MASTER

Proceedings of the
THORIUM FUEL CYCLE

Symposium

Gatlinburg, Tennessee
December 5-7, 1962

BOOK I

UNITED STATES ATOMIC ENERGY COMMISSION
Division of Technical Information

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PROCEEDINGS OF THE
THORIUM FUEL CYCLE SYMPOSIUM

Gatlinburg, Tennessee
December 5-7, 1962

Sessions I-III

Book I

Sponsored by
Oak Ridge National Laboratory
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FOREWORD

The thirty-three papers contained in these two books were presented at the Thorium Fuel Cycle Symposium at Gatlinburg, Tennessee, December 5-7, 1962. The purpose of this symposium was to bring together persons engaged or interested in the use of thorium and uranium-233 in nuclear reactors. While the program was oriented toward fuel cycle technology, discussions of raw materials, reactor physics, and reactor concepts were included. This symposium was sponsored by Oak Ridge National Laboratory* and the Oak Ridge Section-American Nuclear Society.

The program committee for this symposium expresses their gratitude to all who have made this volume possible: D. D. Cowen and H. B. Graham who made the general arrangements for the meeting; D. A. Douglas for his help in technical editing; and especially Imogene Loope, Betty Williams, and Mary Ruth Hall for their invaluable help in preparing the program, conducting the meeting, and preparing the manuscripts for publication.

D. E. Ferguson
J. A. Lane
W. C. Thurber

*Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

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Session I
Paper 1

OBJECTIVES AND PLANS FOR U. S. THORIUM FUEL CYCLE PROGRAMS

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INTRODUCTION

It is easy to understand why work on nuclear fission reactors originated with uranium as the nuclear fuel. Nature provided only one readily fissionable isotope at this particular age of the earth--that is the U-235 which constitutes only about 0.7% of naturally occurring uranium. Recognition of the potential of creating a self sustaining chain reaction of nuclear fissions using this material, and completion of the experimental demonstration of the feasibility of a nuclear fission reactor, is truly one of man's outstanding scientific achievements.

It was also, of course, recognized very early in the history of nuclear reactors that additional fissionable isotopes, Pu-239 and U-233, could be produced in a reactor from the fertile materials U-238 and Th-232. It was also recognized very early that the long term importance of nuclear fuels for power production depends upon our ability to use not only the original fissionable U-235 provided by nature but also at least some appreciable part of the much more abundant fertile materials which can be converted into fissionable isotopes.

The basic physics characteristics of fertile U-238 offers the potential of true breeding in fast reactors where conversion ratios of 1.4 to 1.5 conceivably could eventually multiply our fissile resources energy by about 100, assuming conversion and consumption of all U-238 except that which is lost in the various materials handling processes. However, these same basic physics characteristics allow only a limited breeding effect in thermal reactors where attainable conversion ratios of 0.4 to 0.6 only double the energy attainable from the original U-235. In contrast with these factors, the basic physics characteristics of fertile Th-232, the only significant naturally occurring isotope of thorium, are such that true breeding can occur in thermal as well as fast reactors providing the thermal reactor design avoids the use of highly neutron absorbing structural, cladding, and reactivity control materials and providing fission product accumulation is not allowed to be excessive. Attainment of such a goal, ultimately

multiplies our fissile resources energy by one and one-half to two times that accomplished by U-238 true breeder fast reactors, ie/ the ratio of Th-232 available to U-238 available. Systems using thorium, but not paying the economic penalties associated with sufficient neutron economy to accomplish true breeding, will operate with equilibrium conversion ratios from 0.6 on up giving a continuous spectrum of potential for multiplying our fissile resources energy in the most economic fashion as future basic ore prices gradually tend to increase.

These factors then form the principle basis for our interest in the thorium fuel cycle for nuclear power reactors.

PROGRAM OBJECTIVES

It now appears that the principal near future industrial manifestations of the above factors will come about through the use of thorium in thermal non-breeding reactors where the relatively high conversion ratio will reduce fissile fuel make-up costs and allow longer fuel life without excessive fuel loading and reactivity control requirements. These objectives are being sought in conjunction with the simpler water cooled and moderated reactors, the spectral shift reactor, the all ceramic gas cooled graphite moderated reactor, and the molten salt converter reactor.

In general, the mechanical limitations to the useful life of oxide fuels contained in reasonably thick walled metallic tubes, about 20,000 to 30,000 MWD/T, ave., will preclude substantial lifetime gains in water reactors and will make their principal interest in the use of the thorium fuel cycle be the reduction in U-235 make-up requirements required compared to the uranium fuel cycle. For the simple water reactors, this cost reduction does little more than balance the uncertain increased fuel refabrication costs, thereby making the total energy costs from the thorium and uranium fuel cycles roughly comparable. For the spectral shift water reactor, where the conversion ratio is increased by the use of a variable neutron energy spectrum, and the related variation of the thorium neutron adsorption cross-section in lieu of non-productive control poisons, the fissile fuel make-up savings are substantially larger.

On the other hand, when mechanical fuel lifetime limitations are extended by mixing the fuel and moderator together, such as in the all ceramic graphite moderated gas cooled reactor, fuel specific power can be increased and fuel lifetimes as high as 100,000 MWD/T may be expected. Capsule irradiations to determine mechanical fuel lifetime limitations on coated particle fuel have already been successfully carried as high as 250,000 MWD/T, suggesting that we will be able to live with a peak to average power ratio as high as 2.5 and still reach a reactivity limited 100,000 MWD/T average fuel lifetime goal. This long life fuel greatly reduces the effects of increased refabrication costs and offers the thorium fueled gas reactor the objective of reduced fuel recycle costs as well as reduced U-235 make-up costs when compared to the uranium fueled thermal reactors.

Finally, of course, when thorium is used in a fluid fuel reactor, such as a molten salt converter reactor, mechanical fuel lifetime limitations become practically meaningless and fuel recycle rates are controlled by the necessity to remove accumulated fission products and impurities. In this case, U-235 make-up requirements are also held to a minimum.

It is emphasized that the above objectives imply fuel recycle without government guarantees to buy back the resultant mixed U-235--U-233 bred fuel. It is, therefore, an objective of our program to provide, or assure, adequate development of thorium recycle technology and to ultimately remove fuel buy-back guarantees.

In the longer term future, the governmental and industrial pressures to utilize the thorium fuel cycle will likely take on two distinct but inseparable forms. First, the adoption of systems having higher conversion ratios will extend the useful life of our low cost uranium and thorium ores, thereby acting as an energy conservation program to delay the day when our society will have to mine higher cost ores which will result in higher energy costs. Second, the adoption of systems having higher conversion ratios will reduce the effect of using higher cost ores since, as the over-all system conversion ratio approaches unity, the fissile fuel consumption rate approaches zero. However, inventory

costs will also rise as future ore prices rise. This suggests that, until true breeders can produce and sell sufficient excess bred fuel to override the rising inventory costs, the primary parameter of future concern may well be fuel specific power instead of breeding or conversion ratio.

An illustration of the time dependency of the above arguments can best be illustrated by the following tables which show the projected United States energy consumption and the fission energy content of domestic nuclear resources as reported by the Atomic Energy Commission in its recent report to the President on Civilian Nuclear Power. Figure 1 shows three separate bases for estimating the future energy consumption in the United States. For convenience, the energy values have been indicated in units of Q where Q is defined as 10^{18} BTU. Curve A is an extrapolation of the experience of the last 50 years. Curve B is an exponential curve prepared by the Department of Interior. Curve C has the same initial rate as curve B but incorporates downward trends in relative rates of growth in population and per capita. This curve reaches a maximum of about two Q per year corresponding to a saturation population of about one billion people. More detailed information concerning the basis of these curves is provided in the recent Presidential Report. Figure 2 integrates the consumption rates indicated in Figure 1 and shows the cumulative energy consumption for the same three curves. Figure 3 shows the fission energy content of domestic fissile and fertile nuclear resources, assuming 100 per cent utilization, in increasingly more expensive cost brackets. Again, a more detailed explanation of these figures is provided in the Presidential Report. The significant points on this figure that I would like to call to your attention are that if we were to ignore the fertile fuels and use only the existing U-235 fissile fuel that, in the cost range less than one hundred dollars per pound, we would have only 5 to 10 Q of available energy but that the fuel available at a price up to five hundred dollars per pound provides from 220 to 900 Q of energy. Now, referring back to Figure 2, it can easily be seen that by the end of the first quarter of the next century, about two to three central station plant lifetimes from now, we will have consumed 5 to 10 Q of energy, a value comparable to the total energy

RATE OF ENERGY
USE, Q/YEAR

Fig. 3. FISSION ENERGY CONTENT OF DOMESTIC NUCLEAR RESOURCES

Cost Range, \$ per Pound of Oxide	Energy in U-235, Q		Total Energy Content, Q	
	Reasonably Assured Resources	Estimated Total Resources	Reasonably Assured Resources	Estimated Total Resources
Uranium				
0-10	0.16	0.4	22	50
10-30	0.17	0.3	24	40
30-100	5	10	700	1,400
100-500	220	900	30,000	120,000
Thorium				
0-10	does not apply		6	25
10-30	does not apply		6	13
30-100	does not apply		700	2,200
100-500	does not apply		63,000	190,000

available from U-235 obtained from ore costing up to one hundred dollars per pound. However, the reasonably assured 220 Q of energy for five hundred dollar per pound fuel would last, using curve C, until the year 2260, three centuries from now, and the estimated total value of 900 Q would last several additional centuries. The above arguments quite clearly point to the fact that, if the tables are correct and if one is concerned only with the next several hundred years instead of the next several thousand years, the availability or full utilization of our nuclear resources is not a serious question. However, also by implication from the tables, the increased cost of nuclear energy with increasing ore costs is clearly of importance to us.

Use of \$100 per pound U_3O_8 in a typical water reactor with a conversion ratio of 0.5 would result in a fuel inventory cost of about one mill/kw-hr and a net fuel depletion cost in excess of three mills/kw-hr. These costs clearly point to the necessity of lowering the over-all fuel costs by making fuller use of these expensive ores. This argument, and the argument for extending the useful life of our low cost ores, then forms the real foundation for government support of high conversion ratio or breeder reactors. The development of high specific power high neutron economy thorium fueled thermal reactors, which can operate with a varying conversion ratio depending upon the fuel exposure used, should offer potential operators systems with relatively low inventory charges and the opportunity to gradually change their mode of operation, selecting the most economic balance between fuel depletion costs and fuel reprocessing costs as ore costs gradually increase. The subsequent development and broad industrial application of true breeders will depend not only upon the demonstration of their technical feasibility but, assuming equal capital and operating requirements, will also depend upon their ability to lower the fuel costs through the production and sale of surplus fissile material for use in an expanding nuclear energy industry.

REACTOR PROGRAMS

The application of thorium in nuclear power reactors in the United States has now progressed to the stage that one large pressurized water power reactor,

Indian Point, is in operation, one boiling water power reactor, Elk River, has recently achieved initial criticality, one gas cooled power reactor, Peach Bottom, is under construction, and one fluid fuel reactor experiment, the Molten Salt Reactor Experiment, is under construction. Previous experience also includes operation of thorium cores in the BORAX IV and the Sodium Reactor Experiment. Foreign applications include the OEEC gas cooled reactor, DRAGON, and possibly subsequent cores of German pebble bed or "potato bed" reactor.

Other reactor designs under investigation are such variations as the Spectral Shift Control Reactor, commercial variations of the Elk River boiling water reactor, an Advanced High Temperature Gas Reactor, and the Advanced Epithermal Thorium Reactor.

It is clear from the variety of reactors that I have mentioned that thorium is of some interest in connection with many different types of reactors. Of course, unlike natural uranium, it is not possible to design a power reactor which will operate on natural thorium as the only fuel material. However, it may be possible, in some systems with very excellent neutron economy, to be self-sufficient with a thorium feed stream once an initial inventory of fissionable material is supplied for the reactor and its associated processing pipe lines. If, in fact, breeding can be achieved, it may be possible to supply some of the initial inventory requirements for new reactors from excess bred material.

REACTOR PHYSICS

The ultimate feasibility of achieving breeding or self-sustaining operation, and, in fact, the economics of any thorium based fuel cycle depends among other things upon results of improved measurements of nuclear properties of U-233 and associated materials in the thorium fuel cycle. The value of η for U-233, for example, has been determined to a satisfactory precision at thermal energies, however, its value above 2 ev is sufficiently uncertain that wide variations in the economics of intermediate reactors occur, depending upon the measurements chosen as a basis for calculation.

Also, under the category of basic nuclear data, it is recognized that we need accurate knowledge of thermal and epithermal constants for not only U-233 but U-235 and Pu-239. This includes as many of the cross-section quantities as will give eta to $\pm .5\%$, and fission and non-fission cross-sections to $\pm 1\%$. This $\pm 1\%$ accuracy should be determined up to several Kev along with a 3-5% accuracy determination of these same quantities from several Kev to several Mev. At the present time, it appears we meet these accuracy requirements only at .025 ev. The prospects are bright, however, that utilizing higher resolution choppers and new high intensity linear accelerators, we can obtain most of the data to satisfactory accuracy within the next few years.

Other examples of nuclear data needed are the resonance parameters of Th-232 (principally below 100 ev) and the resonance parameters of Pa-233 (up to 500 ev). Calculations based upon Th-232 resonance parameters differ appreciably from resonance integral measurements. Efforts are now being made to improve both the resonance parameter and the resonance integral measurements. Since Pa-233 is an intermediate product (with a relatively long 27 day half-life) in the formation of U-233 from Th, its cross section can appreciably affect both the reactivity and the U-233 yield. Using a special "hot sample" facility in connection with the MTR fast neutron chopper, work is underway to obtain the necessary resonance parameters of Pa-233.

Other nuclear data of importance to thorium utilization are the fast inelastic and elastic scattering cross-section of Th. The measurements to date have been below 1.5 Mev, however, work is continuing on these measurements and we plan to extend them to higher energies.

Other types of measurements of interest can best be classified as integral measurements made in a neutron spectrum. These include both infinite dilution and effective resonance integrals for the major isotopes Th, U-233, U-235, Pu-239, and Pu-240. These measurements are made not only to resolve discrepancies in existing integral measurements but also to provide data which cannot be readily obtained in a differential form as a function of energy. Recent measurements on Th-232 and U-233 at ORNL can be cited as examples of this type of data. Also

of importance are effective thermal cross sections and resonance integrals of the major fission products. The individual fission product measurements are part of a long term program and depend strongly on the development of samples and techniques. However, we hope to obtain some gross fission product measurements at a much earlier date.

At the MTR, the Advanced Reactivity Measurement Facility is being utilized to make fission product cross section measurements on U-233 and Pu-239 samples (relative to U-235) for various conditions of flux spectra, flux intensities, and sample burnout. Thorium samples are also being irradiated to determine the U-233 production rate, asymptotic U-233 concentration in thorium, the effective cross section of thorium in various flux spectra, the fast fission effects and the Pa-233 cross sections.

A third type of physics data can be classified as reactor lattice studies. There have been major studies of this type at AI, B and W, GA, ANL, LRL, and in the UK. I will not discuss these in detail except to point out that most of these experimental programs utilized U-235 as the fissile material. Only the AI work was with U-233. Since one expects significant differences in the performance of U-233 and U-235 systems (due to differences in the nuclear properties of U-235 and U-233 and the interference of Th-232 and U-233 resonances), we feel it is important to determine the physics of various U-233-Th systems at an early date.

Within the limited quantities of U-233 available we hope to study a wide range of U-233-Th lattices similar to those studied with U-235. The first U-233 lattice studies are expected to get underway at BNL in the spring of 1963. These will include exponential and miniature lattice measurements made up of U-233 O_2 -Th O_2 rods in H_2O . It is hoped that some subcritical measurements can also be made on graphite moderated assemblies in the near future, however, no definite arrangements can be stated at this time.

Ultimately, it is expected that large scale critical experiments will be conducted with thorium and U-233 in order to make detailed predictions of the performance of large power reactors using this cycle. Until sufficient U-233

is available, however, we hope to exploit subcritical studies extensively to better define initial conversion ratios, critical enrichments, variations in excess reactivity with excess fuel loadings, as well as the temperature effects on these quantities.

In summary, there are at this time many unanswered physics questions related to thorium utilization. We are optimistic, however, that significant progress is being made on nearly all of these questions. Efforts to obtain the basic nuclear data, integral data, and reactor lattice data are all essential to the advancement of thorium utilization. We have recently increased our efforts to procure nuclear data and integral data of the type required and we are hoping to increase our efforts to procure clean lattice data on those systems of greater promise.

FUEL MATERIALS

An area of development at least as important, and perhaps even more important than nuclear physics, is that related to nuclear fuel materials. The last several years have seen intensive development of thorium ceramic fuels, particularly the oxides and coated particle carbides which are being used in current reactor development programs.

Uranium oxide fuels, which have been rather extensively developed, fortunately provided a considerable background for the development of the thorium-uranium oxide fuels which are now being used in all thorium fueled water reactors. Current development work is directed principally to application involving U-233 recycle, a subject I will discuss in a moment, and to the development of cladding materials, such as zirconium, which will give improved neutron economy.

The development of uranium carbide fuel, however, had not progressed in the same direction as the thorium carbide fuels being applied in gas cooled reactors. Because of this, there have been substantial programs in recent years for the development of thorium uranium carbide coated particle fuels. This work has involved the development of methods for coating small spheroidal fuel particles with materials, having suitable fission product containment characteristics,

such as pyro-graphite, compacting the coated particles with graphite matrix materials into suitable geometric forms, irradiation testing and subsequent examination and evaluation. Development efforts to date have been directed toward two differing goals, vented fuels, such as will be used in the Peach Bottom HTGR prototype, and non-vented fuels, such as would be used in the pebble bed concept. Although employing the same principles, the latter goal requires a higher degree of success of retaining fission products within the fuel body, since fission product release in this concept is direct to the primary gas coolant stream instead of to a venting gas stream. Irradiation experience to date has allowed decreased emphasis on vented fuel sleeve impermeability requirements, and improved likelihood of maintaining reasonable primary coolant activity levels with non-vented fuels. Efforts to support this latter conclusion have taken the form of plans to utilize coated particle fuel during initial operation of the Ultra-High Temperature Reactor Experiment and discussions with the appropriate West German officials concerning the possibility of utilizing our coated particle fuel technology in their Potato Bed reactor.

While of lesser importance, because of the apparent greater attractiveness of the clad oxide and graphite matrix carbide fueled reactors, work has also been conducted on thorium-uranium alloys and such ceramic variants as unclad thorium oxide pellets. Considerable development work has also been done, of course, in developing suitable fused salt fuels for the molten salt reactor concept. Various speakers will address themselves to these subjects in greater detail later in the symposium.

PROCESSING AND FUEL FABRICATION

Probably the most difficult problem to be found in the development of thorium as a nuclear fuel is the one of developing an economical method for processing irradiated fuel and refabricating the fertile and fissionable material into fuel elements suitable for reuse in the power reactor. This problem is made particularly challenging by the fact that the recovered thorium and U-233,

even after removal of fission products, rapidly become radioactive due to daughter products of U-232. In a matter of less than a week after high level decontamination, the gamma activity becomes sufficiently great that fabrication by direct methods can be permitted only on a scheduled radiation dosage basis.

The magnitude of this problem is directly related to the U-232 concentration buildup which occurs throughout the fuel exposure lifetime. This, in turn, is a function of the integrated fuel exposure, including the neutron energy level incident upon the fuel materials since the principal reaction which produces U-232, the Th-232 ($n, 2n$) Th-231 reaction, does not occur with neutrons with an energy below 6 MEV. As an example, it has been estimated that the fuel discharged from the first core loading of a spectral shift reactor would contain 32 ppm U-232 in thorium compared to a saturation or equilibrium value of 160 ppm after an infinite number of fuel cycles. In contrast, preliminary estimates for fuel discharged from the first core of a typical coated particle graphite matrix fueled reactor indicate a substantially lower U-232 concentration, due in part to the more thermalized average neutron energy spectrum and in part to the effect of finely dispersing the fuel in the moderator so that fewer neutrons have their first collision with fuel when still above 6 MEV. To my knowledge, no estimate has yet been made of the equilibrium U-232 concentration in this type of fuel.

Four different approaches to the problem of radiation from the U-232 daughter products are being considered. You will hear much about them during this symposium so I will merely highlight the different philosophies involved.

First is a system involving high decontamination and direct fabrication. In this system, fuel is chemically reprocessed, to remove essentially all fission products, in a plant which produces separate uranium and thorium product streams. The thorium stream product is stored 10 to 15 years before recycling to allow decay of the Th-228, the first daughter of the U-232 decay series, and virgin or previously stored thorium is used for immediate recycling. The uranium product stream, which contains both U-233 and decaying U-232, is again cleaned up chemically immediately before fabrication begins. Direct fabrication methods

can be used if the work proceeds promptly and if measures are taken to routinely and adequately decontaminate all unshielded process equipment. Since the fabrication process must be done rapidly, it is necessary to avoid complicated processes and materials handling steps. To accomplish this with oxide fuels, the Oak Ridge National Laboratory has developed a process known as the sol-gel process which, simply stated, converts nitrates and oxides to very dense oxides which can be crushed, sized and used in vibratory compacted fuel pins. An initial demonstration of this basic process will be conducted by ORNL when they fabricate 1000 U-233 bearing fuel pins for a set of physics experiments to be conducted at BNL later next year. Additionally, at least one industrial group, the Babcock and Wilcox Company, is constructing a developmental facility and is planning to use this basic process in their commercial nuclear activities.

Little work has been done to date to adapt this high decontamination - direct fabrication system to the recycle of coated particle graphite matrix fuel. Although the refabrication process may be more complicated for this type of fuel, the likelihood that the U-232 concentration will be substantially lower could possibly counteract this effect and make direct fabrication possible.

The second system involves high decontamination and remote fabrication. This system is similar to the first in that it contemplates separation of thorium and U-233 in a conventional chemical separations plant. However, no special chemical clean-up of the U-233 just prior to fabrication would be required, because of the remote fabrication behind shielding adequate for the gamma radiation emanating from the U-232 daughter products. Also, this system contemplates recycling the thorium without a long decay period.

The third system involves intermediate decontamination and remote fabrication. Since all operations are to be remote, only one cycle of solvent extraction is planned, giving fission product decontamination factors of 10^2 to 10^3 , rather than the usual 10^6 to 10^8 . This level of decontamination was chosen because it approximates the level of activity which will be present anyway in recycled U-233 due to the rapid ingrowth of radioactive daughter products. Since irradiated thorium is recycled immediately in this system,

fission product extraction and fuel refabrication both require comparable shielding and can both be carried out in a single building. A plant design based upon this concept has been prepared by the Allis-Chalmers Manufacturing Company for the Italian National Committee for Nuclear Energy and construction has been initiated. Plans are currently being made to furnish the initial Elk River reactor fuel loading for demonstration purposes in this plant upon its completion. Allis-Chalmers has indicated a commercial interest in pursuing this general approach to thorium fuel recycle.

The fourth system of fuel recycle involves little or no decontamination and remote fabrication. This system, in concept, is similar to the pyrometallurgical fuel recycle plant being built for the Experimental Breeder Reactor No. II but adapted to the thorium fuel materials. It is of greatest potential interest in systems in which accumulation of fission product poisoning is relatively unimportant and prompt processing for low pipe line inventory is relatively important. Atomics International has been engaged in developments related to this concept.

While three of the four systems I have described have involved remote fabrication, the actual processes used in specific plant concepts differ in many important respects. This will be apparent as you hear more detailed descriptions of some of the concepts.

SUMMARY

Clearly, the developmental problems related to economic use of thorium as a nuclear fuel span the whole field of reactor technology. A considerable effort has been expended in recent years to get into operation several reactor concepts using thorium as a fuel. Now that this is becoming a reality, a considerable effort is being devoted to the problem of fuel recycle. Additionally, the apparent success of uranium fueled water reactors to meet our near term economic goals has allowed us to place greater emphasis upon the keys to longer term economic goals, i.e./increased fuel specific power and greater neutron economy with its resultant increased fuel utilization.

About a year ago, we established, at the Oak Ridge National Laboratory, a Thorium Utilization Program which we expect not only to furnish directly many of the technical answers, but also to provide a focal point for technical planning for an integrated, over-all program of effort related to the thorium fuel cycle. In some respects, the initiation of this program is comparable to our initiation in mid-1956 of a Plutonium Recycle Program at the Hanford Laboratories.

As the application of thorium fuels becomes more widespread we also predict, hopefully, that additional industrial activity will be exhibited, especially in such fields as reactor construction and operation and the production aspect of fuel reprocessing and fuel refabrication.

Thorium has gotten a relatively late start in serious development as a nuclear fuel. It has many handicaps in its competition with uranium. On the other hand, it has certain advantages that could tip the scales in its favor. Its value, and the uranium fuel cycle value, can be known only after considerably more work has been done and, in particular, after experience has been obtained from operating reactors and associated supply or servicing facilities. Additionally, it should not be forgotten that the ultimate deciding factor on the use of thorium will rest with the decisions of individual utility executives who must weigh its relative economic importance.

Work toward gaining this technology and experience presents an interesting challenge for the years immediately ahead. There are many persons here who have already accepted that challenge and are now working toward making thorium a practical nuclear fuel. I am sure their reports during this very timely Symposium will result in the generation of worthwhile new ideas which will advance the time at which these utility executives can decide that thorium has become an economically practical nuclear fuel.

Session I
Paper 2

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THE ECONOMIC MINERALOGY AND GEOLOGY OF THORIUM

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The geochemistry of thorium, i.e., its chemical behavior in geologic processes, is governed by several principal factors such as its invariant quadrivalence, its periodic grouping with respect to other metals, and its relatively large ionic size. A detailed account of the mineral chemistry and mineralogy of thorium has been presented by Frondel (5). Chemically, thorium occupies an intermediate position between the rare earths, the Group IVa metals (zirconium and hafnium) and uranium. Zachariasen (9) has classified thorium among the quadrivalent thoride elements which are distinguished on the basis of valency from the trivalent actinides. Thorium shows a similarity to both zirconium and hafnium in electron distribution in the outer d and s orbitals, however, its ionic radius in six-fold co-ordination is much larger. Among the rare-earth elements cerium is chemically analogous to thorium, both having four outer electrons in their ground states. However, because all lanthanides have similar chemical properties, thorium is generally associated with these elements as either an essential or vicarious component of their natural compounds. The mineralogical and chemical similarities and dissimilarities of these elements are the result of these properties.

The close chemical relations existing among the lanthanides, which result from the characteristic gradual filling of the 4f shell, are also exhibited by the thoride elements of which Th^{4+} and U^{4+} are the most abundant in nature. The striking difference in the geochemical behavior of uranium and thorium is related to the fact that, whereas thorium is invariantly quadrivalent in minerals, uranium commonly occurs in both the tetravalent and hexavalent states. This dual valency of uranium is perhaps the most important single factor governing the separation of these two elements into their respective ores.

The development of thorium reserves has until recently been chiefly dependent on the market for rare-earth metals. The two minerals which have assumed some measure of economic importance as a source of rare earths are monazite and bastnaesite. Thorite, a silicate containing considerably more thorium than rare earths, has been of little economic value, although it is

one of the most important potential sources of thorium. Interest in these minerals has varied with fluctuations in the demand for thorium and rare earths and has occasionally been prejudiced by the quantity of by-product thorium present in the ores.

Although the major production of monazite has in recent years come from vein deposits in granite gneiss in the Van Rhynsdorp district of the Republic of South Africa, the chief resources of monazite in the USA and the non-Communist world are in recent and fossil placer deposits. The thorium content of placer monazite from North and South Carolina is about 5 to 6 percent, from Florida about 4.5 percent, and from Idaho about 3 to 5.5 percent. Because of its low thorium content (about 0.1 percent) bastnaesite is not important as a source of thorium.

The reserves of thorium in placer monazite in the USA are not large. Although ample for any foreseeable current requirements, it is unlikely that they would be sufficient to meet the long-range demands imposed by an economy relying to an appreciable extent on energy production from thorium reactors. The current estimated resource potential of low-cost thorium, i.e. below \$10 per pound ThO_2 , from unindurated placers is less than 15 thousand short tons, and a two- or three-fold increase in price may make available perhaps only another 60 thousand tons ThO_2 . It is currently impossible from geologic indications to make any additional predictions of resources from this source.

Postulated thorium resources in fossil placers appear to be somewhat larger. The largest known accumulation of monazite in ancient sediments in the USA is at Palmer, Michigan, where monazite has been found in the Precambrian Goodrich quartzite within the Marquette synclinorium. On the basis of a study of the area by Vickers (8) the quartzite is estimated to contain roughly 20 thousand tons ThO_2 available at a cost probably not exceeding 10 dollars per pound. The total thorium resource within the confinement of the Palmer graben, calculated to a maximum depth of about 1,000 feet, is estimated to be in the order of 200 thousand tons. Most of this would be available at not less than 10 and presumably not higher than 50 dollars per pound ThO_2 .

By-product thorium from uranium production at Blind River, Canada, constitutes a major low-cost reserve of the metal on the North American continent. It is estimated (4) that the deposits contain about 200 thousand short tons ThO_2 ; however, low-cost recovery is contingent on production of uranium. Fossil placers, therefore, constitute an important potential source of thorium in the United States and Canada.

The greatest potential for low-cost thorium probably exists in areas of hydrothermal activity. Deposits of this type have been known to exist in the Lemhi Pass area near Salmon, Idaho, since 1949. For many years, prior to informative geologic study, the area was assigned a potential of only about 10,000 tons ThO_2 . However, a recent reappraisal, based largely on the geologic character of the veins and a limited amount of sampling and mapping, indicates a probable reserve of the order of magnitude of 100 thousand short tons and a possible total potential of 400 thousand short tons ThO_2 . The estimates do not take into consideration the possibility of new discoveries or the ultimate exploitability limits of the known occurrences. There is, also, some measure of uncertainty in these figures which is occasioned by the lack of information regarding the tenor of ore at depth and the depth to which the veins can be mined. In the event of a sharp rise in demand for thorium the ores could, however, immediately be drawn upon at a price that will not be markedly higher, and, perhaps, may even be lower than that of present uranium ores.

The question of increasing our low-cost resources to meet ultimate demands may depend on the possibility of finding sufficient additional quantities of vein-type and placer thorium. In lieu of this, a domestic thorium mining industry will probably be obliged to consume ores whose price will be considerably higher, and it may become necessary to draw upon thorium available in granitic rocks.

The two main questions in evaluating the relative merits of a thorium and uranium power economy are the technological advantages associated with each reactor type and the availability of a sufficient fuel supply at a competitive cost. Although the crustal abundances of thorium and uranium have been used as

a yardstick of availability, this ratio (about 4:1) is, in fact, no measure of their productibility within any given cost category.

Although geochemically similar in many respects in the igneous environment, thorium and uranium differ markedly in their chemical behavior in the hydrothermal and sedimentary surroundings in which their major ore occurrences are found. Differentiation into distinct ore types is partly attributable to the fact that the elements follow geochemically separate paths subsequent to release by weathering from igneous host rocks.

The bulk of our domestic uranium reserves is concentrated in sedimentary basins under what are generally considered to be epigenetic or diagenetic circumstances. The formation of these deposits involves the precipitation of uranium from solution and is dependent on the relative solubility and mobility of uranium in its two valence states. The uranyl ion complexed with carbonate or sulfate is very soluble in aqueous solutions, but it is easily reduced in the presence of natural reductants such as hydrogen sulfide. Uraninite (pitchblende) and coffinite, the products of this reaction, are the dominant reduced uranium ore minerals.

Thorium, on the other hand, is known in only one valence state and does not form chemically in its major ores in a manner similar to uranium. The separation of these elements in hydrothermal environments is reflected in the composition of magmatic vein-type uranium ores, which contain relatively little thorium, and in the relative scarcity of uranium in hydrothermal thorite ores. The fractionation mechanism involved is not well understood but undoubtedly involves the chemical properties of these elements. The formation of thorium deposits in sediments, e.g., monazite placers, is a function of the mechanical attrition of crystalline source rocks and the aggregation of refractory minerals by purely physical concentration processes. It is because of these inherent chemical differences affecting their geochemical cycles that the thorium:uranium crustal abundance ratio based on values obtained primarily on igneous rocks has not been found exemplary of the abundances of these elements in minable ore deposits at grades recoverable at comparable costs.

The hydrothermal vein deposits in the Lemhi Pass area of Idaho are virgin, having scarcely been touched for their thorium content. According to Anderson (3) the mineralization occurs along fractures in quartzitic and phyllitic rocks of the Precambrian Belt series. Although thorite is the dominant thorium mineral, allanite, monazite, xenotime(?) and euxenite(?) have also been reported, and rare earths and uranium are present in addition to thorium. The mineralized zones range from less than 1 foot to about 40 feet or more in width and have been observed to extend up to 2 miles in length. The bearing of some of the veins suggests that they may be continuous for distances of several miles. The thorium content of most of the deposits probably ranges from 0.1 to 2.0 percent, the average being somewhat less than 1 percent. The workable deposits on which reserve calculations are based have a minimum width of 1.5 feet and a minimum grade of 0.5 percent ThO_2 .

Regarding genesis, the presumption is that the Lemhi Pass ores were formed from hot solutions derived from a magmatic source enriched in thorium. Another possibility, which has apparently not been suggested for these deposits, is that they are the product of metamorphic assimilation of ancient placers followed by differentiation. Abbott (1) has ascribed deposits of monazite in marble in the Mineral Hill district of northern Lemhi County, Idaho, to metamorphism of sandy, argillaceous sediments of the Belt series and subsequent migration of rare earths, thorium and other elements to their present site. According to Anderson (3) deposits near Salmon, similar to those at Lemhi Pass, cut igneous rock that is presumably related to the Idaho batholith of late Cretaceous or early Tertiary age, but they are apparently older than overlying Tertiary volcanic rocks. It seems apparent, therefore, that the deposits are related to metamorphic or magmatic hydrothermal activity following emplacement of the batholith.

It may be of some significance that these thorium and rare-earth deposits are largely restricted to the Belt series, a thick stratigraphic unit of quartzitic and argillaceous rocks with subordinate amounts of calcareous rocks. The general character of these sediments indicates deposition in or adjacent

to an extensive shallow body of water, and the sediments are, therefore, probably partly continental and partly marine. The Belt quartzites common to Lemhi County may have initially been sands and gravels, and the phyllites and marbles may have formed from marine shales and limestones. If the Belt quartzites, gneisses and schists represent ancient beach or deltaic deposits, it is possible that they contain placers with varying heavy mineral assemblages. Metamorphism associated with Cretaceous or Tertiary igneous activity could have resulted in the assimilation of the heavy elements, with subsequent re-deposition in veins along lines of structural weakness.

Future exploration may depend on this question because it should be possible to predict approximately the limits of regional favorability, if mineralization can be related to placer distribution in Precambrian sediments. The implication of this is that thorium ore deposits will be concentrated more or less in rocks of the Belt series in east-central and, perhaps, northern Idaho and western Montana. Unfortunately, the prospect of delineating local areas favorable for exploration is complicated by the lack of adequate correlation between the Belt strata in various parts of Idaho and Montana and by metamorphic changes which have obliterated to some extent the original character of the sediments. If, on the other hand, we accept the argument by Anderson (2,3) that the mineral assemblages are characteristic of magmatic differentiates, we must conclude that the geologic relation to the Belt series may be largely fortuitous and, in this event, future exploration will probably come to rely on other, as yet unknown, considerations.

An interesting aspect worth mentioning concerns the estimates that can be made about the volume and thorium content of the postulated placer source area at Lemhi Pass. The thorite deposits are distributed along a broad southeast-trending belt approximately 6 miles wide and 8 miles long. Assuming that an underlying placer would have a thickness of about 100 feet, a monazite concentration of 2 pounds per ton (approximate tenor estimated by Overstreet et al, (7) for enriched Carolina Piedmont gravels), an average thorium content of 5 percent in monazite, and a tonnage factor for the host rock of 14 cubic feet

per ton, the quantity of thorium available would be roughly 500 thousand tons which is about the current resource estimated for the area. This calculation indicates that the vein thorium could be accounted for in terms of placer thorium in deeper rocks. Geochemically, however, it is difficult to account for the depreciation in the rare-earth to thorium ratio in the vein deposits, where it is less than 1, as compared to that in monazites which ranges from about 7:1 to 21:1.

Concerning future prospection, in the Mineral Hill district contacts between different lithologies strike generally northwest, the trend of the monazite-bearing zones is nearly paralled (about N. 35° W.; Abbott, 1). To the southeast, in the Lemhi Pass area, the ore bodies trend generally northwest (N. 30° W. to N. 60° W.; Anderson, 3) and more or less parallel the strike of regional fold axes and major fault traces. Since the join between these two districts has a similar direction, there is a suggestion of continuity between the two mineral belts. Whether this is of any consequence insofar as the origin of the ores is concerned is unknown; however, it should focus interest on the area between the two mineral districts.

Since it is not desirable to leave the genesis problem in an unresolved state, one must take account of the limitations of existing geological evidence and employ such approaches as provide criteria which can be further evaluated. Isotopic studies on sulfide and sulfate minerals may be helpful in determining whether the deposits are magmatic or metamorphic hydrothermal, if contemporaneity between the sulfur-bearing minerals and thorium can be established. Wide-ranging radiometric surveys of the Belt series may establish the distribution of syngenetic radioactive constituents which would possibly help to define the initial character of the sediments. The amount of geologic research devoted to thorium deposits has been deplorably small. Inasmuch as there is some indication that it may someday achieve a practical objective, a more aggressive search for knowledge of the factors governing thorium mineralization would appear to be warranted, for it is only through intensive studies that attitudes and beliefs

can be acquired that will ultimately prove helpful in evaluating the extent and resource potential of this and other thorium-bearing areas.

One can ordinarily anticipate the likelihood of increasing mineral resources by expanding the discovery effort. We have just reached the end of a period of accelerated surface prospecting for uranium during which our uranium reserves have been enlarged tremendously, and a number of thorium occurrences have also been uncovered. The prospects of finding additional uranium deposits are now largely dependent on how skillfully our knowledge of uranium geology is applied in subsurface exploration, and there is reason to be optimistic because we know that geochemically favorable areas exist which have not yet been adequately explored. We are not as fortunate with regard to thorium because we know so much less about the conditions favoring its deposition from hydrothermal solutions, and yet we are also faced with the possibility that accelerated exploration for radioactive materials already may have uncovered most of what can be expected to be found from surface indications. Since there is now no great incentive for exploration motivated by either an existing or contemplated market, there seems to be little purpose in expending large sums of money to improve our thorium resource posture. Toward this end, however, an attempt has been made to evaluate, largely on the basis of geologic indications, the potential that exists in the USA for thorium at various price levels (Table 1).

TABLE 1
ESTIMATED DOMESTIC RESOURCES OF THORIUM

<u>Price Range</u> <u>\$/lb. ThO₂</u>	<u>Total Resources</u> <u>(10³ short tons)</u>	<u>Principal</u> <u>Source</u>
5-10	400	Vein deposits
10-30	200	Placers
30-50	10,000	Granitic rocks
50-100	25,000	Granitic rocks
100-500	3,000,000	Granitic rocks

The contraction in estimated resources in the 10-30 dollar range reflects a considerable element of uncertainty concerning resources which are not sufficiently well explored as to remove any doubt concerning their actual existence.

Estimates in the higher cost categories are limited primarily to granitic rocks because of the relative ease of extracting thorium therefrom, as compared to shales, bauxites and other rock types containing above-average (crustal abundance) concentrations of thorium but usually in a more refractory form.

Because of the uncertainties involved in mining and recovery costs, the proportion of leachable thorium in total rock thorium, the homogeneity or heterogeneity of grade and various attendant assumptions, the cost and tonnage figures developed for various granite bodies are not really an adequate expression of these parameters. Therefore, the figures for granite are primarily intended to provide only an indication of a reasonable cost range and order of magnitude of tonnage.

Foreign reserves of low-cost thorium within non-Communist countries have been estimated (6) at about 500,000 tons ThO_2 , with the major portion existing in placers in India and in the Blind River area of Canada.

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Session I
Paper 3

THORIUM RESERVES IN GRANITIC ROCK AND PROCESSING
OF THORIUM ORES

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THORIUM RESERVES IN GRANITIC ROCK AND PROCESSING OF THORIUM ORES

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The past and current demands for thorium have been satisfied chiefly from monazite although significant amounts have been recovered recently as a by-product of uranium milling operations in the Blind River area of Canada. Owing to the present limited thorium market, the relatively high-grade thorite ores recently discovered in the Lemhi Pass area of Idaho have not been exploited as yet, but are available as a source of low-cost thorium for the future (1).

Recovery of Thorium from Monazite

Monazite mineral is usually obtained as a relatively high-grade concentrate from physical beneficiation of fine-grained beach or alluvial sand. It consists principally of the phosphates of rare earths and thorium, the thorium concentration ranging typically from 3 to 9% (as metal). Much lower concentrations of uranium (0.1-0.5%) are also present. An excellent review of monazite processing methods has been made by Wylie (2). The mineral can be decomposed with concentrated sulfuric acid or caustic solutions at elevated temperatures and both methods are used commercially. Chlorination of the ore to produce ThCl_4 has been studied with some success (2-4) but the process has not been applied on a commercial basis.

In the alkaline process, as developed at Battelle Memorial Institute (5), the finely ground monazite is digested with concentrated caustic solution at 140°C and leached with water to remove phosphate. The metal hydroxides are dissolved from the residue with 37% hydrochloric acid and the thorium and uranium

co-precipitated by neutralizing the liquor to pH ~6 with sodium (or ammonium) hydroxide. Further addition of caustic precipitates the rare earths. The thorium-uranium precipitate is redissolved in nitric acid and the elements are separated by tributylphosphate (TBP) extraction. Several variations of the alkaline process are used in industry (6).

In the acid process, the monazite sand is digested at 200-220°C with 93-96% sulfuric acid and the digestion product dissolved in water. Many methods of treating the resulting liquor to recover and separate thorium, rare earth, and uranium products have been investigated and described in the literature. In a process developed at Ames Laboratory (7,8), the elements were partially separated by stepwise precipitation with ammonium hydroxide and the thorium and uranium concentrates were then redissolved in nitric acid and purified by TBP extraction. Subsequently, a modified process (7) was developed which included co-precipitation of the thorium and rare earths with sodium oxalate, conversion of the precipitate to hydroxides by digestion with caustic (which liberated the oxalate for recycle), calcination to oxidize cerium, redissolution of the calcine in nitric acid, and TBP extraction and partitioning to give thorium, cerium, and mixed rare earth products. Other separation schemes utilizing oxalate precipitation, sulfate precipitation, etc., have been proposed by other workers (2,10-13).

More recently, a versatile solvent extraction method, utilizing long chain alkylamine extractants (Amex process) was developed (14-17) for recovering thorium, uranium, and rare earths

from the acid digest liquors. This method is described here in greater detail since the information is more recent and the processes appear to show advantages over the older processes. In addition, they are applicable to all currently known thorium sources and are not restricted to monazite.

The relative extraction power of the amine reagents for thorium and other metal values is strongly dependent on the amine type and alkyl structure. By proper choice of amine, the thorium, uranium, and rare earths can be extracted and efficiently separated from each other and from phosphate in consecutive extraction cycles. Figure 1 shows one arrangement of a 3-cycle flowsheet for treating a monazite acid digest liquor. In the first cycle, thorium is extracted with a primary amine, such as Primene JM,¹ in kerosene diluent. A number of chemical reagents including nitrate, chloride, and carbonate salt solutions are effective for stripping thorium from the solvent phase. The choice of optimum stripping agent depends on several factors including the type of product desired. Uranium is recovered from the first cycle raffinate by extraction with a tertiary amine, or preferably, an N-benzyl-branched-alkyl secondary amine.¹ The rare earths are then recovered by extracting with a primary amine or, alternately, by adding sodium chloride or sodium sulfate to the second cycle raffinate to precipitate the rare earth sodium double sulfate. In bench-scale, mixer-settler demonstrations of this flowsheet, thorium and uranium recoveries were >99.5%. Typical thorium products contained >98% thorium oxide, <10 ppm uranium, <0.2% rare earth oxides, and <0.1% phosphate. This product would require

Fig. 1. Amine Extraction of Monazite Liquors

further purification in a TBP extraction cycle to produce nuclear grade thorium oxide. However, by adjustment of flowsheet conditions it may be possible to eliminate the need for TBP purification. The rare earth extraction flowsheet has not been demonstrated in continuous equipment. Batch tests have shown that rare-earth products only slightly contaminated by phosphate and other metals are obtainable.

Recovery of Thorium from Blind River Ores

In the past few years large tonnages of uranium-thorium ores have been treated in the Blind River district of Canada for uranium recovery, although many of the mills are currently not active. Until recently no provision has been made for recovering thorium as a by-product from the Blind River ores. However, Rio Tinto Dow, Ltd., is now operating thorium recovery plants at two uranium mills, and solvent extraction is used for thorium recovery (18). The particular extractant used has not been announced. The use of di(2-ethylhexyl)phosphoric acid in hydrocarbon diluents for extraction of thorium from these liquors has been studied and found promising provided the iron in the liquor is reduced to the ferrous state prior to extraction (12,19-20). Long chain mono-alkylphosphoric acids, which are somewhat similar extractants, can also be used. With both of these extractants thorium is usually stripped from the solvent with 3-8 M sulfuric acid to give a thorium sulfate precipitate.

Amine extraction of the Blind River liquors has also been studied with considerable success. In this case, reduction of the iron is not required. Both uranium and thorium can be recovered and separated cleanly by a two-cycle amine extraction process (17-21), using a tertiary amine to extract uranium in the first cycle and

a secondary amine to extract thorium in the second cycle. Also, thorium can be recovered from effluents from the ion exchange circuits presently used for uranium recovery (12,17,22-25). Here a primary amine is used if the ion-exchange effluent contains nitrate (added in nitrate elution of uranium from the resin) since nitrate interferes severely with secondary amine extractions of thorium. If chloride elution of uranium is practiced, a secondary amine can be used for the thorium extraction step. Pilot plants using amine extraction have been operated successfully at two mills (25,26).

Processing Thorite Ores

Ores from the Powderhorn and West Mountain districts of Colorado and from the Lemhi Pass area of Idaho, which contain thorium principally as the thorite or phosphothorite mineral, have been successfully treated by a sulfuric acid -- amine extraction flowsheet (27). Thorium recoveries >90% were obtained by leaching with relatively large amounts (300-600 lb/ton ore) of sulfuric acid. The thorium was recovered as a relatively pure concentrate by extracting with a primary amine, stripping with sodium chloride solution, and precipitating thorium from the strip solution with sodium oxalate or with soda ash.

Thorium Recovery from Granite

Although the reserves of high-grade thorium and uranium ores are appreciable, they are limited in regard to the needs of a long-range nuclear power economy (1,28,29). Consequently, if the development of competitive nuclear power is highly successful, the supply of high-grade fissile and fertile materials could change

fairly rapidly from one of plenty to one of scarcity. Although it is conjectural as to just when this will occur, eventually the world will be entirely dependent on low-grade ores for its nuclear fuel supply. For long-range planning of reactor development programs, it is important to know how much uranium and thorium and at what cost the earth can supply in support of a successful nuclear power economy. It is an obvious consideration that the large expenditures of money for reactor development should be aimed at supplying man's power requirements for a very extensive length of time rather than for a relatively limited period.

The large military demand for uranium in recent years has created a significant amount of information (28,29) on low-grade uranium reserves including the outlining of several million tons of uranium in Chattanooga shale, recoverable for \$40-60 per pound. Since comparable information on reserves and recovery costs for low-grade thorium ores was virtually non-existent, a program was initiated at Oak Ridge National Laboratory (ORNL) in 1959 to extend the knowledge in this area. After preliminary tests, and discussions with a number of geologists,² it was decided to place major emphasis on granitic rocks as a thorium source. Low-grade placers, fossil placers, and other types of ore will probably also yield significant amounts of thorium in the future. However, it is known (30-38) that the granitic and related igneous rocks comprise a large fraction of the earth's crust and contain, on an average, about 12 ppm thorium and about a quarter as much uranium. It is also known that some granite formations contain larger concentrations of thorium. It may be considered that if

thorium (plus uranium) could be recovered from granites at costs commensurate with commercial production of power the nuclear fuel requirements could be satisfied for a very long period of time. This possibility was previously proposed by Brown and Silver (39), who described results from cursory leaching tests on several granites and conjectures as to recovery costs. The potential importance of granitic rock as a source of nuclear fuels has also been discussed by Weinberg (40) who dubbed the process "burning the rocks."

The program at ORNL has been aimed at obtaining much more extensive information on the availability, properties, and grades of different types of granites and more definitive estimates of their processing costs. To implement the program, a subcontract was established with the Geology Department of Rice University, under the direction of Professors J. A. S. Adams and J. J. W. Rogers, to collect samples from many large and dispersed granite formations, to determine their thorium content and, where possible, their micromineralization (41). Many of these samples have been evaluated at ORNL as to their amenability to processing (42). The process believed best suited for treating granites, within the limits of present knowledge, involves crushing and grinding, leaching with sulfuric acid, countercurrent decantation to separate the leach liquor from the ore tailings, solvent extraction recovery of the metal values from solution, and finally, neutralization of the waste streams with lime. All of the unit operations employed have been reduced to practice at various places within the domestic metallurgical industry, and this simplifies the estimation of costs. Other process operations, such as preconcentration of the thorium minerals by gravity or magnetic

separation, are being considered but only cursory tests have been made at this time.

With assistance from mining and metallurgical consultants,³ preliminary estimates have been made of the recovery costs covering all of the steps from ore development and mining to production of the final product (thorium oxide concentrate). These costs ranged from \$3.97 to \$5.35 per ton of granite, variations within this range depending on differences in assumed ore/waste ratios for different formations and variations in acid consumption for different granites (Table I).⁴

A summary of test results with a variety of granites from various locations in the United States is shown in Table II. It is apparent that there are a number of large granitic bodies which contain much more than the average concentration of thorium. The thorium recoveries are moderately low from several samples, ranging from 30 to 40%, whereas other samples have responded better, giving recoveries of 45 to 60%, and some have given recoveries of 65 to 80%. The Conway granite from New Hampshire responded unusually well to acid leaching. Uranium recoveries are almost always significantly lower than those for thorium. The variation in thorium (and uranium) recoveries are apparently due mainly to differences in mineralization (31,36,41,43-45). The soluble thorium fraction seems to be associated with unidentifiable interstitial material and such minerals as thorite, apatite, allanite, etc., whereas the insoluble fraction is probably tied up in minerals such as zircon and monazite which are essentially inert to the acid leach.

Table I. Estimated Costs for Treating Granite

Assumptions: Treatment of 100,000 tons of granite per day
 10 year amortization
 14% annual return on capital investment

	Processing Costs, \$/ton granite
Mining	0.45-0.90
Milling	
-crushing to pregnant liquor recovery	0.57
-pregnant treatment to product	0.11
-sulfuric acid plus lime ^a	0.95-1.88
-other chemicals	0.10
Total direct operating costs	2.18-3.56
Overhead	0.29
Contingency	0.31
Amortization ^b	0.50
Return on investment ^b	0.69
Total	3.97-5.35

^aBased on sulfuric acid at \$20/ton and lime at \$18/ton. Assumes use of a countercurrent leach and recycle of the solvent extraction raffinate to the CCD circuit.

^bBased on capital costs of \$35,000,000 for mining and \$145,000,000 for milling.

Table II. Estimated Costs for Recovering Thorium and Uranium from Various Granites

Conditions: -48 or -100 mesh ore^a leached 6 hr at room temperature with
 2 N H₂SO₄, 60% pulp density (130 lb H₂SO₄ per ton of ore)

Granite Source	Head Conc., ppm		Recovery in Leaching, %		Acid Consumption ^b (lb H ₂ SO ₄ /ton ore)	Estimated Recovery Cost ^c (\$ per lb Th+U)
	Th	U	Th	U		
Boulder Batholith, Colorado (A)	8	2	45	20	70	590
Minnesota	12	4	40	20	110	470
Philipsburg Batholith	12	3	35	30	60	450
Washington	16	3	55	20	60	240
Boulder Batholith, Colorado (B)	20	5	45	25	50	220
Enchanted Rock Batholith, Texas	19	4	60	15	90	210
Dillon Tunnel, Colorado	22	8	45	45	65	170
Colorado	40	5	35	15	70	160
Pikes Peak, Colorado	24	4	65	25	85	150
Cathedral Peak, California	23	10	50	45	35	140
Boulder Batholith, Colorado (C)	33	6	45	25	35	130
Owl's Head Granite, N. H. ^d	19	4	75	80	40	120
Lebanon Granite, N. H. ^d	30	5	70	45	35	95
Silver Plume, Colorado ^e	94	2	35	25	60	70
Boulder Creek Batholith, Colorado	76	4	50	50	40	55
Missouri ^d	40	19	80	75	40	45
Conway Granite ^e	74	14	80	68	60	30

^aSubsequent tests with Conway and Pikes Peak granites showed that much coarser grinds (-20 mesh) could be used without loss of thorium leaching efficiency.

^bCalculated by subtracting the residual free acid (by the method of Ingles) in the leach liquor from the head acid.

^cAssumes direct mining costs of \$0.68/ton in each case.

^dLeached at 50% pulp density (195 lb H₂SO₄/ton).

^eAverage test results for two samples.

Estimated recovery costs ranged from \$400-500 per lb Th + U for an average-grade granite such as the Minnesota or Philipsburg samples to ~\$30 for higher grade, more amenable samples. Although the recovery costs from average or somewhat greater-than-average grade granites are high, it has been estimated that they would contribute 2-3 mills/kwhr to power costs assuming future development of an efficient thermal breeder reactor (Figure 2). Such costs should not be prohibitive when demands for large amounts of power become unavoidable. The bulk of the cost is for inventory charges on the fertile fuel since make-up charges are relatively low. No inventory charge is made against the fissile inventory in this estimate since it is assumed that, for a breeder reactor with a reasonably short doubling time, the value of the excess fuel produced would approximately balance the inventory charge.

Conway Granite

The higher-than-average radioactivity in the Conway granite of New Hampshire was reported in 1946 by Billings (31) but no quantitative measurements were made of the thorium and uranium concentrations. Until recently, only a few thorium analyses were available. Four samples by Hurley (46) ranged 32 to 67 ppm in thorium concentration, averaging 51 ppm. Flanagan, et al., (47) reported an average thorium concentration of 70 ppm in 16 samples from the Redstone Quarry at Conway, N. H. Analyses of samples from scattered locations in the Conway formation by Rice University geologists (41) and by Butler of the U. S. Geological Survey (48) indicated that the thorium concentration in the main mass of the Conway granite might be expected to average close to 50 ppm.

Fig. 2. Effect of Raw Material Cost on Power Reactor Fuel Charges

In view of the attractiveness of the Conway granite from the standpoint of thorium content and process behavior, recent studies at ORNL and Rice University have centered principally on this material.

The Conway granite is part of the Central White Mountain magma series which occurs largely in the White Mountains and in smaller outlying areas in New Hampshire (49-52). Figure 3 outlines the major rock types in the central White Mountain magma series as mapped by Billings (52) and modified in certain areas by geologists at Rice University. The major rock unit is Conway granite which is relatively continuous and extensive, having outcrop areas totaling approximately 300 square miles. Other significant rock types are the Mount Osceola granite, which is distinguished from the Conway with difficulty in the field, the porphyritic quartz syenite and the syenite. The outcrop areas for these rocks are approximately 100, 28, and 7 square miles, respectively. During the summer of 1961, over 500 field determinations of thorium were made in the area by Adams, Rogers, and coworkers of Rice University using a portable transistorized gamma-ray spectrometer which counts the 2.62 Mev gamma of Tl^{208} . A statistical analysis of these data (41,53) checked by laboratory radiometric and chemical analyses, indicates that the accessible surface of the Conway granite contains 56 ± 6 ppm Th as an average with few samples being <40 or >100 ppm (Table III). The average thorium content for the Mount Osceola granite, the porphyritic quartz syenite and the syenite were 43, 38, and 23 ppm, respectively. The Mt. Osceola granite, although less extensive and less concentrated in thorium than the Conway granite, still represents a sizeable thorium reserve.

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Fig. 3. Rock Types in Central White Mountain Batholith. A, B, and C show locations of drill sites.

Table III. Major Rock Types and Thorium Contents in the
Central White Mountain Batholith

Rock Type	Number of Stations	Average Thorium, ppm	Square Miles
Conway granite	214	56	307
Mt. Osceola	98	43	100
Porphyritic quartz syenite	28	38	28
Syenite	19	23	7

A number of the outcrop measurements taken on the side of mountains representing over several hundred feet of natural relief showed no dependence of thorium concentration with depth. However, to obtain more definite data on the deep and less-weathered material, three 1-1/8-inch-diameter drill cores were taken during the summer of 1962 at locations A, B and C shown in Figure 3. Core A (off the Kancamagus Highway) and Core B (at Diana's Baths area) reached a depth of 600 ft. Core C (in the Mad River area) reached a depth of 500 ft. As shown in Table IV, analysis of the cores at 5 ft intervals by a field gamma-ray spectrometer revealed a rather constant thorium concentration throughout the core (41,53). Physical observation of the cores indicated typical Conway granite throughout with the exception of a relatively large dike in the Mad River core at the 300-ft level. However, the garbage rock was <0.5% of the total drilled. On these bases, Adams and Rogers have estimated a minimum indicated reserve of 21 million tons of thorium metal in the outer 600 ft of the main Conway granite. There is a probability of at least twice this amount and possibly several times this amount by going to greater depths.

Over a dozen samples from widely scattered locations in the Conway formations have been evaluated with regard to thorium recovery. The thorium concentration in the samples ranged from 36 to 106 ppm, averaging 58 ppm, or essentially the same as indicated by the radiometric field data. A range of 52 to 85% or an average of 72% of the thorium was dissolved by the sulfuric acid (2 N) leach (Table V). The uranium content of the samples ranged from 6 to 14 ppm and averaged 11 ppm. The uranium recoveries were lower than those for thorium, averaging 56% and ranging from 26 to 75%. Acid consumption was relatively high, ranging from 55

Table IV. Thorium Content of Conway Granite Cores

Depth, Feet	Thorium Concentration, ^a ppm		
	Core A (Kancamagus Highway)	Core B (Diana's Baths)	Core C (Mad River)
0-100	54	54	69
100-200	52	55	70
200-300	51	48	76
300-400	47	56	67
400-500	56	58	76
500-600	68	64	

^a Average of radiometric measurements taken at 5-ft intervals.

Table V. Estimated Costs for Recovering Thorium and Uranium from Conway Granite

Conditions: -48 mesh or -100 mesh ore leached 6 hr at room temperature with 2 N H₂SO₄, 50% pulp density

Sample Location	Head Conc., ppm		Recovery in Leaching, %		Acid Consumption (lb H ₂ SO ₄ /ton ore)	Estimated Recovery Cost ^a (\$ per lb Th+U)
	Th	U	Th	U		
North Conway Quadrangle, N. H.	50	13	60	26	93	75
Crawford Notch Quad., N. H.	48	12	52	39	109	89
Plymouth Quad., N. H.	54	12	84	73	80	44
North Conway Quad., N. H.	56	7	53	51	66	70
Plymouth Quad., N. H.	64	12	84	60	60	38
Franconia Quad., N. H.	76	14	58	50	72	46
North Conway Quad., N. H. ^b	70	14	78	60	80	38
North Conway Quad., N. H.	45	6	67	49	93	75
Crawford Notch Quad., N. H.	52	12	67	65	111	62
Ossipee Lake Quad., N. H.	106	13	82	75	80	25
Mt. Ascutney, Vt.	36	6	80	49	55	72
North Conway Quad., N. H.	46	10	85	61	77	53
Mt. Chocorua Quad., N. H.	51	8	81	69	86	52

^a Assumes direct mining costs of \$0.68/ton in each case.

^b Average test results for 5 samples from the Redstone Quarry, Conway, N. H.

to 111 lbs per ton or an average of 85 lbs/ton. Estimated recovery costs ranged from \$25 to \$89 per lb Th + U recovered and averaged \$57. The data in Table V were obtained from tests with outcrop samples. However, recent leaching tests with drill core samples showed no significant variation in thorium leachability with depth in the formation. Consequently no important change in process amenability is expected for granite mined to a depth of at least 600 ft.

Granites from Maine, Massachusetts, Rhode Island

Granitic rock samples from southwestern Maine, Massachusetts, and Rhode Island were, on the average, considerably above the earth's crustal average in thorium content (41). For example, 22 samples from southwestern Maine ranged from 11 to 78 ppm in thorium concentration, averaging 28 ppm; 9 samples from Massachusetts ranged from 9 to 38 ppm, averaging 19 ppm; 4 samples from Rhode Island ranged from 16 to 64 ppm, averaging 32 ppm. A number of these samples have been tested with respect to process amenability and, in general, have responded well (42). Pending further study, granites from these areas could represent attractive large-tonnage thorium sources.

Other Low-Grade Thorium Sources

Other potential low-grade sources including bauxites, sub-lateritic soils, and volcanic rocks have been studied briefly (41,42). For one or more reasons, including, for example, low thorium content, relatively small tonnages available, poor recoveries in leaching, and high acid consumption, none of these sources appear as attractive as granitic rock for long-range thorium production.

Summary

Although the amount of information on thorium reserves has been increased considerably during the last few years, exact relationships between their extent, thorium concentration and treatment costs cannot be drawn in most cases. Nevertheless, for current consideration of a thorium fuel cycle, several reasonable assumptions can be made. For example, it may be assumed that there is a sufficient supply of low-cost thorium to initiate a large-scale thorium fuel reactor industry. Further, it is possible that larger quantities will be found which could support the industry for an appreciable period of time. As these low-cost reserves are depleted, sizeable reserves at moderate costs are attainable from the relatively high-grade Conway granites or others of equivalent or nearly equivalent quality. By accepting lower-grade granites, immense reserves should become available which could supply a nuclearpower industry for a very long period of time, and at nonprohibitive costs, pending development of successful breeder reactor systems. It should also be noted that the granite reserves described in this paper have been entirely from the United States. There is every reason to expect that granites of relatively high thorium content, possibly surpassing the Conway granite, will be found in many other parts of the world.

The processing methods currently available for treating the high-grade thorium ores are acceptable from the standpoint of both operation and economics. Although future improvements can be expected as a natural outcome of advancing technology, they will

probably not be large or dramatic. The present methods for processing low-grade sources are essentially the same as for the high-grade ores and are also technologically and economically acceptable. Owing to greater room and incentive for improvement, larger future advances in these processes are more probable. Sizeable cost reductions are not likely to be attained through modification of existing unit operations, or replacement of a single unit operation with another, unless this considerably improves recoveries. Significant savings might eventually result from combinations of completely new developments such as atomic blast mining and crushing, in situ leaching, bacterial leaching, etc.

Acknowledgments

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Footnotes

1. Descriptions of reagents and suppliers are given in references 16 and 21.
2. An informal meeting on thorium (and uranium) reserves was held at ORNL on February 29-March 1, 1960 and attended by the following: H. H. Adler, A. L. Benson, D. R. Miller, R. S. Nininger, J. M. Vallance, and Jack Vanderryn of the U. S. Atomic Energy Commission; J. C. Olson and George Phair of the U. S. Geological Survey; J. J. W. Rogers of Rice University; E. D. Arnold, K. B. Brown, C. F. Coleman, D. J. Crouse, F. L. Culler, W. K. Ergen, A. T. Gresky, J. A. Lane, H. G. MacPherson, and A. M. Weinberg, of ORNL.
3. Cost estimates were made in cooperation with A. H. Ross and Associates of Toronto, Canada who, in turn, received advice on mining operations from prominent metallurgical companies. Estimation of capital costs for mining were made by C. C. Huston and Associates, Toronto, Canada.
4. The costs given are for open-pit mining to depths of one or possibly several thousand feet. They are not intended to represent costs that would be incurred in, for example, mining most of the earth's crust to depths of several miles.

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Session I
Paper 4

A REVIEW OF THORIUM REACTOR PHYSICS

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A REVIEW OF THORIUM REACTOR PHYSICS

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1.0 Introduction

To a large extent, a review of thorium reactor physics amounts to a review of reactor physics in general, particularly when it is considered that thorium can be utilized with plutonium, and can be used in fast as well as thermal reactors. The object of this review is to place in perspective reactor-physics information as it applies to power-reactor evaluation, and to point out areas where additional information is needed in order to properly guide reactor development programs. Where applicable, emphasis will be placed on thorium systems.

Very much information is involved in a review of this kind, and assimilating and presenting it in a clear and logical fashion requires significant effort. The present paper is not as complete as desired; however, the general conclusions are believed to be valid. In general, this presentation is in summary form rather than one involving detailed discussion. The sections which follow treat special features of thorium reactors, cross-sections of various nuclides, and reactor calculations and critical experiments. This is followed by recommendations concerning areas where special emphasis is needed at this time.

2.0 Special Features of Thorium Reactors

From both the short- and long-term viewpoints, the supplies of thorium and uranium appear adequate for power reactor use, and so the success of thorium as well as uranium systems depends primarily upon the economic success

of reactor technology. Related to this is the basic neutron economy achievable in the systems, as determined by reactor physics considerations. However, it is not realistic to separate reactor physics work from the economic considerations associated with the material physical properties and behavior under irradiation, material costs, fuel fabrication and processing costs, and economic ground rules. Thus, other information should be combined with the reactor physics features in evaluating the desirability of one fuel or reactor type relative to another.

Since natural thorium contains no fissile fuel, it starts from a basic disadvantage relative to natural uranium. However, in certain cases this can be more than compensated by superior physical and/or nuclear properties. In the case of metallic fuels, thorium behaves better under irradiation than does uranium, permitting longer fuel lifetimes relative to radiation damage limitations; such lifetimes of course, must be consistent with achievable reactivity lifetimes. Also, thorium has about the same thermal conductivity as uranium, and a higher melting temperature. Another special feature is the high solubility of thorium and uranium in molten fluoride salts, which permits their use as fluid fuels. Plutonium is not sufficiently soluble in these salts to permit its use as a fluid salt in high conversion-ratio systems. Generally, the molten-salt fuels have better physical properties than other fluid fuels for both thermal and fast reactor applications; also, there presently exists a simple processing scheme for the recovery of uranium from these salts. Thus, the thorium fuel cycle may have a basic advantage relative to achieving low-cost processing and fueling methods. All of the above factors affect reactor design, and in so doing they influence the effective reactivity lifetime to as great a degree as do reactor physics considerations per se.

Another economic feature is the fabrication cost of recycle fuel. Re-fabrication of irradiated thorium fuels is complicated by the presence of radioactive decay products resulting from the $(n,2n)$ reaction on thorium. Although some control of the $(n,2n)$ reaction is possible through proper placement of thorium in the reactor, recycle-fuel fabrication problems are not eliminated by this means.

Associated with thorium systems is a delayed neutron fraction which is smaller than that in similar uranium systems. Also, since U^{233} results from the decay of Pa^{233} which has a 27-day half life, there is a time delay in the production of bred fuel. Following a reduction in reactor power, the formation of U^{233} without concomitant burnup causes the reactivity of the reactor to increase; however, such reactivity changes would occur very slowly. While both of the above features must be treated when properly designing a reactor system, it does not appear that any significant safety, control, or economic difficulties arise because of the above reactivity behavior.

The relatively long half life of Pa^{233} does influence economics in other ways, however. The breeding ratio of the system is of course influenced by neutron absorptions, and Pa^{233} has a significant absorption cross section. Since Pa^{233} absorption removes a potential fissile fuel atom as well as a neutron, a double loss occurs. Also, present processing methods do not remove Pa as a product. The fuel holdup required in order to permit the Pa to decay to U increases the fuel inventory of the reactor system and increases the doubling time.

In the following sections, special features associated with thermal and fast reactors are discussed.

2.1 Thermal Reactors

A primary advantage associated with thermal, thorium reactors is the superior nuclear properties of the bred U^{233} ; specifically, this advantage results from the high η value of U^{233} in the thermal and epithermal energy regions. Relative to the use of plutonium or U^{235} as fissile fuel, U^{233} permits higher conversion ratios over the fuel cycle for a given fuel enrichment; this leads to longer reactivity lifetimes and greater return of fissionable material at the end of the fuel cycle, and these factors are important in reducing fuel costs. The above features are also important economic factors when considering recycle fuel, and tend to favor use of U^{233} -Th rather than Pu- U^{238} as recycle fuels in specific reactor designs optimized on the basis of the initial fuel cycle.

An area which requires considerable further study is the combined use of thorium and uranium. The nuclear properties of these materials and their associated bred fuels are quite different, so that combined use permits more flexibility in the nuclear design of a reactor core. Specifically, thorium has a thermal cross section which is about 2.7 times greater than U^{238} ; the infinitely dilute resonance integral is about one-third that of uranium. Also, the variation of the thorium effective resonance integral with lattice geometry, material concentration, temperature, etc., is different than for uranium, since nearly all the resonances of the two fuels occur at different energies and have different resonance widths. As a result, the resonance capture per fertile atom can be greater in mixtures of Th and U than in the separate materials. For the fertile fuels, Pu²³⁹ has a much higher fission cross section than U^{233} , but also a much higher α value. Because of these different properties, proper combination and distribution of uranium and thorium throughout a reactor can result in longer reactivity

lifetimes, and/or flatter power distributions and smaller reactivity control requirements during fuel exposure, relative to the use of thorium or uranium alone. Another area which has not been investigated thoroughly is the use of recycle plutonium with thorium. Such fuels permit long reactivity lifetimes with relatively little reactivity change over a batch-type fuel exposure; however, the economic virtue of this cycle is very dependent upon the price of recycle plutonium and fuel fabrication costs.

Use of thorium rather than uranium as a fertile material often results in a larger negative Doppler temperature coefficient of reactivity. This feature would normally improve inherent reactor safety. Also, the optimum lattice spacing for a thorium reactor is "tighter" in a nuclear sense than that for a uranium reactor, partly because of the higher epithermal-to-thermal η value associated with thorium systems. Thus, use of thorium may be advantageous in regions of a reactor where the lattice is naturally "tight"; i.e., in the vapor regions of a boiling reactor, or in steam-cooled, superheat regions.

2.2 Fast Reactors

Most studies concerning fast reactors have been of U-Pu systems, since Pu fuels have the highest potential with regard to breeding ratio and doubling time. However, if safety, engineering, and materials considerations lead to a relatively soft neutron spectrum, the nuclear performance of Th-U systems can be comparable with U-Pu systems. Cores utilizing metallic U-Pu fuels have a much higher nuclear potential than cores using metallic Th-U fuels, because of the specific variations in nuclear constants at high neutron energies. A metallic-fueled core has a mean fission energy of about 300 kev, regardless of whether U or Th is used as the fertile material. The greater potential of the U system is associated with the larger fast fission factor

of the fertile material (at high energies the fission cross section of U^{238} is about four times greater than that of Th), and the higher η values of Pu relative to U^{233} at high energies. This higher potential can be realized if fuel processing costs and recycle-fuel fabrication costs become very low. Presently, however, these costs are high and may remain appreciable for a long time; this factor combined with the poor radiation-damage resistance of metallic uranium fuel at high temperatures has led to emphasis of ceramic fuels. On the other hand, metallic thorium exhibits relatively good physical behavior upon exposure, and it may be realistic to compare the nuclear behavior of metallic Th-U cores (or that of cermet) with U-Pu oxide cores.

Core meltdown is a primary safety problem in fast reactors, since its occurrence may lead to the reassembly of a critical mass in a different portion of the core. In particular, avoidance of coolant vaporization in liquid-metal-cooled systems is important, since small amounts of vapor significantly reduce the heat-removal capability of the coolant. Thus, much emphasis is placed on insuring a negative prompt temperature coefficient of reactivity. Some of the same factors which give U-Pu systems breeding-ratio advantages over Th-U systems lead to safety advantages for the Th-U fuel. If coolant such as sodium were lost from the core, there would occur a neutron spectral-hardening effect leading to a reactivity addition, and a neutron-leakage effect causing a reactivity decrease. The spectral-hardening reactivity effect would be due to: (1) the associated increase in average η , (2) the increase of fast fissions in the fertile material, and (3) the decrease in parasitic captures; the first two of these factors have a smaller magnitude in thorium systems, which leads to an inherent safety advantage. Thus, from a safety viewpoint, less emphasis would be required in thorium reactors with regard to increasing the neutron leakage effect, and this design advantage permits a higher breeding ratio than would otherwise be the case.

3.0 Cross Sections

Uncertainty in cross sections can lead to uncertainties in breeding ratio, fuel inventory, and other factors. Specifically, economic penalties result if the nuclear design has not been optimized with respect to the actual attainable fuel lifetime; changes in cross sections can affect the refueling schedule, the reactivity-control requirements and also the spatial power distribution. Still another area in which knowledge of cross sections is important concerns the choice of one fuel over another; uncertainties in cross sections lead to uncertainties with regard to the desirability of one fissile fuel over another.

The accuracy required of cross sections depends on the influence these have on reactor safety and economics. The specific influence varies with each reactor, and so a large variety of conditions need to be evaluated in order to specify cross section needs in detail. Much information on cross sections of the various elements has been accumulated through the years, and presented in reports (such as BNL-325), various journals, and in the newsletters issued by the Cross Section Evaluation Group at BNL. In this review, the cross sections of the heavy elements are of most concern. Within the past few years there have been several competent reviews of the cross sections of fissile materials, primarily in the thermal energy region. Also in this period of time there have been a large number of experimental measurements of heavy-element cross sections. Only the accuracy of cross sections for fissile fuels, fertile fuels, and some other heavy elements is discussed here.

3.1 Thermal Fissile Fuels

U²³³. The total cross section in the thermal energy range up to 0.2 ev has been measured by various investigators, and the reported errors lie in

the range of $\pm 1/3$ to $\pm 1\%$. In general, it appears that the total cross section in this energy range is accurate within $\pm 1/2\%$; the fission cross section is probably accurate within $\pm 1\%$, its accuracy being less than that of the total cross section because of uncertainties in the scattering cross section. In the energy range of 0.2 to 5 ev, the total cross section of U^{233} appears to be accurate within $\pm 1-3\%$, while from 5-10 ev the accuracy is probably within $\pm 3-5\%$. The fission cross section in this energy range is not known as well as the total cross section, although it appears better known than the variation of η . This latter quantity is probably known within $\pm 5\%$ up to 5 ev, and to within $\pm 10\%$ up to 10 ev. At energies greater than 10 ev, the cross section data are not very accurate, with values probably known within $\pm 10\%$ from 10-30 ev, and within $\pm 10-20\%$ at energies up to about 65 ev. Measurements have been made of the fission resonance integral and the average resonance value of α within about $\pm 10\%$. Also, values for α^{23} over discrete energy ranges from 30 kev to 1 Mev have been obtained with estimated errors of $\pm 10\%$.

Better measurements are currently being made and are being extended to cover wider energy ranges; this is particularly true for the higher energies. Values of cross sections, resonance parameters, η , ν , and α are being obtained.

U^{235} . The accuracy of the present U^{235} cross section values appears to be either the same or slightly better than that for U^{233} , particularly at low energies. Because of the large quantities available and its low radioactivity, the cross sections of U^{235} could be determined with higher accuracies and less effort than for U^{233} . In the range of 30 kev to 1 Mev, discrete-energy values for α^{25} were obtained, having an estimated error of $\pm 10\%$. Experiments are planned to measure α^{25} from 10 ev to 500 kev.

Pu²³⁹. Because of its natural radioactivity, there are special difficulties in accurately measuring the cross sections of plutonium. Thus, in general, the Pu²³⁹ cross sections are not known as well as those of U²³³ or U²³⁵. Up to 1 ev, the total cross section of Pu²³⁹ is probably accurate within $\pm 2\%$; the accuracy of the fission cross section is perhaps $\pm 5\%$. The shape of the fission cross section is known better than the absolute values, and is probably accurate within 2% , up to 1 ev. Measurements of η^{L9} in the 5-10 ev range have a probable accuracy of $\pm 5\%$; up to 50 ev, measurements of the fission cross section and η^{L9} have an accuracy of about $\pm 10\%$ in the resonances (regions of most importance). Discrete-energy measurements have been made of α^{L9} from 30 kev to 1 Mev, with an accuracy of about $\pm 10\%$. Experiments are planned to measure α^{L9} in the 10 ev - 500 kev energy range.

Pu²⁴¹. Fewer measurements have been made of the Pu²⁴¹ cross sections than of the Pu²³⁹ cross sections, due to lack of adequate samples in the past. At the present time, the fission cross section of Pu²⁴¹ up to about 100 ev has been measured to about the same accuracy as that of Pu²³⁹. The total cross section is not as well known as that of Pu²³⁹.

3.2 Thermal Fertile Materials

Th²³². The cross section of thorium is well known in the thermal energy range; however, the resonance integral and resonance parameters often employed at the present time may have errors of about $\pm 15\%$. Above about 100 ev, the absorption cross section appears to be known satisfactorily; below 100 ev the measurements are fairly old, and the accuracy of the measurements could be improved.

U²³⁴. The thermal absorption cross section of U²³⁴ is known within about $\pm 5\%$, and the resonance integral is known within $\sim \pm 10\%$.

U²³⁸. The cross sections and resonance parameters of U²³⁸ are apparently known more accurately than those of any other nuclide considered here.

Pu²⁴⁰. The cross sections up to and including the 1-ev resonance appear to be adequately known for reactor calculations. The thermal cross section is known within $\pm 5\%$; the first resonance accounts for most of the measured resonance integral.

3.3 Some Other Heavy Elements

Pa²³³. The measured thermal cross section and the gross resonance integral of this element appear to be accurate within about $\pm 10\%$. Cross-section measurements in the energy range of 0.5 - 10 ev are continuing; current results account for only about 1/3 of the measured resonance integral.

U²³⁶. The accuracy of the thermal cross section is about ± 20 - 30% , and that of the resonance integral is perhaps $\pm 10\%$.

Pu²⁴². The thermal cross section is known within about $\pm 10\%$, and the accuracy of the resonance integral is perhaps $\pm 20\%$.

3.4 High-Energy Cross Sections

The above cross-section information concerned measurements in the thermal- and resonance-energy regions primarily. Considerable information about the high-energy cross sections of the heavy elements has been accumulated, with emphasis placed on those elements which are fissionable in fast reactors. Thus, measurements have been made on thorium, uranium, and plutonium, and include data on fission, capture, and inelastic cross sections. The fission and total cross section measurements are usually accurate within about $\pm 3\%$. However, based on comparisons of experimental and theoretical results for fast critical assemblies, it appears that there are some cross sections, particularly the scattering and absorption cross sections of coolant and structural materials, which are not known as accurately as desired for reactor calculations. Also, experimental measurements of the inelastic scattering cross section of thorium are required.

3.5 Gross Fission-Product Cross Sections

The best estimates for gross-cross-section values are obtained from yield and cross section data for the individual fission fragments, together with theoretical calculations. The probable error associated with the calculated gross-fission-product thermal cross section appears to be $\pm 10\text{--}20\%$ for a given fuel, while that associated with the gross resonance integral is perhaps $\pm 20\text{--}30\%$. In high energy reactors the probable error associated with the gross cross section is estimated to be about $\pm 50\%$. In calculating the gross cross section, it is important that non-steady-state conditions, decay processes, and higher order reactions be specifically included, since each of these items can have a significant influence on the effective gross-cross-section value.

Measurements of gross cross sections have been restricted to U^{235} fission products; most of the associated values based on the experimental data are of sufficient variation so as to neither prove nor disprove the adequacy of calculated gross values. However, the latest measurements appear to have sufficient precision for thermal reactors, and give very good agreement with the calculated thermal values (within a few per cent); the measured resonance-integral values were within 15% of calculated values.

Relative to thermal reactors, reducing the error in the gross fission-product cross section from $\pm 20\%$ to $\pm 10\%$ for a given fuel could provide fuel cost savings of about 0.02 mill/kwh(e) because of better definition of the nuclear design associated with minimum fuel costs. When a choice of two fuels exists and there is a 20% difference between the gross fission-product cross sections associated with the two fuels, utilization of the fuel with the lower fission-product cross section can result in fuel cost savings of about 0.2 mill/kwh(e) due to differences in cross section per se.

4.0 Reactor Calculations and Critical Experiments

Within the past few years a large number of reactor computations and critical experiments have been performed. The majority of work has been done on uranium systems, but the accuracy of results should be representative also of that obtainable in thorium systems, if the basic nuclear data of the two fuel systems are known to the same degree. It is important that criticality calculations give agreement with experimental results, since the nuclear potential and the final nuclear design of a reactor system are at least partially based on such calculations. The ability to correctly predict reactivity and power distributions depends upon the reactor geometry, size, and composition, the mathematical model which can be utilized in a practical manner, and the availability of proper nuclear constants. This part of the presentation briefly considers thermal reactors, fast reactors, and the use of machine computations.

4.1 Thermal Reactors

In general, the use of sophisticated, yet practical calculational models presently available permits estimation of reactivity within $\pm 1\%$, and power distributions within $\pm 10\%$, provided the necessary cross section data are available. For H_2O reactors, this degree of accuracy is achievable with few-group diffusion-theory computations if the few-group constants are based on fast- and thermal-spectrum calculations and include self-shielding and disadvantage-factor calculations. This over-all agreement between calculations and experiment is often achieved in spite of areas in which better understanding is needed. An absolute evaluation often cannot be made because of the uncertainty in some of the cross-section data and/or the experimental measurements, and to the difficulty of evaluating in retrospect the effect of different calculational methods and input data on the results.

Few-group diffusion-type calculations, with group constants based on relatively elaborate one- or non-dimensional spectral computations, have also been used successfully for reactors having a moderator other than H_2O ; e.g., D_2O , Be or graphite. In general, sophisticated multigroup calculations are required for cases where neutron leakage effects are quite important. For beryllium-moderated reactors, small changes in the energy distribution of the $(n,2n)$ cross section, even though within the experimental uncertainty of the cross section, can significantly affect the computed multiplication constant. Also, the use of isotropic- rather than anisotropic-scattering cross sections for Be can change the calculated reactivity by several per cent. In large graphite reactors it is important to calculate thermal neutron spectra in detail in order to properly estimate the temperature coefficients of reactivity and the reactivity control needed in safety rods. Large-lattice reactors, such as those using D_2O moderator and clustered-rod fuel elements, require accurate formulations of the resonance escape probability as a function of the lattice geometrical complexity and material composition.

4.2 Fast Reactors

The computations usually performed for fast reactors consist of multigroup calculations using transfer coefficients; both diffusion-theory and transport-type approximations have been employed. Agreement between calculations and experimental results has improved with time; this improvement was achieved by considering the detailed energy variation of scattering cross sections, proper evaluation of geometrical factors, updating the cross section data, and also by arbitrary adjustment of group cross-section values. While there are cases of good agreement between results of calculations and experiments (e.g., a difference of less than 1% in reactivity), group cross

sections which were adequate over a large range of moderately dilute assemblies have not been sufficiently accurate for some subsequent, highly dilute cores.

Usually the differences between calculations and experiment are attributed to inaccuracies in group cross sections. In particular, it appears important to know the detailed energy variation of the scattering cross sections of thorium, coolants, and structural materials. For some structural materials, the absorption cross section as a function of energy has not been adequately determined.

4.3 Machine Computations

Nearly all calculations of a repetitive nature can be performed faster, more accurately, and more economically by large-scale computers than by hand calculations; also, fewer arbitrary safety factors are being included in reactor designs and this requires increased accuracy in design calculations. As a result, elaborate and sophisticated computations are often required. A large number of such machine programs have been written, particularly in the reactor physics field. These programs are extremely useful in reactor design and evaluation, and relatively easy to use. The specific calculations vary with the reactor program and the personnel involved, the capacity of the computing machines employed, and the cost of machine time.

Generally, the more sophisticated calculations are associated with specific design problems, with comparative-reactor-evaluation studies utilizing combined programs; these latter consist of several individual machine codes which have been combined into a single program. Often these combined (or automated) programs make use of relatively simple and/or moderately complex individual machine codes. Updating these combined programs as better nuclear data and

computations become available is an area which needs emphasis in evaluating the relative merits of thorium and uranium reactors. There is a tendency to utilize a given set of group constants without evaluating its consistency with the latest available information; this is often due to the need of obtaining an answer quickly and the convenience of not changing data already written in the program. Because of this, comparisons of calculated results from one installation with those from another often have little meaning if only the over-all results are examined. Thus, a continuing effort is required by reactor evaluation groups with regard to: (1) keeping abreast of information on cross sections and available computer codes; (2) evaluating the adequacy of reactor physics data and the mathematical models employed; (3) keeping machine programs up to date as better information becomes available; and (4) knowing what nuclear constants are used and what computations are performed by other evaluation groups.

5. Summary and Recommendations

Thorium reactors are of particular interest because of the relatively high values of η^{23} associated with thermal and epithermal systems, the good physical behavior of thorium and some of its compounds, and because of certain inherent nuclear characteristics (associated with safety considerations) of fast reactors operating on the Th-U²³³ cycle. Also, the combined use of thorium and uranium as fertile materials permits flexibility with regard to relative absorptions in fissile and fertile materials as a function of neutron spectrum, for a given concentration of fissile fuel. Thus, thorium and uranium should be considered as possible complementary materials which may be utilized together advantageously. Also, combined use of Th-U-Pu is possible in core-blanket arrangements of either thermal or fast reactors; such combined fuel cycles can be advantageous under special economic conditions.

The accuracy of cross section information for thorium reactors is generally about the same as that for uranium systems. Good agreement between critical calculations and experiments has been obtained in many cases; however, there are nuclides and energy ranges where better cross section data are required, and situations where complex mathematical models need to be utilized. Thermal reactors require accurate formulations of resonance escape probability as a function of composition, size and geometrical complexity of heterogeneous lattices. Epithermal and fast reactors require additional information concerning the absorption and fission cross sections of U^{233} , the absorption cross section of Pa^{233} , the inelastic cross section of thorium, and the absorption and scattering cross sections of structural and coolant materials as a function of neutron energy. Experimental measurements are needed of the gross cross section of U^{233} fission products as a function of energy and of reactor fission spectrum, relative to those for other fuels. When calculating gross fission-product poisoning, it is important to consider non-steady-state conditions, decay processes and higher-order reactions.

More work is needed regarding the importance of one cross-section measurement relative to another. General reactor-evaluation studies should consider various combinations of nuclear constants (whose values fall within the uncertainty of the experimental data) in order to better determine the priority of cross-section needs. Such studies should also include investigation of the effect of cross section values on reactor safety characteristics.

There have been few general evaluations of the relative merits of Th-U and U-Pu fuels, and those which have been made often did not use present cross-section information. Also, the use of different calculational models and nuclear constants by different groups often makes it difficult to compare results.

Much additional work is needed in order to obtain a comprehensive view of proper fuel utilization. In such studies, use should be made of nuclear constants which are consistent with the latest cross-section data, and the mathematical models employed should be adequate for the reactor under consideration. Improvements in cross-section values and calculational methods should be incorporated as they become available.

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Special Features

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Cross Sections

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Reactor Calculations and Critical Experiments

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Session I
Paper 5

COMPARISON OF CRITICAL EXPERIMENTS AND
THEORY FOR SOME THORIUM-WATER LATTICES

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COMPARISON OF CRITICAL EXPERIMENTS AND THEORY FOR SOME THORIUM-WATER LATTICES

I. Summary

An extensive series of critical and exponential experiments has been performed with uniform lattices of fuel rods composed of fully enriched UO_2 in ThO_2 . These lattices were moderated by either H_2O or mixtures of H_2O and D_2O ranging up to 82 mole % heavy water. Lattice spacings ranged from those yielding a somewhat over-moderated core to those yielding an extremely tight lattice in which more than half of the fissions were epithermal. The experimental measurements included buckling, ratio of epithermal to thermal captures in Th-232 , ratio of epithermal to thermal fissions in U-235 , the thermal disadvantage factor, and water height reactivity worths leading to $\frac{\partial K_{\text{eff.}}}{\partial B^2}$.

II. Experimental Technique

Four different types of rods containing thorium as the fertile material have been used in the experiments. Their characteristics are reviewed in Table 1. The fuel rods were comprised of pellets using an organic resin binder and sintered to density indicated in the slide. The cladding was type 304 SS in the case of the CETR pins and type 25 aluminum for the TUPE pins. The CETR pins contained 19 and 11.5 grams of U-235 in the 15/1 and 25/1 pins, respectively. The TUPE pins

TABLE 1
FUEL ROD CHARACTERISTICS

<u>Fuel Designation</u>	<u>TH U</u>	<u>Clad Material</u>	<u>Fuel Density</u>	<u>Rod Diameter</u>	<u>Fuel Diameter</u>
CETR-4	25.8	SS	8.35 (gm/cm ³)	.792	.660 cm
CETR-7	15.0	SS	8.35	.792	.660
TUPE-4	25.3	Al	8.45	.785	.594
TUPE-7	15.0	Al	8.45	.785	.660

contained 24 and 12 grams in the 15/1 and 25/1 pins, respectively. The rods designated CETR were used for the design of the Consolidated Edison Thorium Reactor and the TUPE-4 rods were used in a series of Thorium-Uranium Physics Experiments in collaboration with Argonne National Laboratory who performed similar measurements in heavy water. The TUPE-7 rods were used in the Spectral Shift Control Reactor program with mixtures of H_2O and D_2O as moderator.

All lattices had uniform square pitch. Care was taken to obtain right circular cylindrical configurations and criticality was achieved with control blades removed by adding fuel rods or by adjusting the moderator height. The lattice configurations are listed in Table 2. For the critical experiments the water moderator was raised to the full height of the fuel rods. Radial and axial bucklings were measured with gold, indium, or U-235 foils. Radial measurements were fitted by least squares to $J_0(B_r \gamma)$ over the asymptotic region. Axial measurements in the critical experiments were fitted to $\cos B_z Z$ and in the exponential experiments to $\exp(-B_z Z)$.

For the epithermal effects in U-235, thin aluminum - U-235 alloy foils with and without cadmium covers were inserted in a fuel rod and the fission product activities were compared with a pre-calibrated decay curve for U-235 fission products. Experimental values of δ_{25} (ratio of epithermal to thermal fissions in 235) were

TABLE 2
LATTICE CHARACTERISTICS

<u>Fuel Designation</u>	<u>Pitch, cm</u>	<u>M W</u>	<u>% D₂O in Moderator</u>	<u>Type of Experiment</u>
CETR-4	1.023	.890	0	Critical
CETR-4	.966	1.116	0	Critical
CETR-7	1.933	.152	0	Critical
CETR-7	1.367	.358	0	Critical
CETR-7	1.115	.656	0	Critical
CETR-7	1.023	.890	0	Critical
CETR-7	.966	1.116	0	Critical
TUPE-4	1.446	.301	0	Critical
TUPE-4	1.222	.480	0	Critical
TUPE-7	1.222	.480	0	Critical
TUPE-7	1.023	.860	0	Critical
TUPE-7	.978	1.024	0	Critical
TUPE-7	.983	.990	55.38	Exponential
TUPE-7	.983	.990	60.40	Critical
TUPE-7	.983	.990	71.94	Exponential
TUPE-7	.983	.990	81.16	Critical
TUPE-7	.983	.990	81.96	Exponential

then determined from the cadmium ratios. The cadmium ratios for Th-232 activation were measured using either thorium metal foils or ThO₂ wafers. These were inserted in a section of the fuel rod for activation. For the cadmium-covered runs, a cadmium sleeve replaced a section of the metal clad around the fuel rod. Values of ρ_{02} (the ratio of epithermal to thermal absorptions in Th-232) were then determined from these cadmium ratio measurements.

The rate of change K_{eff} with buckling was obtained from the usual straight line variation of the reciprocal cube root of the reactivity derivative with respect to height and the water height itself.

III. Theoretical Analysis

The theoretical analysis of these lattices utilizes a 39 group, extended Grueling-Goertzel slowing down model in the B_1 approximation to the neutron transport equation. The system of multigroup equations resulting from this approximation is given in equations (1) through (5):

$$B J(u) + \Sigma^A(u) + \Sigma^{in}(u) \phi(u) = S(u) - \sum_k \frac{dq_k}{du} - \frac{dq_F}{du} + I(u) \quad (1)$$

$$h(u) \Sigma^T(u) - \mu(u) \Sigma^S(u) \quad J(u) = \frac{B}{3} \quad (u) = \sum_m \frac{dp_m}{du} \quad (2)$$

$$r_k(u) \frac{dq_k}{du} + q_k(u) = \xi_k(u) \Sigma_k^S(u) \phi(u) \left[1 - \frac{d\tau_k}{du} \right] \quad (3)$$

$$q_F(u) = \sum_{\ell} \xi_{\ell}(u) \Sigma_{\ell}^S(u) \phi(u) \quad (4)$$

$$\zeta_m(u) \frac{dp_m}{du} + p_m(u) = \eta_m(u) \Sigma_m^S(u) J(u) \left[1 - \frac{d\zeta_m}{du} \right] \quad (5)$$

where

- u = lethargy
- $\phi(u)$ = flux
- $J(u)$ = current
- $q(u)$ = slowing down density from elastic scattering
- $p(u)$ = anisotropic component of slowing down density
- $I(u)$ = source from inelastic scattering
- B^2 = buckling
- $\Sigma^A(u)$ = absorption cross section
- $\Sigma^{in}(u)$ = inelastic scattering cross section
- $\Sigma^S(u)$ = elastic scattering cross section
- $\Sigma^T(u)$ = total cross section
- $S(u)$ = neutron source (usually from fission)
- $\mu(u)$ = average cosine of the scattering angle (laboratory system)
- $\xi(u)$ = average lethargy gain per collision
- $\tau(u), \zeta(u), \eta(u)$ = slowing down parameters

For the bare reactor in which asymptotic theory as characterized by Wigner is applicable, the Fourier transform variable with respect to space becomes the geometric buckling allowing the separation and removal of the spatial variation of the flux. The equations in the slide then, denote only lethargy dependent functions. The equations are solved for the unknown slowing down density, flux, and current in the BPG code which has been written for the Datatron 205. Spectrum weight averages are then performed to yield 4 group constants which can be used in one- or two-dimensional multiregion calculations.

Anisotropic scattering in the center-of-mass coordinate system was not considered in the calculations performed on these lattices except in the case of $\bar{\mu}$, where a quadratic variation in the differential scattering cross section was assumed and the Legendre coefficients calculated from the experimental differential scattering cross section data for oxygen and deuterium. Since all the Grueling-Goertzel parameters will be affected by anisotropy in C-system scattering, this treatment is somewhat inconsistent. To bring the code up-to-date a four term Legendre expansion of the Grueling-Goertzel coefficients as defined by Hurwitz and Zweifel has been made, and using the experimental differential scattering cross section data of Gerardo, the energy variation of these parameters has been computed and incorporated into the BPG library.

As mentioned previously the resonance absorption in a finite lethargy group is computed by obtaining the product of the slowing down density into the group and the absorption probability summed over the single peaks in the group, i.e.,

$$\text{Absorptions in a peak} = q_i (1-p)$$

Resonance integrals of single peaks are obtained from the resonance parameters using a Doppler broadened Breit-Wigner shape following the method given by Roe. The effects of lump size are accounted for by using the simple Wigner approximation to the escape probability in the rod and computing an effective σ_p^* , the potential scattering cross section per absorber atom in the lump. The lattice effects were computed using the Dancoff-Ginsberg formulation for the shielding factor which, in turn, was applied to the surface fraction of the resonance integral following the calculations of Nordheim. The effective lattice resonance integral was obtained from

$$R_{O2} (\text{lattice}) = R_{O2} (\text{single lump}) (1 - \delta) + \gamma \delta$$

where

δ = the surface fraction of the resonance integral

γ = the Dancoff factor

For the analysis, the calculated distribution in energy of the resonance integral was renormalized to agree with the Hellstrand and Weitman single pin ThO_2 data. Lumping and self-shielding effects for U-235 resonance absorption was included also. Resonance

parameters were used to compute the effective resonance integral of each line assuming a Breit-Wigner shape. In this case, however, the Dancoff factor was applied directly to the surface area in the definition of σ_p^* .

VI. Results

A comparison of a portion of the experimental and calculated parameters is shown in Table 3. The critical bucklings agree well over the range

$$5 \text{ M}^{-2} \leq B^2 \leq 115 \text{ M}^{-2}$$

with few exceptions. The k_{eff} agree quite well, the maximum error being about 2% in four lattices. Measured and calculated values of $\frac{\partial K_{\text{eff}}}{\partial B^2}$ are in fair agreement over the range 30 to 70 cm^2 . For the most part they agree with a Gaussian non-leakage probability. The values for this quantity are quite sensitive to computed values of the delayed neutron fraction and the results depend on the axial reflector savings being constant. Table 4 shows a comparison between experimental and calculated values δ_{25} , ρ_{02} , and the disadvantage factor for some of the lattices. The largest discrepancies appear in ρ_{02} . This is certainly partially due to the fact that resonance parameters for thorium are not as well known as, say those for U-238.

TABLE 3
COMPARISON OF EXPERIMENT AND THEORY I

<u>Fuel Designation</u>	<u>Critical Buckling</u>		<u>Calc. K_{eff}</u>	<u>$\partial_{eff}/\partial B^2$</u>	
	<u>Expt.</u>	<u>Calc.</u>		<u>Expt.</u>	<u>Calc.</u>
CETR-4	29.3	27.7	.994	39.8	38.2
CETR-4	26.2	21.5	.981	-	41.3
CETR-7	57	64.8	1.022	-	27.6
CETR-7	94	93.7	.999	-	27.6
CETR-7	84	82.7	.996	-	30.9
CETR-7	72	70.6	.995	-	33.9
CETR-7	61	60.0	.996	34.5	36.9
TUPE-4	53.5	55.8	1.007	-	32.3
TUPE-4	64.0	66.0	1.007	33.5	34.1
TUPE-7	114.2	115.5	1.004	27.7	29.7
TUPE-7	94.2	92.1	.993	39.4	35.8
TUPE-7	85.3	83.1	.992	43.7	38.5
TUPE-7	44.8	41.7	.981	-	61.3
TUPE-7	39.0	37.1	.988	59.3	65.1
TUPE-7	31.4	26.1	.961	-	76.2
TUPE-7	--	16.6	-	-	88.8
TUPE-7	22.7	15.8	.940	-	89.8

TABLE 4
COMPARISON OF EXPERIMENT AND THEORY II

Fuel Designation	δ_{25}		ϕ_{Fertile}		$\phi_W/\phi_{\text{Fuel}}$	
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
CETR-4	.157	.163	-	1.01	1.14	1.12
CETR-4	.210	.206	1.28	1.26	-	-
CETR-7	.221	.244	1.49	1.58	-	-
CETR-7	.292	.310	2.08	1.99	-	-
CETR-7						
CETR-7						
CETR-7						
TUPE-4	.053	.046	-	-	1.22	1.14
TUPE-4	.085	.070	-	-	1.16	1.13
TUPE-7	.130	.123	-	-	1.22	1.21
TUPE-7	.181	.220	-	-	1.12	1.19
TUPE-7	.266	.263	-	-	1.22	1.18

Session I
Paper 6

EPITHERMAL THORIUM REACTOR PHYSICS

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INTRODUCTION

For the past four years Atomics International has been studying the physics of U-235-Th epithermal systems under a research program sponsored by the Southwest Atomic Energy Associates. The main tool has been the Epithermal Critical Assembly (Figure 1), a multiregion, split-table assembly. The loading of core materials into the drawers and the drawers into the matrix is designed so that the boundaries of the core regions (Figure 2) approximate concentric spheres, as nearly as permitted by the rectangular matrix and the 2" by 2" by 1/8" building blocks. The regions are designed to satisfy two requirements: 1) to provide a test region at the center with a required spectra and 2) to provide a critical assembly for driving the test region and allowing reactivity measurements to be done. In order to minimize the disturbance of the neutron flux at the center, the test region is made as large as permitted by the limited amount of U-235 available (25kg). The U-235 is in the form of U_3O_8 clad in stainless steel and contains 14.7 grams of U-235 per plate. Other materials in this region typify other full-scale reactor materials: graphite, aluminum (for sodium), stainless steel, and thorium. The test region is surrounded by buffer region with nearly the same material composition as the test region, except for the substitution of U-235 for U-235 as the fuel. The buffer fuel plates are 93% enriched U metal plates which are clad on both sides with Al. Each plate contains about 40 grams of U^{235} . The amount of U^{235} in this region is determined so that the nuclear characteristics here will match those of the test region as nearly as possible, and thus reduce the boundary disturbance of the central neutron flux. Surrounding the buffer region is the decoupler region, which

Fig. 1. Epithermal Critical Assembly Machine.

PSEUDOSHERICAL, CONFIGURATION OF THE MULT-REGION CRITICAL ASSEMBLY

Fig. 2. Pseudospherical Multi-Region Core Used in Experiments.

is a shell of thorium that absorbs thermal neutrons, preventing their leakage from the driver region where the average energy is low to the inner regions where it is much higher. The next region is the driver, in which over 90% of the fissions take place. The driver fuel pieces are 50-mil-thick plates of 93% enriched U-Al alloy, each of which contains ~ 2 grams of U^{235} . It is this region which determines the characteristics of the assembly as a whole and is used to satisfy the second requirement - a critical assembly. The sizes of the regions are determined by their functions, the driver region size is adjusted to produce criticality. The entire assembly is surrounded by a polyethylene reflector.

Table I lists the compositions and sizes of nine cores. The cores comprised a series of spectra ranging from ~ 9 ev to 422 kev in median fission energy and included some specially designed cores to test certain properties of the multiregion cores (for example in determining the necessity of using U-233 to produce spectra for studying U-233 systems). By studying the nuclear characteristics of many materials in the wide range of spectra we are developing data to help study the economic possibilities and optimization of fast power reactors. Data on other aspects of affecting the reactor are being developed by other groups at Atomics International.

The calculations of both predicted and experimental data have been made using AIM-6, a multiregion, multigroup diffusion code. An 18-group set of cross sections, mainly from LAMS-2255 was used. The effective cross sections for thorium were calculated using ARES-I, a resonance integral code which gives group cross sections for lumps

TABLE I

COMPOSITIONS OF CORE 1 - 9

REGION	MATERIAL	CORE 1	CORE 2	CORE 3	CORE 4	CORE 5	CORE 6	CORE 7	CORE 8	CORE 9
Test	U-233 (kg)	--	9.85	--	1.68	19.73	23.18	4.26	24.45	24.45
	U-235 (kg)	29.77	--	22.20	--	--	--	--	--	--
	U-238 (kg)	2.24	--	1.67	--	--	--	--	--	--
	Th (kg)	--	88.11	88.05	46.71	138.52	196.68	117.86	219.97	219.97
	C (kg)	--	5.57	5.57	2.64	25.23	109.92	173.19	14.06	--
	Be (kg)	--	--	--	24.73	--	--	--	--	--
	Al (kg)	9.68	17.44	20.60	10.26	31.11	60.17	39.34	43.23	53.96
	Stainless Steel (kg)	20.11	34.12	35.41	13.31	69.02	59.51	11.92	88.32	88.32
	O (kg)	--	1.86	--	0.32	3.72	4.37	0.80	4.61	4.61
	Radius (cm)	14.02	18.85	18.85	18.85	24.26	31.52	32.18	25.53	25.53
Buffer	U-235 (kg)	46.35	--	--	--	33.30	--	--	44.08	44.08
	U-238 (kg)	3.49	--	--	--	2.51	--	--	3.31	3.31
	Th (kg)	--	--	--	--	58.59	--	--	167.87	167.87
	Al (kg)	4.00	--	--	--	63.93	--	--	48.70	46.49
	Stainless Steel (kg)	97.56	--	--	--	134.60	--	--	58.58	58.58
	C (kg)	--	--	--	--	--	--	--	10.22	--
	Radius (cm)	19.10	--	--	--	29.67	--	--	30.63	30.63
Decoupler I	C (kg)	--	--	--	47.85	--	--	--	--	--
	Al (kg)	--	--	--	7.31	--	--	--	--	--
	Radius (cm)	--	--	--	24.18	--	--	--	--	--

TABLE I

Compositions of Core 1 - 9

REGION	MATERIAL	CORE 1	CORE 2	CORE 3	CORE 4	CORE 5	CORE 6	CORE 7	CORE 8	CORE 9
Decoupler II	Th (kg)	824.57	824.57	824.57	489.28	724.44	507.30	401.39	625.00	625.00
	Al (kg)	17.60	17.60	17.60	10.30	14.74	10.62	8.91	13.16	13.16
	Radius (cm)	29.77	29.64	29.64	29.59	35.03	35.05	35.08	35.10	35.10
Driver	U-235 (kg)	13.35	15.85	15.85	15.78	17.58	16.37	18.17	16.76	16.70
	U-238 (kg)	0.98	1.16	1.16	1.16	1.29	1.21	1.34	1.23	1.23
	Polyethylene(kg)	105.05	125.00	125.00	124.46	137.74	128.16	142.48	131.13	130.68
	Al (kg)	122.35	137.57	137.57	137.10	158.99	150.44	162.60	152.93	152.54
	Stainless Steel (kg)	54.11	60.53	60.53	60.53	81.25	77.59	77.59	76.82	76.82
Reflector	Radius (cm)	41.15	42.42	42.42	42.37	46.38	45.90	46.74	46.02	46.00
	Polyethylene (kg)	98.87	98.87	98.87	98.87	121.41	121.40	121.40	121.40	121.40
	Al (kg)	34.37	34.07	34.07	34.07	42.75	42.75	42.75	42.90	42.90
	Stainless Steel(kg)	30.83	31.97	31.97	31.97	44.47	44.47	44.47	44.17	44.17
	Radius (cm)	46.51	47.55	47.55	47.52	51.69	51.28	51.97	51.38	51.36

and mixtures. The inelastic scattering cross section of thorium used was the nonelastic cross section of U-238 minus the fission cross section of thorium; the (n, γ) cross sections were assumed negligible in this energy range. The same type of probability distribution for the inelastic matrix as that used for U-238 was assumed for thorium. Table II gives some data on the first nine cores.

TABLE II

CORE DATA

Core	Fuel	Mod. Vol. %	Median Fission Energy kev	Keff* (Calc)
1	U-235	0	422	1.0000
2	U-233	12 (C)	127	0.9972
3	U-235	12 (C)	140	0.9997
4	U-233	50 (Be)	0.0096	1.0099
5	U-233	25 (C)	63	1.0074
6	U-233	50 (C)	4.7	0.9959
7	U-233	73 (C)	0.0085	0.9933
8	U-233	12 (C)	127	1.0012
9	U-233	0	189	1.0012

* Measured keff = 1.000

REACTIVITY MEASUREMENTS

Figure 1 shows the reactor with the central $7/8$ -in.-square hole along a diameter parallel to the oscillator motion. The oscillator carriage is on rails at one end of the assembly so that the carriage can be moved away from the reactor when the experiments are completed; the oscillator support is completely separated from the reactor. A steel bar is driven into the reactor by means of an electric motor and screw. The bar can then be oscillated on a 24-in. stroke by means of a double-ended air piston.

The bar has two pockets; the first for a dummy sample so that it has no effect on values to be measured; the second for the sample of interest. Steel was chosen to prevent streaming through the hole and because of its similarity to the test region materials; tests have been made with a brass bar and no difference in the measurements was noted. The piston will interchange sample positions in less than 200 msec (speed is important because of the high cross section ratio between the driver and the test regions). The in and out times are adjusted to be nearly the same.

The sample changers and sample are seen in Figure 1. Each changer has ten positions and is controlled and monitored from the control room. The samples are 2 by $1/2$ inch in diameter so that the perturbation and self-shielding effects in the fast spectra are small. In addition, several weights of the same material are used for the more reactive samples. The reactor was made spherical and with thin plates to simplify the calculations. In addition, the flux and adjoint values were experimentally checked with threshold detectors and neutron sources; these measurements are described later. The system was designed so that the major reactivity effect is produced by the sample and not in some extraneous manner.

Figure 3 shows the data recording system. Current from a BF_3 ion chamber is amplified with a vibrating-reed electrometer whose output voltage is converted to a pulse train, with a frequency proportional to the reactor power. This train is counted over 0.6-second intervals on a 200-channel time analyzer. Since the oscillation cycle is one minute, two complete cycles are recorded on the analyzer in one pass. Immediately after the pass the analyzer is started again, making the signal in phase with that already recorded. Many passes of this type can be made. The signal shape is completely retained while the noise averages itself out. The chamber is sensitive enough and in such a position to allow the major noise to come from the reactor itself. It is also insensitive to radiation not directly from fission, and which hence does not perturb the reactivity measurement. The timer controls both the firing of the oscillator and the start of the time analyzer. The relative times are independent.

Figure 4 shows a typical output of a large sample, $\sim 1\text{g}$, with a large scale expansion. This data is printed out and then fed into the digital analysis code.

Figure 5 shows the type of calculation done. The data include several contributions in addition to the wanted data. The time between firing the oscillator and starting the analyzer has been adjusted so that the fundamental component of the signal is in phase with the cosine and then an approximate Fourier analysis is performed. This eliminates the contribution from the constant B term and the linear $C\theta$ term, as well as any term D of a double frequency. One such effect occurs from the passage of the sample through the driver twice during each cycle. If this can be kept exactly 180° out of phase, it is completely

Fig. 3. Schematic of Data Recording System.

Fig. 4. Reactivity Measurement Data on Analyzer Screen.

$$ANS = \frac{\int_0^{2\pi} [S(\theta) + N(\theta) + B + C\theta + D(2\theta) + OTHER(\theta)] \cos \theta d\theta}{AB.}$$

$$\Delta k_e = \frac{\int_0^{2\pi} S(\theta) \cos \theta d\theta}{AB}$$

Fig. 5. Calculation Performed in Oscillator Data Analysis.

eliminated; it is also kept small by fast movement. The effect of noncriticality is eliminated to the first order in the cosine analysis, and calculations and experiments show that a 25,000-sec period is more than sufficient for measurement of $10^{-8} \Delta k$. This has proven easy to obtain with our reactor because of its stability and the regulated temperature of the room.

The remaining term is noise from the reactor which finally limits the sensitivity of an oscillator experiment. The method of data taking preserves the signal information and has started reducing the noise. The cosine integration quite nearly performs a least squares fit on the 100 data points per cycle. Little improvement can be gained from a larger number of channels or the higher order components in the analysis. Provision is made in the digital computer to enter the number of passes, a bucked out current and scale expansion factors. The output is the cosine component and reactivity in cents as well as the sine, sum, and phase angle. The system is calibrated by finding the reactivity by a second method (Δk vs t), but can also be done by calculation of the transfer function. Agreement is about 1%. On several samples per core, the first three Fourier components are calculated to check the system, especially the absence of the second component and relative amplitudes of the first and third, and phase shifts. The final answer is the result given by the code corrected for the bar oscillation with no samples.

Two sensitive checks are performed on the system. The transfer function is measured around the measurement frequency and compared to theory. Also, the reactor power is calibrated by observing the noise output at the measurement frequency as well as several others. The source

insertion method with a mock fission source gives 1.10 scale division per watt on the reactor linear power recorder; 0.94 on the experimental channel; 0.945 by absolute fission counter; 0.98 source oscillation compared with $0.93 \pm 10\%$ by noise at 7.6 watts, and $1.06 \pm 10\%$ at 66 watts. The comparison is good and the variation in measurements is the same. The sensitivity is then $\pm 10^{-8} \Delta k$ for measurements at 200 watts for 133 min.

Results have been obtained from the cores for ~ 40 samples of 25 different elements. These results are available to any interested.

Reactivity is also found as a function of radius and is calculated from the power history data which are taken in the same manner as in the oscillator experiment, except that only one pass is taken and the interval can be adjusted for the particular measurement desired. For the measurement of reactivity as a function of radius, the interval is again 0.6 sec and a complete traverse is taken in 2 min. The sample is driven out of the reactor in 2.5-in. steps. A second run is made without the material of interest to correct for the reactivity change due to the bar and sample pocket. The restrictions on the counter linearity, sensitivity, etc., are stronger than for the oscillator.

The kinetic equations shown in Figure 6 are combined so that the sum term, for reactivity plus source strength, can be calculated from relative power levels with the boundary condition that rate of flux change, dn/dt , has been zero for a sufficient time. The flux, n , is taken from each analyzer channel and the equation solved at the time the channel ends. It is assumed that n is constant over the channel. If large times are used or changes are fast, then that data can be either curve fit or straight line segments used where the slope is

$$\textcircled{1} \frac{dn}{dt} = n \frac{\Delta k_p}{\beta_e} + \sum_i \lambda_i C_i + S_e$$

$$\textcircled{2} \frac{dC_i}{dt} = \frac{n \beta_i k_e}{\beta_e} - \lambda_i C_i$$

$$\frac{\Delta k_e}{\beta_e} + \frac{\beta_e S_e}{n \beta_e} = k_e + \frac{1}{n} \left[\frac{\beta_e}{\beta_e} \frac{dn}{dt} - \sum_i (n_0 a_i e^{-\lambda_i t} + \lambda_i e^{-\lambda_i t} \int_0^t n k_e e^{\lambda_i t} dt) \right]$$

($n = n_0$ for $t = 0$ to $t \approx -10 \text{ min}$)

Fig. 6. Calculation Performed in Reactivity Versus Time.

found from the before and after points and the $\int n dt$ from the point. For this experiment, source, S, is made zero, while in the importance measurement two runs are made at different powers to separate the terms. β_{eff} can also be found using fission counter data, also the power to the accuracy of β_{eff} .

Extensive checks have been made with other methods and interchecks using different paths. Figure 7 shows typical results for radial traverses. The many points are where the samples stopped for a time. This is the form of the IBM output combined with the usual digital values. The point variation is about $\pm 0.01\%$ for each 0.6-sec interval with a reactor power of 150 watts. The method is also used for rod drops, rod calibrations, table separation, etc. In the rod drop case the channel width is only 20 msec.

Fig. 7. Typical Results for a Radial Reactivity Traverse.

NEUTRON IMPORTANCE

In order to provide a direct check on calculations of neutron importance, various neutron sources are being used to measure the importance in the AETR critical assemblies.

The sources used in these measurements are Po-Be, Po-B¹¹, mock fission, Po-CaF₂, Po-Li⁷, and Sb-Be. Neutrons from these sources have different energy distributions that are characteristic of each source. The sources are described in Table III.

Relative source strengths were determined in a manganese sulfate bath; these relative values were normalized to the long-counter calibration of the Po-Be source at Mound Laboratory. However, since only relative values of the importance are significant, the absolute source strength is not needed. Uncertainties in the relative values are less than 2%.

The source being calibrated was left in the tank overnight. After removal of the source the solution was mixed while bubbling nitrogen through it. The Mn⁵⁶ activity produced by absorption of the source's neutrons in the solution was then measured by an NaI (Tl) scintillation counter placed in the center of the tank. The counting system used is shown in Figure 8, to the right of the tank. Raw count data were corrected for counter dead time, background, residual activity from the previous source, and activity induced by the previous day's reactor operation. The values used for these sources are shown in Table IV.

The corrections for leakage and source absorption were calculated using the AIM-6 diffusion code. Correction for the stainless steel tube was determined from the difference between the run with the plastic

TABLE III
DESCRIPTION OF NEUTRON SOURCES

Source	Dummy	
Po-Be 5.25×10^6 n/sec $\pm 0.8\%$	2.53 curies Po ²¹⁰ 6.25 grams Be	6.25 grams Be
Po-B ¹¹ 2.93×10^6 n/sec $\pm 1.3\%$	9.75 Curies Po ²¹⁰ 1.22 grams B ¹¹	1.22 grams B ¹¹
Mock Fission 4.92×10^6 n/sec $\pm 0.5\%$	15.63 curies Po ²¹⁰ 0.0946 grams Be 0.388 grams B ¹¹	0.0953 grams Be 0.391 grams B ¹¹
Po-CaF ₂ 1.306×10^6 n/sec $\pm 0.8\%$	2.676 grams Li ⁷ F 22.06 curies Po ²¹⁰ 2.91 grams CaF ₂	2.695 grams Li ⁷ F 2.62 grams CaF ₂
Po-Li ⁷ 0.981×10^6 n/sec $\pm 0.8\%$	23.01 curies Po ²¹⁰ 2.18 grams Li ⁷	2.54 grams Li ⁷
Sb-Be I 9.34×10^6 n/sec $\pm 2.0\%$	17 grams Sb 6.7 grams Be	17 grams Sb 6.7 grams Be
Sb-Be II * 9.14×10^6 n/sec $\pm 2.0\%$	17 grams Sb 6.7 grams Be	17 grams Sb 6.7 grams Be

* All activities referred to are January 16, 1961, except *March 1, 1962

SOURCE CALIBRATION APPARATUS

Fig. 8. Source Calibration Apparatus.

TABLE IV

NEUTRON SOURCE CALIBRATION CORRECTIONS

SOURCE	LEAKAGE (%)	SOURCE ABSORPTION (%)	THRESHOLD REACTIONS (%)
Po-Be	1.2 ± 0.4	0.3 ± 0.2	2.5 ± 0.4
Po-B ¹¹	1.1 ± 0.4	0.4 ± 0.2	2.3 ± 0.4
Mock Fission	0.5 ± 0.2	0.6 ± 0.3	0.5 ± 0.1
Po-CaF ₂	0.2 ± 0.1	0.6 ± 0.3	0.2 ± 0.1
Po-Li ⁷	0.1	0.8 ± 0.4	0.0
Sb-Be	0.0	3.5 ± 1.7 Source	0.0
		5.4 ± 1.0 SS Tube	

holder and those runs with the stainless steel tube. This agrees well with correction computed from the AIM-6 calculations. Corrections for threshold reactions came from published experimental and theoretical results.

For each source there is an inactive dummy differing only by absence of radioactive material. For polonium source dummies, the Po^{210} was omitted. The Sb-Be dummy was constructed in the same manner as the Sb-Be sources but was not irradiated. These dummies are used to cancel reactivity effects of the source material. The greatest amount of material thus omitted is 5 mgm of polonium, in the Po-Li^7 dummy. The other differences in content of the dummies produce trivial reactivity changes.

Since test regions of the critical assemblies are designed to mock-up neutron flux and importance spectra of various reference cores, the variation of importance with energy is measured at the center of the test region. The neutron importance at the center of the test region averaged over the source spectrum, is measured by a reactor oscillator technique.

Since some neutrons from the source in its "out" position may enter the reactor, a shadow shield was interposed between this position and the reactor. This shield is shaped like a cone and consists of stainless steel, polyethylene and cadmium, with cadmium adjacent to the reactor. Some neutrons still reach the reactor, both directly and by reflection from the steel critical assembly table, and this effect must be measured. This is done by determining the reactor power level due to subcritical multiplication of the neutrons when the source is

at the center and when it is outside the reactor. This correction is $\sim 10\%$ for the high energy sources (Po-Be, Po-B¹¹, Mock fission) and less for the others.

As sources decay, reactor power at which the source importance is measured has been reduced and this has required an additional correction. At very low power the reactor is subcritical due both to source neutrons and an inherent source. This inherent source is due primarily to the (α, n) reaction on aluminum contained in U²³³ fuel packets. The calculated reactor transfer function, which relates the change in reactor power to the change in reactivity, varies by $\sim 10\%$ in the range zero to six cents subcritical. The measured importance values must be corrected for this change.

The measurements of central source importance for the first eight AETR critical assemblies are shown in Figure 9. For comparison, the experimental values are normalized to the calculated values for the mock fission source. Source spectra were obtained from recently published measurements, supplemented by our own measurements with a stilbene spectrometer which discriminates against gamma rays.

The Sb-Be source was not used in Core 4 since this core contained approximately 4000 times as much beryllium as the source. Gamma rays from the Sb¹²⁴ would have produced many more neutrons in the test region beryllium than in that contained in the source.

Source importance is also measured as a function of radius. This is done by moving each source in discrete steps through the reactor, recording the output of the ion chamber integrated over two-second

CENTRAL SOURCE IMPORTANCE

Fig. 9. Central Source Importances for Eight Cores.

intervals. This is done at two power levels; one low, so that the effect of the source neutrons is large, the other high, so that the reactivity effect of the source material predominates. Using the reactor kinetic equations, a computer code calculates an apparent reactivity for each time interval at two power levels and then solves for the term proportional to source importance. This code corrects for the inherent source and the fact that the reactor is subcritical at low power because of this source.

A radial traverse in a graphite moderated core (core 6) with a Po-Be neutron source is shown in Figure 10. Agreement between the experimental points and the calculated curve is moderately good. The errors indicated are random errors associated with the individual points only. The magnitude is uncertain by about 4% due to errors in normalization, source strength, and corrections.

The ratios of central source importance measured with the oscillator agree well with those from the radial measurements.

Fig. 10. Typical Radial Importance Distribution.

SPECTRAL MEASUREMENTS

Energy threshold reactions in fission counters and various foil materials aid in establishing the neutron spectra of AETR cores. Reaction cross sections are measured and compared with calculated values as a function of position in the epithermal critical assemblies.

Fission counters are prepared by placing an electroplated foil of the desired fissionable material in a cavity in an aluminum cap as shown in Figure 11. A solid-state detector is placed on top of the foil and a set screw tightened to make the assembly secure. Fission counters have been manufactured utilizing materials highly enriched in Th^{232} , U^{233} , U^{234} , U^{235} , U^{236} , U^{238} , Np^{237} and Pu^{239} .

A 4-ft - long, hollow stainless-steel tube was fabricated to insert the fission counter into the reactor and to serve as a coaxial cable. This tube is attached to a remotely controlled drive unit so that the fission counter can be located anywhere along a radius of the reactor. Commercially available electronic equipment is used to amplify the signals from the fission counter and discriminate between true fission events and other reactions in the critical assembly.

The fission counters are calibrated before they are inserted into the reactor. All the fissionable materials are alpha emitters with well-known half-lives. Hence a knowledge of the number of alpha particles per second striking the solid-state detector indicates the mass of material in contact with the detector. This information is sufficient for an absolute calibration.

Figure 12 shows an alpha spectrum obtained for Th^{232} with a solid-state detector. This figure shows the most complex alpha spectrum

Fig. 11. Fission Counter and Solid State Detector.

Fig. 12. Alpha Particle Spectrum of Th-232 and Impurities.

resolved for the alpha normalization. The Th^{232} alpha peak is the only one of importance for calibration purposes.

A fission particle energy spectrum obtained from a U^{233} fission counter inside the reactor is shown in Figure 13. The low energy peaks are due to alpha particles and to neutron-induced reactions in the silicon detector. The two fission peaks are seen clearly at a much higher energy. A discriminator setting is used which counts none of the low-energy events and virtually all the fission events.

Individual foil measurements are performed in the following way. Materials in the form of foils 1/2 inch in diameter and from 0.005 inch to 0.020 inch in thickness are placed either in a milled slot in the reactor plates or on a 7/8-in.-square by 20-in.-long aluminum bar. This bar is then inserted in the central drawer of the fixed and movable halves of the reactor. After irradiation, the foils are removed and either monitored for gamma ray activity by means of a NaI(Tl) scintillation crystal or beta-counted with an anthracene scintillation detector. The associated electronic equipment and automatic sample changers used for the counting operations are commercially available.

The materials used as thresholds detectors are Al, S, Pb^{204} , and Mg. Other materials - In, Au, Mn, and Dy, both with and without 0.020-in. cadmium covers, are used to detect thermal and epithermal neutrons.

Metal foils of Th^{232} and U^{235} are also irradiated in the AETR cores. The former is used to determine relative neutron capture in thorium and the latter relative neutron fission activity in U^{235} .

Fission ratios, with U^{235} as the standard, are calculated from the fission counter measurements. The absolute calibration obtained from

U^{233} FISSION SPECTRUM

Fig. 13. Alpha Particles and Fission Events in U-235 Fission Foil.

alpha counting is sufficient for this purpose. In addition, there is a relative calibration which applies to four materials. The U^{234} , U^{235} , U^{236} , and natural uranium counters have appreciable isotopic fractions of U^{235} . When one of these fission counters is placed in a thermalized neutron flux, most of the fission counting rate is due to the U^{235} isotope. The isotopic abundances of the various materials are known from mass spectrographic data. The driver region of the AETR cores is sufficiently thermalized for the normalization. Table V shows the results of these two methods for core 3. The results from the absolute calibration of a U^{238} fission counter which is highly depleted in the U^{235} isotope is also shown. Agreement between the two methods is good.

The fission ratio experimental results are shown in Table VI. The data are listed in the order of decreasing calculated median fission energy to show trends. Thus, we can see that the fission ratio of U^{238} relative to U^{235} decreases from 0.076 in the hardest spectrum to 0.0023 in the softest spectrum. This trend is also true of the other threshold detectors (Th^{232} , U^{234} , U^{236} , and Np^{237}). The fission ratios of the thermal neutron detectors (U^{233} and Pu^{239}) relative to U^{235} do not show a systematic trend.

Table VI also shows the initial calculated values of the fission ratios for comparison purposes. The agreement between the two sets of values is good for the five hard cores.

Figure 14 shows a fission traverse for U^{235} in core 6. The alpha-counting technique gives an absolute calibration of the U^{235} fission counter so a direct comparison with the calculated results is possible. There is $\sim 10\%$ uncertainty in the relative position of the two curves

TABLE V

NORMALIZATION COMPARISON

NUCLIDE (RELATIVE TO U^{235})	THERMAL-NEUTRON NORMALIZATION	ALPHA-COUNT NORMALIZATION
U^{234}	0.229	0.228
U^{236}	0.0678	0.0727
U^{238} (Natural)	0.0298	0.0312
U^{238} (Depleted)	--	0.0304

TABLE VI

FISSION RATIOS

EXPERIMENTAL

Nuclide (Relative to U ²³⁵)	Core 1 (422 kev)	Core 3 (140 kev)	Core 8 (127 kev)	Core 2 (127 kev)	Core 5 (63 kev)	Core 6 (4.7 kev)	Core 4 (9.6 ev)	Core 7 (8.5 ev)
Th ²³²	--	0.0069	0.0064	--	0.00504	0.0034	0.00060	0.00048
U ²³³	--	--	1.44	--	1.392	1.45	1.85	1.60
U ²³⁴	0.52	0.228	0.191	0.194	0.175	0.095	0.021	0.018
U ²³⁶	0.153	0.0705	0.0585	0.0545	0.0545	0.0316	0.0060	0.005
U ²³⁸	0.076	0.0306	0.0281	0.0248	0.0240	0.0150	0.00265	0.0023
Np ²³⁷	--	0.233	0.196	--	0.169	0.093	0.0200	0.016
Pu ²³⁹	--	--	--	--	0.96	0.98	--	--

CALCULATED

Nuclide (Relative to U ²³⁵)	Core 1	Core 3	Core 8	Core 2	Core 5	Core 6	Core 4	Core 7
Th ²³²	0.01696	0.00722	0.0060	0.00588	0.00565	0.00368	0.00100	0.00103
U ²³³	--	1.497	1.44	1.434	1.406	1.364	1.74	1.69
U ²³⁴	0.466	0.2399	0.205	0.1984	0.1746	0.0996	0.0265	0.0241
U ²³⁶	0.167	0.07505	0.0629	0.0613	0.0572	0.0351	0.0098	0.00951
U ²³⁸	0.0763	0.03239	0.0270	0.0264	0.0255	0.0167	0.00456	0.00460
Np ²³⁷	0.484	0.2463	0.203	0.2035	0.180	0.0997	0.0277	0.0253
Pu ²³⁹	--	1.049	0.995	1.004	0.952	0.9065	1.56	1.62

Fig. 14. U^{235} Fission Traverse.

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due to the power calibration. The relative shapes of the two curves are similar except for the peak in the reflector region that the diffusion calculations predict. The calculated counting rate is considerably higher in the test region than the measured value. This traverse is typical of materials which fission with thermal neutrons.

Figure 15 shows the Np^{237} fission traverse for core 6. The agreement between calculated and experimental curves is good in the driver when one takes the 10% uncertainty into consideration. The calculated counting rate is much higher in the test region than the fission counters indicate. These results are typical of all the absolute fission counter data. There is good agreement in the driver region but the calculated values are too high in the test region even though the ratios are quite good.

Fig. 15. Np-237 Fission Traverse.

ANALYSIS

The data of reactor size, composition and experimental measurements are compared with the 18 group AIM-6 and perturbation theory calculations. Adjustments are being made in the cross section values to better describe the data. Both flux and adjoint flux information is available as well as the reactivity data. Any changes affecting the core calculation are iterated and readjusted. The ARES code is used to obtain effective multigroup cross sections for lumps and mixture of fertile materials. Some facts relating to fast systems are directly available from the measurements. For example Table VII gives the relative fission rates of the fertile materials, relative Pu, U-233 and Th, natural uranium reactivity values.

By observing the fuel materials reactivity changes on the several cores the variation of ν with energy can be determined, the value for U-233 is $2.47 + .127E$, for U-235 $2.43 + .100E$ and for Pu is $2.92 + .17E$ assuming a straight line fit (where E = energy in Mev).

Preliminary analysis of the first eight critical assemblies has verified the breeding potential of U-233 systems over a wide neutron energy ranges, plutonium only above 60 kev and U-235 above 150 kev. Appropriate adjustment on fissile and fertile material cross sections have been factored into full-scale power reactor design studies. As one of the final products of the critical experiment data a set of cross sections are being developed which can be used in further power reactor studies. They will be used to calculate many values of interest such as critical mass, breeding potential, some burnup information, flux distributions, control worths etc.

TABLE VII

PER ATOM RATIOS

	Core 1 422 kev*	Core 3 140 kev	Core 8 127 kev	Core 2 127 kev	Core 5 63 kev	Core 6 4.7 kev	Core 4 9.6 ev	Core 7 8.5 ev
Fission U^{238}/Th		4.4	4.4		4.8	4.4	4.4	4.8
Reactivity U^{233}/Pu		1.06	1.00	1.01	1.05	1.37	1.68	1.73
Reactivity Th/U^{238}	1.33 (+)	1.86	1.78	1.63	1.72	1.40	1.16	1.31

 * Median Fission Energy

Session II
Paper 7

SOME ASPECTS OF THE PHYSICS OF THORIUM FUELED,
HIGH TEMPERATURE, GAS-COOLED REACTORS

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INTRODUCTION

The most interesting aspects of the physics of the high-temperature, gas-cooled reactor concept result from the following characteristics:

1. The very high moderator temperature and the large coolant temperature rise required by the gaseous coolant.
2. The semihomogeneous configuration of the fuel.
3. The small parasitic neutron capture associated with the nonfuel components.

These characteristics result in reactors which can achieve large fractional burnups, excellent neutron economy, high thermal efficiencies, and low fuel costs. However, realizing these four goals simultaneously necessitates high moderator temperature and heavy loadings of fertile and fissile materials. Consequently, the epithermal spectrum is far from $1/E$, and the thermal spectrum is relatively hard. The thorium-uranium fuel cycle is best suited to exploit these characteristics, and thus the physics of high-temperature, gas-cooled reactors invariably involves the physics of thorium-fueled reactors.

THERMAL SPECTRA

In the calculation of thermal spectra, the principal problems are associated with the chemical binding of the moderator and with the presence of strong absorption. Both of these effects are found in all thermal reactors to some degree. In graphite-moderated reactors, the crystalline binding of the carbon atoms should be considered at temperatures below 900°K ; ⁽¹⁾ free-gas scattering kernels are adequate at higher temperatures. The effects of crystalline binding on thermal spectra at 300°K are indicated in Fig. 1, which shows the flux per unit energy as a function of energy. Spectra consistent with a free-gas scattering kernel ⁽²⁾ and the Wilkins ⁽³⁾ heavy-gas

Fig. 1. Thermal Flux Spectra in Graphite at 300°K.

model are also shown for comparison. In all three models the source strengths are equal. It is obvious that the graphite binding results in a considerably hardened spectrum. When the temperature is increased to 1200°K, the three models are in good agreement.

The effects of strong absorption on thermal spectra are best demonstrated when nuclides with thermal-energy resonances are present. Figure 2 shows the spectrum obtaining in graphite at 1200°K in a reactor having a carbon-to-plutonium ratio of 2000 and plutonium composition similar to that produced in Calder Hall type reactors;⁽⁴⁾ i. e., 78% Pu²³⁹, 17% Pu²⁴⁰, and 5% Pu²⁴¹. Again, the heavy-gas model, with equal source strength, is shown for comparison, and it is quite clear that it cannot adequately represent the case of strong absorption. The spectrum from the free-gas kernel, on the other hand, agrees quite well with that from the crystal kernel. The large difference in magnitude far from the resonances is due to the overestimate of the Pu²⁴⁰ absorption rate in the heavy-gas calculation.

That these spectral differences are important in the design of reactors is demonstrated in Table 1, which shows the thermal cross sections of several nuclides under various temperature and loading conditions. With the exception of (1/v), all the nuclides shown have some resonance structure, and, consequently, the absorption cross sections can either increase or decrease as the spectrum hardens. Thus, it is very difficult to characterize these very broad spectra by a simple hardness parameter (as in the heavy-gas model), and the errors resulting from such simplification for the various nuclides vary over a wide range. At high temperature and moderate U²³⁵ loading, the cross sections are all in good agreement. However, when the heavy plutonium loading is considered, the Pu²⁴⁰ cross section is overestimated by 64%, whereas the Xe¹³⁵ and Sm¹⁴⁹ cross sections are underestimated by 22% in the heavy-gas calculation. From the spectra shown in Fig. 2, it is clear that the error associated with Pu²⁴⁰ is caused by the inability of the heavy-gas model to represent the spectrum in the

Fig. 2. Thermal Flux Spectra in Graphite at 1200°K.

Table 1
EFFECTS OF CRYSTALLINE BINDING AND NUCLIDE CONCENTRATION
ON THERMAL^a CROSS SECTIONS

	Scattering Model							
	Crystal	Free Gas	Heavy Gas	Crystal	Free Gas	Heavy Gas	Crystal	Free Gas
Moderator temp., °K	300			1200			1200	
C:U ²³⁵ ratio	4000			4000			∞	
C:Pu ratio	∞			∞			2000	
	σ (barns)	Diff. (%)	Diff. (%)	σ (barns)	Diff. (%)	Diff. (%)	σ (barns)	Diff. (%)
U ²³⁵ absorption	321	+14	+17	227	+1.0	+1.5	99.3	-8.7
Pu ²³⁹ absorption	940	-1.0	+1.7	1,340	-0.22	+0.22	489	-8.8
Pu ²⁴⁰ absorption	1,100	+11	+5	982	+0.11	+1.6	1,940	+64
Xe ¹³⁵ absorption	1,540,000	+7.4	+11	800,000	+1.8	+2.0	187,000	-22
Sm ¹⁴⁹ absorption	41,800	-3.6	-1.1	25,300	+1.1	+0.75	6,680	-22
(1/v) ^b absorption	0.515	+11	+14	0.374	+0.86	+1.2	0.210	-6.4

^aThe cross sections are averaged over a group from zero to 2.38 ev.

^bThe (1/v) represents a nuclide whose 2200 m/s absorption cross section is unity and varies inversely with velocity.

vicinity of a strong resonance. Since the Pu^{240} reaction rate is almost entirely due to the 1.05-ev resonance, this error should be expected. All nuclides with large thermal-energy resonances will behave similarly; consequently, the computation of one-group thermal cross sections must be done by a method that can account for strong absorption. Further, the degree of flux shielding in a resonance will depend on the nuclide concentration and therefore will vary during the lifetime of a core.

SPATIAL VARIATION OF THE THERMAL SPECTRUM

In graphite-moderated reactors, the thermal diffusion length varies from 10 to 30 cm, depending on the core loading. Thus, neutrons from the reflector can penetrate quite far into the core. The spectrum prevailing in the side and bottom reflectors is much softer than that in the core for two reasons:

1. The coolant flows through the side and bottom reflectors first; consequently, the reflector temperature is only slightly higher than the inlet temperature. On the other hand, the average core temperature is much higher than the average coolant temperature, since all the fission energy must be transferred to the coolant.

2. The fuel content of the core results in a hardened thermal spectrum.

These variations in thermal spectra are illustrated in Fig. 3, which shows the neutron flux per unit energy as a function of energy at three locations in a reactor. It is clear that the spatial variation of the spectrum must be considered if accurate power and temperature distributions are required. Furthermore, multiple thermal-group methods can adequately handle the problem (see Fig. 4).

EPITHERMAL SPECTRA

The slowing-down spectrum in a high-temperature, gas-cooled reactor is shown in Fig. 5; the fissile and fertile loadings are consistent with high

Fig. 3. Thermal Flux Spectra at Various Temperatures.

Fig. 4. Power Distribution in a High-Temperature Gas-Cooled Reactor.

Fig. 5. Flux Per Unit Lethargy as a Function of Lethargy.

conversion ratios and low fuel costs. It is clear that the slowing-down spectrum is far from $1/E$, especially between 6 and 13.5 lethargy units. This is principally due to thorium captures. At lethargies above 13.5, the spectrum is still not $1/E$ because of captures in the low-lying resonances of U^{235} . This depletion in the slowing-down flux is particularly significant with relatively heavy moderators, such as graphite, since the removal cross section is principally determined by the flux at the thermal cutoff. Figure 6 shows the flux above 13.5 lethargy units for the same loading at several exposures up to 0.93 fissions per initial fissile atom (fifa). The increase in flux at $u = 13.5$ is the result of depletion of the thorium and consequently reduced resonance captures. However, at $u = 14.25$ the gain in flux level is completely wiped out by the captures in the 5.49--ev resonance of U^{236} and at larger exposures by the 5.2-ev resonance of U^{234} . A second large neutron loss occurs at $u = 15.25$ owing to the low-lying resonances of U^{233} . There are many other small losses due to the various fission products, but the principal contributors are U^{233} , U^{234} , and U^{236} in thorium-uranium-fueled reactors. This effect is clearly due to the high conversion and long exposure attained by the reactor. Similar information is shown in Fig. 7 for the same reactor but with a reduced thorium content. Now the softening due to thorium depletion is nearly equal to the hardening due to the production of U^{233} , U^{234} , and U^{236} at 0.62 fifa. Clearly, if even more thorium were removed, over-all epithermal spectral softening would occur but at the expense of the conversion ratio. An even stronger effect is to be expected in uranium-plutonium-fueled reactors because of the large resonance integrals of all the plutonium isotopes.

The effect of epithermal spectral hardening requires that depletion calculations be performed using multiple fast groups. For the fuel loading shown in Fig. 6, the errors in the multiplication factor associated with few-epithermal-group calculations are shown below:

Fig. 6. Epithermal Neutron Spectra at Several Exposures.

Fig. 7. Epithermal Neutron Spectra at Two Exposures.

	Number of Epithermal Groups					
	1			3		
Group lethargy boundaries	0-17			0-4.5 4.5-13.5 13.5-17		
Exposure, fima	0.31	0.62	0.93	0.31	0.62	0.93
Resonance escape probability	0.518	0.509	0.504	0.509	0.494	0.485
Error in k associated with epithermal spectral hardening, %	2.2	3.9	5.2	0.4	0.8	1.3

Power reactors are generally designed to produce high conversion ratios and small reactivity variations during the burnup cycle. Therefore, errors in multiplication factors greater than 1% will result in considerably overestimated reactivity lifetimes and correspondingly underestimated fuel-cycle costs. Therefore, multi-fast-group depletion calculations should be used for fuel-cycle analysis.

FUEL UTILIZATION

The semihomogeneous fuel configuration makes it possible to achieve a large fractional burnup without severe damage to the fuel element. Thus, it is possible to attain 10% total atom burnup (thorium and uranium) in a single pass through the reactor. If the refabrication losses are 1%, 90% of the thorium is utilized in the reactor. On the other hand, in a fast reactor limited to 5 at.-% burnup, only 80% of the thorium can be utilized for the same refabrication losses. If the burnup is limited to 1 at.-%, then half of the thorium is lost in refabrication.

A second advantage associated with the semihomogeneous fuel is a sizable reduction in the production of U^{232} . Since this nuclide is the primary source of the radiation hazard in recycled fuel, the penalty associated with refabrication should be much smaller than for the more heterogeneous

fuel designs. We have estimated that the U^{232} production rate in a semi-homogeneous-type fuel element will be decreased by a factor of 8 from that of a 0.27-in. thorium oxide rod and by a factor of 20 from that of a 0.75-in. thorium-metal rod.

NEUTRON ECONOMY

In specifying the loading for a high-temperature, gas-cooled reactor one would like to achieve a high conversion ratio, a large fractional burnup, and a large energy production simultaneously. However, these requirements are not mutually consistent and some compromises must be made. That is, high conversion ratios and large fractional burnups are best realized with light fuel loadings, which result in relatively small energy production. Conversely, heavy uranium loadings result in reduced values of η and consequently reduced conversion ratios. This is illustrated in Fig. 8, which shows the average η value for U^{233} and U^{235} as a function of uranium and thorium content. It is clear that the carbon-to-uranium ratio principally determines the value of η and that the effect of the carbon-to-thorium ratio is negligible. The value of η as a function of uranium content and fractional absorptions in U^{233} is shown in Fig. 9. The achievement of high conversion ratios clearly requires that at least 80% of the fuel absorptions occur in U^{233} and that the carbon-to-uranium ratio should be larger than 5000.

Some examples of the neutron losses encountered in a large high-temperature, gas-cooled reactor are shown in Table 2. It should be emphasized that the reactor loadings shown here have not been optimized and represent only a few isolated cases. In all cases the reactor power is 1225 Mw(t), the power density is 7 w/cm^3 , and the exposure is determined only by reactivity considerations. Case A represents batch loading, and Case B is the same core refueled by quarters. The use of partial refueling results in a 58% increase in fractional burnup and a 3% increase in conversion ratio. In Case C the uranium loading has been halved and the

Fig. 8. Spectral Averaged η as a Function of Uranium and Thorium Loading.

Fig. 9. Effective η Values as a Function of Fissile Loading and Composition.

Table 2

NEUTRON BALANCES FOR LARGE HIGH-TEMPERATURE,
GAS-COOLED REACTORS

	Case				
	A (Fully Enriched Fuel)	B (Fully Enriched Fuel)	C (Fully Enriched Fuel)	D (U ²³³ Fuel)	E (Recycled U+U ²³⁵ Fuel)
Fraction of core refueled each time at each shutdown	1.0	0.25	0.25	0.25	0.125
Carbon-to-thorium ratio, in feed	150	150	250	185	200
Carbon-to-uranium ratio, in feed	3000	3000	6000	6000	~5800
Burnup, fwa	0.73	1.15	1.44	1.62	1.15
Average conversion ratio	0.78	0.80	0.79	0.96	0.89
Average η	2.00	2.02	2.07	2.19	2.13
Losses per fuel absorption, %:					
Leakage	2.6	2.7	2.9	3.0	2.9
Th+U ²³⁴ +U ²³⁸ +Pu ²⁴⁰	79.3	81.6	80.9	97.4	89.5
Pa ²³³ +Np ²³⁹	1.2	1.2	1.7	1.8	0.8
U ²³⁶ +Pu ²⁴²	1.1	1.4	1.0	----	1.6
Xe ¹³⁵	3.1	3.1	4.2	4.0	3.9
Cd ¹³³ +Sm ¹⁴⁹ +Gd ¹⁵⁵ +Gd ¹⁵⁷	0.9	0.8	0.9	0.7	0.8
Low cross-section fission products	0.8	1.3	1.3	1.6	0.6
Mo ⁹⁵ +Tc ⁹⁹ +Rh ¹⁰³ +Nd ¹⁴³ +Nd ¹⁴⁵ +Pm ¹⁴⁷	3.4	4.5	4.8	4.6	2.2
Xe ¹³¹ +Cs ¹³³ +Sm ¹⁵¹ +Sm ¹⁵² +Eu ¹⁵³	1.8	2.4	2.3	2.4	1.2
Graphite	1.6	1.7	4.2	3.3	3.3
U ²³³	31.8	40.3	42.4	98.4	70.4
U ²³⁵	67.1	58.6	56.9	1.6	29.1
Pu ²³⁹ +Pu ²⁴¹	1.1	1.1	0.7	----	0.5

thorium reduced by 40%. Although the value of η increased by 0.05, the conversion ratio remained roughly the same. This was due to increased absorptions in graphite, fission products, and control rods.

Case D represents a limiting condition, in that pure U^{233} is the feed fuel. The effective value of η goes up to 2.19 and the conversion ratio is larger than 0.95. The losses to the rapidly saturating fission products are reduced slightly because U^{233} has a lower fission yield for these nuclides than U^{235} . The thermal flux is slightly smaller because of the somewhat larger fission cross section of U^{233} relative to U^{235} in the spectrum of high-temperature, gas-cooled reactors.⁽⁵⁾ Therefore, the losses to graphite are reduced 17% relative to Case C.

Case E represents an actual uranium recycle with enriched uranium makeup. Nearly 30% of the fuel absorptions occur in U^{235} , and, consequently, the effective η is only 2.13. This loss in η is directly reflected in a 7% loss in conversion ratio relative to Case D. The fission-product losses are considerably reduced owing to the 29% decrease in fractional burnup; however, most of the advantages gained by this reduction are offset by increased losses to the control rods.

From the neutron balances shown in Table 2, it is clear that enriched-uranium-fueled, high-temperature, gas-cooled reactors can achieve conversion ratios above 0.8, and uranium recycle can result in conversion ratios in excess of 0.9. If a source of pure U^{233} were available, conversion ratios larger than 0.97 would seem to be attainable.

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Session II
Paper 8

EPITHERMAL THORIUM REACTORS

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INTRODUCTION

Atomics International has had a long time interest in reactors operating on fuel cycle involving the conversion of thorium into uranium ²³³. The principal basis for this interest lay in some data on U²³³ reported by the Russians at the 1955 Geneva conference which indicated that η (neutrons produced per neutron absorbed in U²³³) was nearly constant over the entire energy and greater than 2, thus showing promise of breeding. The breeding ratio (BR) may be defined as $BR = \eta - 1 - C - L$. To obtain the maximum breeding ratio, the capture (C) and leakage (L) terms must be made as small as possible. The leakage term is small for large (thermal) reactors, while the capture term is small for high energy (fast) reactors, and since η for U²³³ is nearly constant for all energies, it was considered that an intermediate energy reactor large enough to reduce leakage and fast enough to produce capture losses to structure, coolant, and fission products could be designed.

In 1958, Atomics International engaged in a research and development program for the Southwest Atomic Energy Associates (SAEA) with the objective of developing a reactor concept promising economically competitive power production in the Southwest area of the United States within ten to fifteen years. The concept selected for evaluation was the Advanced Epithermal Thorium Reactor (AETR), operating on the Th-U²³³ cycle with a neutron spectrum ranging from above thermal to fast. This reactor concept involves fixed fuel elements cooled with liquid sodium and utilizes stainless steel for the structural material. The moderator, if used, would be graphite or beryllium metal.

The purpose of this report is to summarize the results of evaluation studies on U²³³-Th fueled reactors, which are sodium-cooled and which operates with a spectrum in the above thermal energy range. These studies have not only demonstrated the feasibility of such reactors from an engineering and materials standpoint but also have shown the potential capability for producing economic power in low fuel-cost areas. In addition, these studies have served to delineate possible problem areas which require resolution before construction of a full-scale plant should be initiated.

I. SUMMARY

The Advanced Epithermal Thorium Reactor (AETR) concept is high-performance, sodium-cooled, above-thermal-neutron energy, U^{233} -Th fueled power source to generate economically competitive electrical energy in the Southwest area. The principal emphasis during the Advanced Epithermal Thorium Reactor (AETR) program has been to develop accurate nuclear parameters on which to base the evaluation of economic potential and technical feasibility of the AETR concept. To accomplish this goal, a critical assembly and laboratory were constructed and experiments were conducted to improve the knowledge of certain nuclear parameters, especially in the epithermal- and intermediate-neutron energy range. Data from the epithermal critical experiments and data from other sources have been incorporated into codes for nuclear analysis of possible AETR designs. Parameters have been surveyed over the full practical range of energies and fuels of interest. At the same time, engineering concepts, fuel materials, safety and control, and economics have been evaluated. Although these studies have not been completed, they have already shown that the AETR concept offers great potential in attaining its goal of economical, electrical-energy generation.

An AETR can be operated as an epithermal reactor using beryllium as a moderator and U-Th oxide or carbide as fuel. Economic fuel cycles can be realized over three to four fuel recycles at fuel burnups between 50,000 and 75,000 Mwd/T. Although the in-core breeding ratio is high (~ 1), fuel loadings larger than desirable (800 to 1000 kg of U^{233}) are required to overcome fission product and heavy isotope poisoning incurred during long burnup operation. Total breeding ratio, including the blankets, could be about 0.8 to 1.0.

An AETR can also be operated as an unmoderated reactor using U-Th oxide or carbide, or other high performance fuel. Due to high in-core breeding ratio (0.80 to 0.90) and negligible fission product and structural poisoning at the higher neutron energies, long burnup periods of 100,000 Mwd/T (or longer) are practical. In comparing unmoderated systems, U^{233} and Pu could offer similar economic advantages when a free-market, supply-demand price exists for fissile material. General plant layout, heat transfer, and plant control are the same for either system, however, the systems do have different advantages.

The principal advantages of U^{233} -Th fueled system over that of a Pu- U^{238} fueled systems are:

- 1) Design Flexibility. A Pu- U^{238} cycle operates more efficiently the harder the neutron spectrum, whereas a U^{233} -Th cycle has greater spectral latitude allowing a wider choice of material shape, size, and composition.
- 2) Safety. All temperature and power reactivity coefficients are inherently negative for U^{233} -Th systems.
- 3) Bred Fuel Value. High quality of U^{233} bred in the blanket has potentially high value as a thermal reactor fuel.

Relative disadvantages of using the U^{233} -Th cycle stem from:

- 1) Lack of U^{233} fuel. There are only small experimental quantities of U^{233} . Only two, relatively small, power reactors will produce U^{233} (Indian Point and Elk River).
- 2) Less Technology. Less effort has been devoted to improving the technology of thorium and U^{233} , than that devoted to uranium and Pu.

Two technical disadvantages exist: (1) In a high energy neutron spectra, U^{238} fissions four to five times more than thorium (fast fission effect), which reduces the critical loading, increases the average neutron energy, and improves effective in-core breeding for a Pu- U^{238} cycle, and (2) although of minor importance, control of U^{233} -Th systems is slightly more difficult because (a) the delayed neutron fraction is $\sim 0.3\%$ ($\sim 0.4\%$ for Pu- U^{238}), and (b) protoactinium (Pa^{233}) decay at shutdown requires 1.2 to 1.8% $\Delta k/k$ shim control.

II. ANALYSTS OF VARIOUS REACTOR CONCEPTS

Survey studies to evaluate potential AETR cores require accurate nuclear data in various energy ranges. In the past, effort had been placed on data for thermal reactors and, to a lesser extent, on fast reactors. Very little effort had been expended on reactors to operate in the epithermal or intermediate energy range. Resolution of parameters for this range has been limited. The AETR nuclear studies reported in this section have been made using reliable multigroup nuclear cross sections derived from or confirmed by measurements from the AETR critical assembly.⁽¹⁾ In addition, advanced reactor theory, methods, and codes developed under the AETR program have been employed.

Data obtained from the AETR critical assembly show that η , and therefore the breeding potential, for U^{233} is satisfactorily high over the energy range from thermal to fast and higher than either U^{235} or Pu, below about 60 kev (See Figure 1). The plutonium η is higher above median fission energies of 60 kev. Only in very fast (high neutron energy) cores does U^{235} show any breeding potential. Since the neutron scattering parameters are subject to doubt, calculated spectra are, in general, higher than in the actual case which means that predictions for Pu fueled cores may be optimistic, whereas U^{233} core calculation may be slightly pessimistic. In any event more latitude in spectra is possible for U^{233} systems than for plutonium systems without serious economic consequences.

Early AETR survey calculations examined the important nuclear characteristics of U^{233} -Th fueled reactor cores ranging in energy from epithermal to fast. Typical results are shown in Figures 2, 3, and 4, in which critical mass, critical diameter, and breeding ratio for clean, just critical cores are plotted against core moderator volume fraction. The data shown assume the use of graphite moderator and mixed carbide fuel; however, comparable information was also developed assuming the use of paste and oxide fuels and beryllium moderator. The figures show that as moderator volume fraction is decreased and neutron spectrum hardens, breeding ratios increase and core sizes decrease. Critical loadings increase as would be expected considering the decrease in fission cross section with energy.

Fig. 1. Evolution of Eta (η) Values Since 1956.

Fig. 2. Critical Mass of Spherical Reactors.

Fig. 3. Size of Critical Spherical Reactors.

Fig. 4. Breeding Ratio of Critical Spherical Reactors. (Assumed volume ratios are Na: Th/U = 1.28 and Na: Fe = 2.25.)

Rough screening using clean, just critical nuclear data showed that operation in either of two spectra appeared about equally attractive on an economic basis. These were: (1) the epithermal energy region, corresponding to median fission energies centering around one ev and achieved in reactor design employing ~ 50 vol % beryllium moderator, and (2) the spectrum attained by operation of unmoderated U^{233} -Th fueled reactors containing practical sodium coolant volume fractions, i.e., operation at median fission energies of ~ 50 to 200 kev. Operation at intermediate median fission energies (between 10 ev and 10 kev) results in increased parasitic neutron losses due to resonance absorption in various materials, producing somewhat higher fuel cycle costs.

In a power reactor operating for long periods of time, neutron captures in the fuel lead to higher isotope formation and neutron-induced fissions result in fission fragments. Effects of isotope buildup and fission fragments on reactor core performance are important in evaluating the excess fuel (reactivity) that must be built into the core or introduced during the reactor power life cycle. This adds to fuel cost and is a very important parameter in optimizing neutron economy of AETR cores. For this reason, a comprehensive burnup program (SIZZLE) was designed and written in digital machine language for use in studying the complicated Th- U^{233} chain. Reactivity-lifetime calculations which considered the nuclear effects of higher isotope formation, fission product poisoning, and long-term reactivity changes could then be made.

Detailed analyses as described above were made for heat transfer limited cores employing both oxide and carbide fuel in epithermal and fast reactors. Multizone refueling schemes utilizing both isotopically clean fuel and fuels contaminated with equilibrium amounts of higher isotopes were considered.

Table I summarizes nuclear and heat transfer information on the following epithermal reactors, which were moderated with 50 vol % beryllium and operated with median fission energies in the vicinity of 1 ev:

- 1) $U^{233}O_2$ -ThO₂ fueled cores employing 0.29-in.-and 0.40-in.- OD fuel pins.
- 2) A U^{233} C-ThC fueled core using 0.43-in.-OD fuel rods.

TABLE I

HEAT TRANSFER AND BURNUP DATA FOR EPITHERMAL REACTORS

	Epithermal AETR, Oxide Fuel			Epithermal AETR, Oxide Fuel			Producer Reactor, Oxide Fuel			Epithermal AETR, Carbide Fuel		
Fuel Material	U ²³³ O ₂ -1hO ₂			U ²³³ O ₂ -ThO ₂			U ²³⁵ O ₂ -ThO ₂			U ²³³ C-1hC		
Blanket Material	ThO ₂			ThO ₂			1hO ₂			1hO ₂		
Design Parameters												
Thermal Power (Mw)	1160						1160			1160		
Core Height (ft)	7.40						9.20			7.18		
Core Diameter (ft)	7.52						9.32			7.18		
Fuel Rod OD (in.)	0.29						0.40			0.43		
Glad Thickness (in.)	0.02						0.025			0.01		
Bond Thickness (in.)										0.02 (sodium)		
Fuel Slug Diameter (in.)	0.25						0.35			0.37		
Radial Blanket Thickness (ft)	0.66						0.66			0.66		
Reflector Thickness (ft)	1.50						1.50			1.50		
Beryllium Volume Fraction	0.50						0.50			0.50		
Sodium Temperature Rise (°F)	400						400			400		
Maximum Sodium Velocity (ft/sec)	32						28			33		
Maximum Heat Flux (Btu/hr-ft ²)	830,000						600,000			1,390,000		
Nuclear Parameters												
Discharge Fuel Exposure (Mwd/T)	54,700	87,800	127,500	36,000	55,000	86,700	34,000	72,300	107,800	39,500	69,000	108,000
k _{eff} initial	1.149	1.190	1.234	1.107	1.145	1.190	1.094	1.184	1.234	1.128	1.166	1.205
k _{eff} final	1.006	1.005	1.008	1.002	1.008	1.002	1.001	1.004	1.004	1.003	1.002	1.003
Delta k per cycle	-0.143	-0.185	-0.226	-0.105	-0.137	-0.188	-0.093	-0.180	-0.230	-0.125	-0.164	-0.202
Cycle time (full power days)	217	344	489	315	476	741	301	629	921	141	245	378
Isotopic Compositions (total U ²³³ + U ²³⁵ in core, kg)	980	1244	1579	1490	1881	2381	1961	2995	3991	750	985	1293
Clean Core Fuel In (kg)												
U ²³³	373	504	688	532	710	960				274	380	535
U ²³⁵							751	1308	1881			
Th ²³²	4341	4221	4051	9757	9593	9364	9655	9152	8625	3935	3852	3724
Irradiated Fuel Out (kg)												
U ²³³	223	250	278	403	462	519	153	202	222	182	213	245
U ²³⁴	43	55	67	63	84	106	18	30	35	29	40	50
U ²³⁵	20	33	48	26	45	69	330	434	561	12	22	36
U ²³⁶	2	5	9	2	6	11	150	307	454	1	3	6
Pa ²³³	12	9	7	16	12	10	10	5	3	14	11	9
Th ²³²	4147	3965	3736	9398	9102	8733	9386	8740	8142	3799	3654	3463
Fission Products	265	404	588	376	586	865	354	732	1073	171	286	446
Radial Blanket Out (kg)												
U ²³³ + Pa ²³³	43	73	110	48	81	137	34	93	145	30	55	90
Breeding Ratio												
In Core	0.68	0.58	0.48	0.84	0.73	0.62	0.65	0.49	0.42	0.76	0.65	0.54
Radial Blanket	0.12	0.15	0.16	0.09	0.11	0.14	0.05	0.07	0.08	0.11	0.14	0.17

- 3) A $U^{235}O_2$ - ThO_2 fueled core with 0.40-in. -OD fuel rods. This system represents a startup in "producer" reactor, which is necessary since the 750 to 1500 kg U^{233} loading required for operation of an epithermal AETR is not likely to be available for reactor startup in the early 1970's.

All of the above cores employ ThO_2 radial blankets.

Table II presents comparable data for the following unmoderated, oxide-fueled fast spectrum reactors employing 0.25-in.-OD fuel pins.

- 1) U^{233} -Th fueled core with ThO_2 blanket. This system mocks up conditions existing in an unmoderated AETR operating at steady state several years after startup.
- 2) U^{235} - U^{238} core and ThO_2 blanket. The reactor burns mostly U^{235} while producing plutonium in the core and U^{233} in the blankets.
- 3) U^{235} - U^{238} core with UO_2 blanket. This reactor burns mainly U^{235} while producing plutonium in both the core and blankets.
- 4) "Fast Plutonium" - U^{238} fueled core and UO_2 blanket. Fast plutonium is the Pu^{239} , Pu^{240} , Pu^{241} and Pu^{242} isotopic mixture formed during long exposure and recycle of plutonium in an unmoderated reactor.
- 5) "Thermal Plutonium" U^{238} core with UO_2 blanket. Thermal plutonium is the isotopic mixture produced in a one-cycle exposure of U^{238} in a high burnup ($\sim 25,000$ Mwd/T) thermal sodium graphite reactor. Thermal plutonium will be available sooner than the other mixtures considered, and thus represents a possible startup fuel for an unmoderated AETR.
- 6) Pu^{239} -Th core with ThO_2 blanket. This system represents a combined startup unmoderated AETR and U^{233} production reactor. The present calculation considers the use of clean plutonium fuel feed, i.e., relatively pure Pu^{239} formed in a production reactor or in the blanket of a fast plutonium breeder

Unmoderated reactors fueled with plutonium were examined in parallel with U^{233} -fueled reactors, since preliminary economic analysis indicated that the two fuel systems were approximately competitive.

TABLE II
HEAT TRANSFER AND BURNUP DATA FOR FAST REACTORS

	Uranium-Fueled Fast Reactors			Plutonium-Fueled Fast Reactors		
				Fast Pu	Thermal Pu	Clean Pu
Fuel Material	U ²³³ -ThO ₂	Enriched UO ₂	Enriched UO ₂	Pu-U ²³⁸ O ₂	Pu-U ²³⁸ O ₂	PuThO ₂
Blanket Material	ThO ₂	ThO ₂	Nat. UO ₂	U ²³⁸ O ₂	U ²³⁸ O ₂	ThO ₂
DESIGN PARAMETERS						
Height (ft)		5.1			3.25	
Diameter (ft)		5.45			6.50	
Fuel Rod Diam (in.)		0.268			0.250	
Clad Thickness (in.)		0.025			0.025	
Oxide Diam (in.)		0.218			0.200	
No. of Fuel Elements		120			150	
Max. Sodium Velocity (ft/sec)		25			19	
Reactor Press Drop (psi)		45			25	
Sodium Inlet Temp (°F)		785			785	
Sodium Outlet Temp (°F)		1205			1190	
Sodium Temp Rise (°F)		420			405	
Max Heat Flux (Btu/hr-ft ²)		890,000			960,000	
Reactor Power (Mwt)		1160			1160	
NUCLEAR PARAMETERS						
k _{eff} Initial	1.053	1.039	1.039	1.023	1.002	1.011
k _{eff} Final	1.005	0.984	0.989	0.998	0.971	0.984
Δk	-0.048	-0.055	-0.050	-0.025	-0.031	-0.027
ISOTOPIC COMPOSITION						
Clean Core Fuel In (kg)	U ²³³ 500 U ²³⁴ 144 U ²³⁵ 14 U ²³⁶ 2 Th 2409	U ²³⁵ 644 U ²³⁸ 2647	U ²³⁵ 629 U ²³⁸ 2662	Pu ²³⁹ 405 Pu ²⁴⁰ 175 Pu ²⁴¹ 20 Pu ²⁴² 28 U ²³⁸ 2412	Pu ²³⁹ 334 Pu ²⁴⁰ 79 Pu ²⁴¹ 74 Pu ²⁴² 28 U ²³⁸ 2480	Pu ²³⁹ 568 Th 2296
Irradiated Fuel Out (kg)	U ²³³ 387 U ²³⁴ 154 U ²³⁵ 17 U ²³⁶ 4 Pa ²³³ 14 Th 2184	U ²³⁵ 327 U ²³⁶ 61 U ²³⁸ 2401 Np ²³⁷ 1 Pu ²³⁹ 154 Pu ²⁴⁰ 9	U ²³⁵ 323 U ²³⁶ 59 U ²³⁸ 2419 Np ²³⁷ 1 Pu ²³⁹ 154 Pu ²⁴⁰ 9	Pu ²³⁹ 362 Pu ²⁴⁰ 187 Pu ²⁴¹ 22 Pu ²⁴² 2 U ²³⁸ 2149	Pu ²³⁹ 335 Pu ²⁴⁰ 107 Pu ²⁴¹ 37 Pu ²⁴² 22 U ²³⁸ 2188	Pu ²³⁹ 305 Pu ²⁴⁰ 37 Pu ²⁴¹ 2 U ²³³ 149 U ²³⁴ 12 Pa ²³³ 17 Th 2046
Clean Blanket In (kg) (radial)	Th 7145	Th 7145	U ²³⁵ 55 U ²³⁸ 7735	U ²³⁸ 5860	U ²³⁸ 5860	Th 5280
Irradiated Blanket Out (kg) (radial)	U ²³³ 90 U ²³⁴ 1 Pa ²³³ 12 Th 7038 U ²³³ 30 Th 1500	U ²³³ 101 U ²³⁴ 1 Pa ²³³ 12 Th 7038 U ²³³ 21 Th 1446	U ²³⁵ 48 U ²³⁶ 1 U ²³⁸ 7605 Pu ²³⁹ 113 Pu ²³⁹ 30 U ²³⁸ 1555	Pu ²³⁹ 78 Pu ²⁴⁰ 1 U ²³⁸ 5783 Pu ²³⁹ 46 U ²³⁸ 2300	Pu ²³⁹ 90 Pu ²⁴⁰ 1 U ²³⁸ 5771 Pu ²³⁹ 50 U ²³⁸ 2300	U ²³³ 62 U ²³⁴ 1 Pa ²³³ 9 Th 5208 U ²³³ 40 Th 2200
BREEDING RATIO						
Incore	0.81	0.75	0.76	0.90	0.89	0.83
Blanket	0.28	0.21	0.22	0.29	0.33	0.19
Total	1.09	0.96	0.98	1.19	1.22	1.02

For heat transfer studies, maximum $\int kdt$ values of 5000 Btu/hr-ft were used in analyzing oxide fuel rods, while for the carbide-fueled epithermal core, fuel central temperatures of 2050°F maximum were assumed. Coolant temperature rise was approximately 400°F in all cases.

Nuclear calculations on epithermal reactors were made using a combination of multigroup nuclear programs. Corrections to the resonance region cross sections of fertile materials were made on the basis of a "rubber band" calculation of the surface-to-mass ratio of a fuel cluster. The "out-in" three-zone fuel shuffling scheme was employed. Important conclusions reached in nuclear and heat transfer studies of epithermal reactors are:

- 1) Epithermal reactors can be operated to relatively high fuel exposures with moderate losses in reactivity. Typically, $\Delta k/k$ changes of 15 to 20% would be expected for a reactor utilizing a three-zone loading scheme and discharging fuel exposed to 75,000 Mwd/T.
- 2) Core fissile loadings of at least 1000 to 1200 kg U^{233} are required for epithermal reactors capable of reaching fuel exposures of 75,000 Mwd/T.
- 3) Reactor startup using U^{235} -Th results in production of U^{233} badly diluted with U^{234} , U^{235} , and U^{236} unless the U^{235} and thorium are physically separated before insertion into the reactor.
- 4) Recycle of fission-product-free fuel cannot be continued indefinitely due to continuous buildup of higher isotopes, particularly U^{236} .
- 5) Problems presented by Li^6 and helium formation in beryllium moderator appear to be readily soluble.

Heat transfer and burnup studies for unmoderated systems showed that (1) all unmoderated systems examined can be operated for considerable lengths of time with relatively small losses in reactivity. This favorable situation results because in-core conversion ratios are high; thus there is little net burnup of "fuel" isotopes in the core, (2) all uranium, plutonium, thorium, and protoactinium isotopes are fissionable to some extent in a high energy spectrum reactor and help sustain reactivity, and (3) fission product poisoning is of minor importance at these energies. The cores can be operated

for 240 to 285 full power days (300 to 355 operating days at 0.8 plant factor) with reactivity losses of only 2.5 to 5.5% Δk . Unmoderated reactors are therefore not reactivity limited, and oxide fuels, which appear capable of achieving fuel exposures up to 100,000 Mwd/T, can be used to full advantage. It is found that rather complex isotopic mixtures of fuel result from exposure of fuel fertile material mixtures in the reactor cores, but relatively pure fuel is bred in the blanket regions. With U^{238} fertile material, about 15% of core power is developed from U^{238} fission, while in the reactors containing in-core thorium, only about 3 to 4% of the core power is developed from thorium fission. This results in larger initial fuel loads for reactors using Th as the in-core fertile material than when U^{238} is used.

The effectiveness of thorium or U^{238} as a blanket material is about equal for capturing neutrons. Thorium may be considered the preferred material on several points because energy production is not desirable in the blanket (thorium has a small fast fission cross section), and material bred in the blanket is relatively pure (pure U^{233} is more valuable to thermal reactors than Pu^{239} or U^{235}).

III. EVALUATION OF POTENTIAL AETR FUELS

A number of fuel elements have been evaluated for the AETR program. Fuel materials including metallic alloys, cermets, pastes, carbides, and oxides in the form of plates, rod bundles, or calandria-type elements have been considered. These studies have shown that fuel for an epithermal or fast spectrum sodium-cooled reactor should have the following important characteristics:

- 1) Fuel should be capable of achieving discharge exposures of at least 50,000 Mwd/T and preferably 75,000 to 100,000 Mwd/T, without serious fuel swelling or cladding failure; this is in contrast to burnup requirements for thermal reactors where fuel cycle costs are minimized at about 25,000 Mwd/T.
- 2) Fuel specific powers on the order of 1 Mwt/kg of fissionable isotope are desirable in order to minimize core inventory charges.
- 3) Fissile plus fertile isotope density in the fuel material should be as high as possible. As a minimum requirement, heavy metal density should exceed 7 g/cm^3 of fuel.
- 4) Fuel rod cladding must be compatible with sodium coolant at temperatures up to 1200°F and with fuel at temperatures exceeding 1300°F .
- 5) In order to attain economical fuel cycle costs, fabrication charges for core elements should not exceed \$300/kg contained fuel. In addition, facilities should be available for reprocessing fuel at costs consistent with an economic fuel cycle.

It was concluded that metallic fuels, such as Th-U alloy, are not economically attractive for either epithermal or unmoderated systems because of their relatively low allowable exposures (10,000 to 25,000 Mwd/T). Cermets are capable of achieving higher exposures, but fuel density is low. Pastes, including oxide-sodium and carbide-sodium mixtures have high burnup capabilities and potentially low fabrication and reprocessing costs, but suffer from fission gas evolution problems and low fuel density, and are limited to central temperatures below 1600°F .

Both mixed oxide and mixed carbide fuels show promise for use in epithermal and fast spectrum reactors. Table III presents a summary of comparable data for the two fuel materials. It will be noted that experimental conductivity and irradiation data for $\text{UO}_2\text{-ThO}_2$ and UC-ThC under fast reactor conditions have not been measured directly. Information on UO_2 , $\text{PuO}_2\text{-UO}_2$, and UC is available, however, and it has been assumed that thermal and irradiation characteristics will be the same for the thorium-containing components as for the uranium-plutonium mixtures.

TABLE III
COMPARISON OF OXIDE AND CARBIDE
FUELS FOR EPITHERMAL AND UNMODERATED REACTORS

	$\text{UO}_2\text{-ThO}_2^*$	Present* UC-ThC	Advanced* UC-ThC
Fuel form	gas-bonded rod	Na-bonded rod	gas-bonded rod
Theoretical density at operating temperature (g/cm ³)	10	11	11
Thermal conductivity (Btu/hr-ft-°F)	2.0	13.0	13.0
Max fuel cent temp (°F)	4,800	1,750	4,000
Max $\int k \, dT$ (Btu/hr-ft)	5,000	7,300	13,600
Max linear power gen- eration (kw/ft)	18	27	50
Max demonstrated fuel exposure (Mwd/T)	99,000 (2)	25,000	25,000
Estimated fabrication cost for 0.3 in. diam- eter rod (\$/kg)	125	175	175

* Thermal and irradiation data actually measured for UO_2 , $\text{Pu}_2\text{-UO}_2$, or UC; assumed the same for thorium-containing fuels.

(2) G. W. Wensch, et al., "A Summary of U.S. AEC Fast Breeder Reactor Program," (March 1962).

Table III indicates that oxide fuel is in a more advanced state of development, having demonstrated fuel exposures close to 100,000 Mwd/T in test capsules. Oxides are inherently more compatible with both stainless steel and air than are carbides. Mixed oxide fuels also have fabrication cost advantages over carbides since carbide fuels must first pass through an oxide stage. Mixed carbides, on the other hand, display higher thermal conductivity and fuel density which may make them attractive for possible use in more advanced epithermal and unmoderated concepts. For this reason, we are currently establishing some of the basic design characteristics of AETR-oriented thorium-uranium monocarbides. Results of this phase of the work are reported in a paper presented in another session of this symposium.⁽³⁾

(3) L. Abraham, "Thorium-Uranium Monocarbide Fuel Development," presented at Thorium Fuel Cycle Symposium, Gatlinburg, Tennessee December, 1962.

IV. STUDY OF CONTROL AND SAFETY PROBLEMS

Neutron lifetime is effective in determining the rate at which reactivity changes can be reflected as power changes. This coupled with a low thermal conductivity of oxide fuel increases the Doppler effect in the fuel which suppresses the net reactivity level in the reactor and increases power rise time for period and level control shutdown action. The delayed neutron fraction determines the control latitude and worth of external reactivity changes. Plutonium- U^{238} systems have a 30% greater fraction than U^{233} -Th systems due to the contribution of fast fissions in U^{238} . What is gained in increased β_{eff} for control is lost to some extent in lower Doppler effect because of the harder spectrum.

Median fission energies are higher for Pu- U^{238} systems than for U^{233} -Th systems due to the greater number of fast neutron fissions in U^{238} . In addition, losses of sodium or lower densities due to temperature rise lead to higher neutron energies. Since plutonium fissions increase more rapidly than captures, and U^{238} fissions also increase with increased neutron energy spectra, sodium and void coefficients of reactivity tend to be positive for Pu- U^{238} systems. A counteracting mechanism is operative as sodium density decreases; this is due to neutron leakage which results from two effects: (a) higher energy neutrons travel further between collisions, and (b) there are less sodium atoms to scatter the neutrons. For this reason large Pu- U^{238} reactors are designed for high leakage at the expense of breeding ratio. Optimization of design using U^{233} and/or thorium mixed with the Pu- U^{238} fuel may reduce the sodium coefficient problem at less expense to breeding ratio than present method of increasing leakage.

Another consideration related to the neutron energy spectrum is its effect on the fuel or Doppler coefficient of reactivity. Although it is expected that the Doppler coefficient is negative for both the U^{233} -Th and Pu- U^{238} systems, it is surely very small and will be smaller the higher the neutron energy. In addition, plans to operate the fuel center temperature near melting to take advantage of radiative heat transfer and in-pile sintering of ceramic fuel leave less latitude in the amount of temperature rise in the fuel before fuel meltdown, which may lead to coolant channel choking and resultant sodium void formation.

Because of the high specific powers in unmoderated reactor cores and the high coolant velocity, the temperature in the upper sodium pool increases rapidly during power transients. Preliminary calculations indicate that the upper grid and structure expand rapidly and produce sizeable negative reactivity effect of importance in transient limitation. This is not normal in thermal reactors where core expansion is of minor importance.

Control and safety studies show that either moderated or unmoderated reactors, operating with median neutron energies in the range of interest for the AETR concept, can be designed as safe sources of power. For transient analysis a digital computer program, called OSCAI I, was developed for use with the IBM 7090. The code calculates multichannel reactor conditions during excursions extending into a partial fuel meltdown and choked coolant condition. It is specifically intended for unmoderated sodium-cooled reactors using oxide or carbide fuels in which fuel temperatures are substantially higher than coolant temperatures.

Use of this digital program demonstrated that rapid reactivity ramps from full power can result in fuel melting without unstable oscillations in power, but that power may be cut back only temporarily after individual or groups of fuel elements are successively melted. Radical geometry change associated with fuel melting is expected to be the ultimate shutdown mechanism but this topic has not yet been investigated in detail. Increase in temperature of the outlet coolant plenum may result in significant pressurization, relief for which should be taken into consideration in plant design. Normal operational transients would be smaller in magnitude and much more rapidly corrected, and would not damage the reactor fuel elements or core.

Reactor safety is largely determined by the materials, safety parameters, and sequence of events during abnormal operations. Use of sodium coolant provides safety through high heat transfer, low vapor pressure, and retention of major radiologically troublesome fission products. Safety parameters such as prompt neutron lifetime, delayed neutron fraction, and temperature coefficients of reactivity generally favor the moderated reactor.

However, the unmoderated reactor is less inclined toward stability problems which may be associated with delayed and positive reactivity feedbacks; it may be designed with a sufficiently strong negative fuel temperature coefficient to give an adequately safe response to reactivity inputs during credible accidents. With U^{233} -Th fuel the AETR also has negative reactivity feedback from loss of coolant. If adequate negative coefficients can be assured by further experimentation and analysis, the unmoderated AETR can be designed to be essentially as safe as a moderated reactor. A better knowledge of the Doppler coefficients in a ceramic fueled fast reactor is essential before any realistic assessment can be made of the safety features of large ceramic fueled fast reactors and of the design criteria and economics for such reactors.

V. COMPARISON OF U^{233} -Th and Pu-U ECONOMIES IN A FREE MARKET

Fissile material produced in a reactor has value only if it can be utilized in either the reactor producing the material or some other reactor. Its value to any reactor must then be related to the cost of using an alternate fissile material.

Studies at Oak Ridge and Hanford have attempted to determine the value of U^{233} or plutonium to a given concept. The value of the reactor-produced fissile material is set at that value which equates the fuel cycle costs of the reactor system regardless of whether it is utilizing U^{235} or a fissile material produced by a nuclear reactor. These studies arrive at a different value of U^{233} or plutonium for each reactor concept studied. This is to be expected since each of the concepts uses fissile materials (U^{235} included) somewhat differently.

When consideration is given to a free market in nuclear fuel, the conclusion is reached that there can be basically only one price for any given fissile material. Any kind of economic setting resembling the equating of supply and demand seems to dictate one price for one kind of fuel regardless of the reactor used.

Certainly, fossil-fuel prices do not vary to a utility depending upon how efficiently each of its boiler units uses the fuel. The problem is then one of determining what market interactions set the price of reactor-produced fissile material. An examination of the general behavior of fuel cycle costs of various reactor concepts for various values of fissile material provides the basic answer.

Generally, all reactors which use U^{235} as a fissile material and produce fissile materials such as U^{233} or plutonium will have decreasing energy generation costs as the value of the produced fissile material increases. In contrast, reactors which use these fissile materials will have increasing generation costs as the value of the fissile material increases. These phenomena can be seen in Figure 5 where the crossover point of the two curves represents the market price of the fissile material.

Only those systems which yield the lowest total power generation costs will be built in quantity in an actual economy. Hence, it can be seen that

Fig. 5. Evaluating Fissile Material Produced by U^{235} Fueled Thermal or Unmoderated Reactors.

once an equilibrium condition is reached where supply and demand are approximately equal, producing and using systems must have about the same total power generation cost, since it is that criterion which equates the supply and demand. Unbalances that may arise because of new, more economic reactor concepts will only be temporary, because when either group of reactors in Figure 5 changes cost, there will be a change in the market value of the fissile material and corresponding change in the cost of power from the other group of reactors in order to equate supply and demand.

Based upon the above model, analyses were made of the U^{233} -Th economy and of the Pu-U economy. From a nuclear viewpoint, U^{233} appears a better fuel in thermal or epithermal systems than plutonium, while plutonium is a better fuel in unmoderated systems.

When U^{233} and plutonium values are equal, Th- U^{233} thermal systems have a lower cost than thermal Pu-U systems. However, the unmoderated systems which ultimately use recycled U^{233} have steeper cost curves than to the corresponding Pu-U systems; thus, at equivalent U^{233} and plutonium values above a few dollars per gram, such Th- U^{233} systems have a higher fuel cost than do the Pu-U systems. The result is that free market value of U^{233} appears to be lower than the similar value for plutonium. This is, of course, in direct contradiction to the present artificially guaranteed prices for these materials set by the AEC.

The free market value is, of course, only significant in its effect on the energy costs arising from each economy. Cross-plotting the results of the analyses of the two economies leads to the conclusion that there is little difference between two economies, especially in the region of interest rates which would represent ownership of fuel by investor-owned utilities. This may be seen from Figure 6 where unmoderated reactor fuel costs are plotted as a function of interest rate for a range of values of U^{233} and plutonium typical of the spread of possible market values shown in the previous analyses. Figure 7 also illustrates the similarity in cost using the most probable market values of the respective fissile materials.

Fig. 6. Fuel Cycle Costs for Unmoderated Reactors, Best Estimates of Cost Range.

Fig. 7. Fuel Cycle Cost, Best Estimates for Most Probable Fissile Material Values.

Session II
Paper 9

WATER COOLED THORIUM REACTORS

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WATER COOLED THORIUM REACTORS

BY

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I. Introduction & Scope of Discussion

Several water cooled thorium reactor concepts have been developed and studied by the Babcock & Wilcox Company. The use of thorium in pressurized water reactors and the spectral shift reactor are discussed. Emphasis is placed on the thorium fuel utilization in the SSCR concept. Comparisons of nuclear parameters, fuel utilization, and fuel composition are presented for batch cycled cores and zonal cycled cores. These comparisons are made for both the poison controlled cores and the spectral shift controlled cores as a function of cycles including the initial cycle, the intermediate cycles and the equilibrium cycle.

The scope of the thorium reactor study includes the cases outlined in Table 1.

TABLE 1

SCOPE OF THORIUM REACTOR DISCUSSION

- A. Spectral Shift Controlled Reactor
 - 1. Batch Recycled Core Without Blanket
 - 2. Shuffled Recycled Core Without Blanket
 - 3. Batch Recycled Core With Lateral and End Blankets

- B. Soluble Poison Controlled Reactor
 - 1. Batch Recycled Core Without Blanket
 - 2. Shuffled Recycled Core Without Blanket
 - 3. Batch Recycled Core With Lateral and End Blankets

II. General Description and Assumptions

The calculations in this study were done using standard methods. Nuclear parameters, as a function of D_2O to H_2O ratio, were calculated by the BPG 40-group spectral code. These quantities as functions of the D_2O/H_2O ratio were used in a spatially dependent lifetime or depletion code to calculate the core lifetime, the integrated conversion ratio and isotopic buildup and depletion. Power peaking factors for the spectral shift control reactor were obtained from two-dimensional PDQ calculations.

A list of important core parameters that are applicable to the batch and shuffled recycle SSCR and the batch and shuffled soluble poison controlled core is given in Table II.

For calculational purposes all of the core was approximated by right circular cylinders. The cores, batch and shuffled, contained three radial zones with the thorium to uranium ratio highest in the central zone, intermediate in the second zone and lowest in the outer zone. The ratios of fissionable material in the central, second, and outer zone were about 1.0, 1.2, 1.5 respectively.

A brief summary of methodology and assumption used in the fuel recycling is given.

The following system is used during the reshuffle recycle study. The initial loading is chosen such that the lifetime will fall between 350 and 400 F.P.D. At the completion of Cycle I the innermost zone (zone 1) is removed from the core, and the fuel elements making up zones 2 and

TABLE 2

CORE PHYSICS PARAMETER LIST

<u>Item</u>	<u>Batch Recycle</u>	<u>Shuffled Recycle</u>
Power Level (MWT)	1355	1355
Metal/Water Ratio	0.8	0.8
Pin OD (inches)	0.420	0.420
Clad Thickness (inches)	0.026	0.026
Average Moderator Temp. (F)	520	520
Core Active Height (inches)	116	116
Core Equivalent Diameter (inches)	102.8	120
Blanket Equivalent Diameter (inches) (Where Applicable)	108.8	126
Power Maximum/Power Average	1.9	2.5

3 are moved inward to zones 1 and 2 respectively. For this study the zones are numbered out from the center. Thus zone 3 is the outermost zone. A fresh zone 3 identical to that used in Cycle I is then loaded into the core and Cycle II is begun. During Cycle II the fuel contained in zone 1 of Cycle I is recovered. At the end of Cycle II, zone 1 is removed and zones 2 and 3 are moved into zones 1 and 2. Additional fully enriched U-235 is added to the fuel recovered from Cycle I, the mixture is blended with fresh thorium, and a new zone 3 is fabricated and placed in the core. This process continues from cycle to cycle with 3 zones in the core producing power and a fourth zone in the recovery and fuel element fabrication plant.

Batch recycle involves removing the entire core at the end of life rather than just one zone. After reprocessing and addition of makeup fuel, a new core is fabricated which may be used on a subsequent cycle or in a companion reactor. The output of cycle I is input to cycle II in the lifetime calculations. Actually, cycle I would feed cycle III if only one reactor is used, with cycle II being identical to cycle I. This has no influence on the mass balances or on the approach to equilibrium.

The fashion in which the core with blanket is handled is similar to the batch recycle. At the completion of a cycle the fissionable material in the core and in the blanket is reduced by 2% for losses. Bred fuel from the blanket is added to the fuel removed from the core and the mixture is blended with fresh ThO_2 in the appropriate thorium

to uranium ratios. A new ThO_2 blanket was added and the next cycle started.

The recycling schemes involved the following assumptions:

1. 2% of the recycled fuel is lost during recovery and fabrication.
2. The cooling period of the out of core elements is long enough that all of the Pa-233 decays into U-233.
3. Overage requirements are neglected.
4. Reshuffling takes enough time for Xe and iodine to decay out, and for Pm-149 to decay to Sm-149 but not long enough for an appreciable amount of Pa-233 to decay into U-233.

III. Spectral Shift Controlled Thorium Reactor

Spectral Shift Control, which has been under development by B&W for six years, utilizes a mixture of ordinary and heavy water as the moderator-coolant (rather than only ordinary water) in a conventional pressurized water reactor. The name derives from the principal that the neutron energy spectrum in the core is gradually changed, or shifted, over the lifetime of the core by decreasing the heavy water content of the moderator-coolant. The spectral shift principle is a means of reactivity control which permits the reactor to operate with a minimum of control rods and avoids the need for the parasitic, neutron absorbing poisons in the core.

Changing the heavy water concentration of the moderator-coolant affects core reactivity primarily because heavy water absorbs less energy per collision from a neutron than light water and a change in the relative amounts of heavy and light water therefore produces a change in the total moderation, or slowing down, of the neutrons. Thus, with a high concentration of heavy water, there is a relatively high population of neutrons of intermediate energy in the core, whereas with a preponderance of light water, the neutron spectrum is predominantly thermal.

Use is made of the fact that relatively more absorptions of neutrons will take place in the fertile material (Th-232) than in the fuel (U-235 or U-233) when the neutron spectrum is in the intermediate

energy range rather than when the spectrum is thermal. Thus, variations in the heavy water concentration can be used to control the relative absorptions of neutrons between fuel and fertile material.

The relatively high absorption of neutrons in fertile material rather than in parasitic poisons results in a high conversion ratio (i.e., a high conversion of Th-232 to uranium fuel). Further the ability of the heavy water to control a large amount of excess reactivity or excess fuel at the start of core life permits the core to be designed for long life. The additional fuel created during the core life - because of the improved conversion ratio - also permits the core to achieve a long lifetime. The higher conversion ratio in the spectral shift controlled reactor results in lower fuel burnup costs than those present in a pressurized water reactor controlled by parasitic poisons.

The mass balances for the shuffled recycle core with no blanket and spectral shift control are given in Table 3. This table gives the masses of important materials for Cycle I through VII and the equilibrium cycle. Mass balances are given at the beginning and end of each of the 400 day cycles. The integrated conversion ratio (ICR) starts at 0.75 for Cycle I and increases to 0.85 for the equilibrium cycle.

A neutron balance which shows the fraction of neutrons absorbed in each isotope, moderator and structural material is given in Table 4 at the beginning of Cycle VII with 48% D₂O in the water in the core and at 400 days of core life of Cycle VII with all H₂O in the core. The studies

TABLE 3
MASS BALANCE

SSCR Reshuffle Recycle

	CYCLE I		CYCLE II		CYCLE III		CYCLE IV	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
U-235 Kg	1670	1154	1474	998	1167	780	958	648
U-233 Kg	-	317	198	485	415	627	596	745
Pa-233	-	48	29	47	30	47	29	47
U-234 Kg	-	12	7	29	19	46	37	67
U-236 Kg	-	97	63	149	125	189	168	215
Th-232 Kg	54340	53880	53940	53420	53700	53190	53700	53190
U-235 Kg Makeup	-	-	636	-	82	-	154	-
Core Life (Days)	-	350	-	400	-	400	-	400
ICR		.75		.75		.76		.78
Initial % D ₂ O	48	-	44	-	44	-	49	-

TABLE 3 (Cont'd)
 MASS BALANCE
 SSCR Reshuffle Recycle

	CYCLE V		CYCLE VI		CYCLE VII		EQUILIBRIUM	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
U-235 Kg	723	492	661	469	583	406	450	345
U-233 Kg	757	818	829	890	870	920	1050	1050
Pa-233 Kg	30	47	31	47	29	47	30	47
U-234 Kg	66	96	86	114	101	128	180	180
U-236 Kg	215	245	247	267	250	268	280	280
Th-232 Kg	53730	53210	53670	53150	53700	53184	53620	53100
U-235 Kg Makeup	81	-	102	-	107	-	105	-
Core Life (Days)	-	400	-	400	-	400	-	400
ICR		.81		.82		.83		.85
Initial % D ₂ O	50	-	50	-	51	-	51	

of the shuffled recycle core with lateral and end blankets have not been completed. Preliminary results which are not reported in detail indicate that the blanket increases the equilibrium cycle conversion ratio to about 0.90.

Table 5 gives the mass balances of the 1000 day batch recycle core without blankets for Cycles I - IV and equilibrium. The conversion ratio of Cycle I is 0.71 and increases to 0.82 at equilibrium conditions.

Table 6 reports the mass balances for the 1000 day batch recycle core with lateral and end blankets. Cycle I conversion ratio is 0.73 and reaches 0.86 under equilibrium conditions. The increase of conversion due to the blanket can be obtained by a comparison of Tables 5 and 6. This comparison shows that the three inch thick blanket increases the equilibrium cycle conversion ratio by about five per cent, i.e., from 0.82 to 0.86.

TABLE 4

SSCR SHUFFLED CYCLE SEVEN

NEUTRON BALANCE NORMALIZED TO ONE
ABSORPTION IN U-233 + U-235

Elements	Zero Days			400 Full Power Days		
	Reson.	Thermal	Total	Reson.	Thermal	Total
Th-232	.5799	.2554	.8353	.4246	.3478	.7724
U-233	.3182	.3108	.6290	.2601	.4578	.7179
U-235	.1218	.2492	.3710	.0593	.2228	.2821
U-236	.0379	.0011	.0390	.0304	.0016	.0320
Pa-233	.0063	.0011	.0074	.0082	.0028	.0110
U-234	.0315	.0059	.0374	.0302	.0107	.0409
Pm-149	-	-	-	-	-	-
Xe-135	-	-	-	-	.0404	.0404
Sm-149	-	.0054	.0054	-	.0083	.0083
Fission Products U-233	.0203	.0082	.0285	.0360	.0275	.0635
Fission Products U-235	.0166	.0060	.0226	.0244	.0167	.0411
H ₂ O (in fuel)	.0088	.0278	.0366	.0123	.0737	.0860
D ₂ O (in fuel)	-	-	-	-	-	-
S. Steel	.0109	.0203	.0312	.0079	.0278	.0357
Zircaloy	.0041	.0084	.0125	.0030	.0116	.0146
Leakage from fuel	.0166	.0890	.1056	.0136	.0620	.0756
Total	1.1729	.9886	2.1615	.9100	1.3115	2.2215

TABLE 5
MASS BALANCE
SSCR BATCH RECYCLE

	CYCLE I		CYCLE II		CYCLE III		CYCLE IV		EQUILIBRIUM	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
U-235 Kg	1700	593	886	345	685	298	621	288	550	273
U-233	-	568	598	743	770	800	826	816	850	825
Pa-233	-	43	-	43	-	43	-	43	-	43
U-234	-	64	60	122	120	158	155	178	228	233
U-236	-	204	200	258	253	276	271	284	300	306
Th-232	38,801	37,587	38,734	37,492	38,709	37,480	38,604	37,384	38,549	37,307
U-235 Makeup			305		347		329		276	
Core Life (Days)		1000		1000		1000		1000		1000
ICR		.709		.784		.801		.810		.820
Initial P ₂ O %	70.2		75.4		74.5		73.0		71	

TABLE 6
MASS BALANCE
SSCR-ThO₂ BLANKET BATCH RECYCLE

Cycle	I		II		III		IV		EQUILIBRIUM	
	Begin	End	Begin	End	Begin	End	Begin	End	Begin	End
U-235	1,693	616	827	328	646	300	516	258	530	280
U-233	-	611	642	808	836	884	910	907	920	890
Pa-233	-	43.7	-	44.8	-	44.4	-	44.3	-	44
U-234	-	61.2	60.0	126	123	165	162	188	210	214
U-236	-	207	203	256	250	271	266	273	280	286
Th-232	43,669	42,386	43,630	42,325	43,526	42,236	43,508	42,210	43,500	42,200
¹⁸⁶ Δ U-235	-		223		324		223		250	
ICR	0.731		0.819		0.837		0.850		0.86	
Initial D ₂ O %	67.5		73.5		72.5		71.0		67.0	

Core Life = 1000 days for all cycles

IV. Soluble Poison Controlled Thorium Reactor

The soluble poison controlled reactors have been studied for a number of years. The fuel cycle neutron economy and conversion ratios in water reactors controlled by chemical poisons are essentially the same as for pressurized water reactor controlled with control rods. However, soluble poison controlled cores are able to achieve longer core lifetimes and flatter power distributions than rod controlled cores are able to achieve.

In the soluble poison control studies that has been completed it is assumed that the soluble poison control core is able to achieve the same maximum to minimum power peaking factor that is achieved in the spectral shift control reactor. For heat transfer calculations a 1.9 power peaking factor was used for the batch recycle soluble poison core and a 2.5 power peaking factor was used for the shuffled recycle soluble poison core.

Table 7 shows the mass balance for the 400 day soluble poison reshuffle recycle core for Cycles I-VII and equilibrium. The conversion ratio of Cycle I is 0.71 and increases to 0.75 at equilibrium.

The same information is given for the 1000 day soluble poison batch recycle core in Table 8 where the conversion ratio starts at 0.59 for Cycle I and increases to 0.65 at equilibrium conditions.

Table 9 gives the mass balances of the 1000 day soluble poison batch recycle core for Cycles I - V and equilibrium. The conversion ratio changes from 0.61 to 0.69 from Cycle I to the equilibrium cycle.

TABLE 7
MASS BALANCE
Soluble Poison Reshuffle Recycle

	CYCLE I		CYCLE II		CYCLE III		CYCLE IV	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
U-235 Kg	1710	1129	1474	996	1239	832	1014	685
U-233 Kg	-	336	214	476	412	610	586	719
Pa-233 Kg	-	47	29	45	30	45	30	45
U-234 Kg	-	13	8	28	19	43	36	63
U-236 Kg	-	106	71	154	131	198	177	227
Th-232 Kg	54300	53810	53850	53380	53660	53190	53640	53170
U-235 Kg Makeup	-	-	636	-	182	-	167	-
Core Life (Days)	-	400	-	400	-	400	-	400
ICR		.71		.70		.71		.72
Initial H ₃ BO ₃ (g/l)	4.0	-	3.5	-	3.8		4.1	

TABLE 7 (Cont'd)
MASS BALANCE
Soluble Poison Reshuffle Recycle

	CYCLE V		CYCLE VI		CYCLE VII		EQUILIBRIUM	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
U-235 Kg	833	568	775	535	720	498	600	440
U-233 Kg	730	811	785	846	834	880	975	975
Pa-233 Kg	30	46	31	45	30	45	30	45
U-234 Kg	63	90	79	105	95	120	180	180
U-236 Kg	226	262	254	284	273	300	330	330
Th-232 Kg	53680	53190	53650	53176	53750		53650	53150
U-235 Kg Makeup	153	-	155	-	165	-	60	-
Core Life (Days)	-	400	-	400	-	400	-	400
ICR		.74		.74		.75		.75
Initial H ₃ BO ₃ (g/l)	4.3	-	4.4	-	4.4		4.4	

TABLE 8
MASS BALANCE

Soluble Poison Batch Recycle

	CORE I		CORE II		CORE III		CORE IV		CORE V		EQUILIBRIUM	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
U-235 Kg	1959	727.1	1330	528.9	1170	497.2	1087	474.7	1066	482.8	1030	475
U-233 Kg	-	502.7	531.7	675.8	701.2	736.0	759.5	755.7	778.7	761.4	800	778
Pa-233 Kg	-	39.8	-	39.7	-	38.9	-	38.9	-	39.0	-	39.0
U-234 Kg	-	45.5	44.6	97.6	95.6	134.6	131.9	158.7	155.5	173.6	200	204
U-236 Kg	-	220.1	215.7	323.4	316.9	378.2	370.6	423.1	414.6	454.9	540	551
Th-232 Kg	38,523	37,522	38,713	37,718	38,582	37,604	38,484	37,505	38,439	37,458	38,270	37,280
U-235 Kg Makeup	-	-	620	-	650	-	600	-	580	-	565	-
Nominal Life (days)	-	1000	-	1000	-	1000	-	1000	-	950	-	1000
ICR		.59		.62		.63		.64		.65		.65
Initial H ₃ BO ₃ (g/liter)	12.64	-	15.4	-	16.1	-	15.4	-	14.8	-	14.0	-

TABLE 9
MASS BALANCE

Soluble Poison - ThO₂ Blanket Batch Recycle

Cycle	I		II		III		IV		V		EQUILIBRIUM	
	Begin	End	Begin	End	Begin	End	Begin	End	Begin	End	Begin	End
U-235	1,917	708	1,218	474	1,101	468	976	422	972	431	977	447
U-233	-	535	568	713	739	775	799	793	817	801	823	800
Pa-233	-	41.3	-	41.5	-	40.4	-	40.8	-	40.6	-	40
U-234	-	46	45	101	99	139	136	164	161	180	186	190
U-236	-	220	218	317	311	377	369	413	405	440	470	480
Th-232	43,400	43,400	43,295	42,243	43,109	42,093	43,077	42,050	43,003	41,985	43,000	42,000
Δ U-235	-		521		631		522		547		550	
ICR	0.61		0.65		0.65		0.67		0.68		0.69	
Initial H ₃ BO ₃ (g/Li)	12.9		15.3		16.4		15.3		15.1		15.0	

Core Life = 1000 days for all cycles

V. Summary and Conclusions

A summary of the conversion ratios for shuffled and batch recycled core utilizing both spectral shift control and soluble poison control are tabulated in Table 10.

This table shows that the spectral shift control reactor offers a conversion ratio of at least 0.1 higher than the shuffled soluble poison controlled reactor. Further, the recycling of fuel is more attractive in the SSCR than the PWR, because as shown in the tabulation the SSCR conversion ratio increases by from 0.10 - 0.13 between Cycle I and equilibrium, while the PWR conversion ratio increases by about 0.04 - .08 between Cycle I and equilibrium.

Additional studies that are not yet tabulated show that a three inch thick blanket increases the equilibrium cycle conversion ratio of the SSCR shuffled core to 0.89. This conversion was achieved with the 400 day cycle length and the 0.8 metal to water ratio. Studies have also shown that the conversion ratio can be increased significantly above 0.9 if a shorter cycle length is used, the blanket thickness is increased, and the metal to water ratio increased.

TABLE 10
CONVERSION RATIO AS A FUNCTION OF CYCLE NUMBER FOR
VARIOUS SSCR AND SOLUBLE POISON PWR CORES
CONVERSION RATIO

<u>Reactor Type</u>	<u>Cycle 1</u>	<u>Cycle 2</u>	<u>Cycle 3</u>	<u>Cycle 4</u>	<u>Cycle 5</u>	<u>Cycle 6</u>	<u>Cycle 7</u>	<u>Cycle Equilibrium</u>
SSCR - 400 Day Shuffle Recycle	.75	.75	.76	.78	.81	.82	.83	.85
Soluble Poison PWR - 400 Day Shuffle Recycle	.71	.70	.71	.72	.74	.74	.75	.75
SSCR - 1000 Day Batch Recycle	.71	.78	.80	.81				.82
Soluble Poison PWR - 1000 Day Batch Recycle	.59	.62	.63	.64	.65			.65
SSCR - 1000 Day Batch Recycle With Blanket	.73	.82	.84	.85				.86
Soluble Poison PWR - 1000 Day Batch Recycle With Blanket	.61	.65	.65	.67	.68			.69

Session II
Paper 10

MOLTEN SALT AND AQUEOUS POWER REACTORS FOR
THORIUM UTILIZATION

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Introduction

The essential economic advantage of fluid fuel reactors is that fuel fabrication costs are negligible and that fuel reprocessing may, in principle, be performed continuously on-site, and, when integrated with the reactor, costs very little.

Other advantages, such as the absence of excess reactivity and control poisons, the absence, in circulating fuel reactors, of internal heat transfer and associated structure and coolant, the capability for continuous operation, etc., more than offset disadvantages such as the inventory of valuable materials in external heat exchange loops, the difficulty of containment of irradiated fuel in these and the requirements for remote maintenance (though the last may eventually prove to be an advantage).

But the overriding advantage of fluid fuel reactors stems from the chemical engineering of the fuel. It is the purpose of this paper to show how this basic advantage, taken together with the unique advantages of molten-salt and aqueous fuels, makes the use of thorium economically attractive in power reactors both in the short and long run.

Molten Salt Reactors

Beginning with the Aircraft Nuclear Propulsion Project, molten fluoride reactors have been the object of research and development at ORNL and elsewhere for over fifteen years. In 1954, the Aircraft Reactor Experiment, a 2.5-Mwt circulating fuel molten-salt reactor was successfully operated for more than 90,000 kwhr at temperatures up to 1650°F. The potential usefulness of molten-salt fuels for civilian power was recognized from the start. The unique features that attracted attention were the high temperatures attainable (permitting use of modern steam technology and attainment of high thermal efficiency) at low pressures, ample solubility for thorium and uranium fluorides, and the applicability of the well-developed Fluoride Volatility Process for recovery of isotopes of uranium, and the ease of recycling U^{233} and irradiated thorium.

The Molten Salt Reactor Program, instituted at ORNL in 1956, comprised an evaluation program to select the most promising reactor concepts for civilian power and to pinpoint crucial development problems; an extensive materials development program for fuels, containers, and moderators; an equally extensive program for the development of components, especially pumps, valves, and flanges suitable for extended use with molten salts at 1300°F; a modest program for the discovery of supplemental chemical process for recovering valuable components (other than uranium) from irradiated fuel; and a program for the development and definitive demonstration of a remote maintenance facility for molten-salt reactors. These programs have substantially reached their initial goals, and a project has been instituted to design and construct a molten-salt reactor experiment (MSRE) to demonstrate the utility of these achievements and resolve remaining areas of uncertainty.

1000-Mwe Molten Salt Converter Reactor¹

This one-region, one-fluid, near-term system is essentially a scale-up of the MSRE² with power generation added, and does not require any technology beyond the scale-up that already developed in the laboratory or to be demonstrated in the MSRE. The INOR-8 reactor vessel, measuring 20 ft in diameter and 20 ft high, is filled with vertically stacked, cylindrical graphite logs 6 inches in diameter and 24 inches long. The fuel, a mixture of the fluorides of Li⁷, Be, Th, and U, having a density of 190 lbs/ft³ and a heat capacity of 0.38 Btu/lbs°F enters at 1100°F and 80 psig, flows upward through the passages (10 volume percent) formed by the logs at a velocity of 6 ft/sec, and is discharged at 1300°F through eight pumps having salt-lubricated bearings to an equal number of heat exchangers where the heat is transferred to an intermediate salt coolant (63-Li⁷F, 37-BeF₂) chemically and nuclearly compatible with the fuel salt. Steam saturated at 2400 psi is superheated to 1000°F in a shell-and-tube exchanger; part of the steam is routed to the turbines, the rest is recirculated to Loeffler boilers where saturated steam is generated by injecting the superheated steam into liquid water. Thermal contact of the

coolant salt with sub-cooled boiling water is avoided, thus holding thermal stresses in the tube walls to tolerable levels. Thermal efficiencies in excess of 40% are easily obtainable. Twenty-five hundred Mw of heat are easily extracted from a single core at average power densities in the fuel salt of not more than 35 watts/cc.

Irradiated fuel is removed from the reactor daily, collected into processing batches, and treated with fluorine for recovery of isotopes of uranium (fully decontaminated) as the hexafluoride. The stripped salt is discarded, since the HF Dissolution Process (which permits recycle of carrier salt) is not sufficiently advanced to label it "current technology." Recovered UF_6 is reduced to UF_4 , blended with fresh salt, and recycled to the reactor. Deficiencies in the breeding ratio are compensated by addition of 95% enriched U^{235} .

MSCR Nuclear and Thermal Performance

The limiting criteria (e.g., maximum allowable fuel temperature, maximum allowable thermal stress in graphite, etc.) were chosen conservatively throughout, and provide considerable margin for improvement in later designs. The key variables (core diameter, volume fraction of fuel in core, carbon/thorium ratio, and processing rate) were optimized with respect to the fuel cycle cost. Characteristics of the optimized system are listed in Table 1, where it is seen that the optimum conversion ratio, with full loss of neutrons to xenon, is 0.84.

TABLE 1

NUCLEAR AND THERMAL PERFORMANCE OF 1000-MWE MOLTEN SALT CONVERTER REACTOR

Thermal capability	2500 Mwt
Net thermal efficiency	41.5%
Diameter and height of core	20' x 20'
Volume fraction of fuel in core	0.10
C:Th atom ratio	~ 300
Th:U atom ratio	~ 30
Volume of circulating fuel stream	2500 ft ³

TABLE 1 (cont.)

Circulation rate	160 ft ³ /sec
Processing rate (Fluoride Volatility)	$\left\{ \begin{array}{l} 1.7 \text{ ft}^3/\text{day} \\ 53 \text{ kg Th/day} \end{array} \right.$
Power density in core (av.)	14 w/cc
Power density in fuel salt (av.)	35 w/cc
Fertile material specific power	30 Mwt/tonne Th
Fissile material specific power	0.9 Mwt/kg U
Fertile material exposure	47,000 Mw·days/tonne Th
Mean neutron production	2.21
Optimum conversion ratio	0.84 (0.90*)

* With improved graphite to occlude Xe.

These calculations were based on the assumption that fission product gases would be absorbed by the moderator and that the full loss of neutrons to xenon-135, etc., would result. Modest improvements in graphite properties (by reduction of porosity and/or diffusivity) would nearly eliminate the xenon penalty, and result in an optimum conversion ratio of 0.90 and a maximum of 0.93 at a processing rate of 5 ft³/day.

MSCR Fuel Cycle Cost

The estimation of inventory and replacement charges for the MSCR is straightforward and unequivocal. Processing costs are less well defined; however, the processing contributes only a small part of the total fuel cost, and the aggregate is not sensitive to large errors in the processing cost estimates.

A central Fluoride Volatility facility capable of processing 30 ft³/day of salt (1000 kg/day of thorium for the MSCR fuel) was designed and costed.³ Only isotopes of uranium are recovered; carrier salt and thorium are discarded along with fission products. The capital investment was estimated to be about \$30 million and the annual operating expense about \$3 million, which leads, with a turn-around-time of two days and 6000 kg processing batches, to a processing cost of ~ \$35/kg thorium. Shipping costs were estimated to be ~ \$10/kg of

thorium. With thorium (as the fluoride) at \$19/kg thorium, carrier salts at \$1130/ft³, and fissile isotopes at \$12/gram, the cost schedule shown in Table 2 was computed for the case with full xenon poisoning loss.

With modest improvements in the graphite, as discussed above, burnup and inventory charges may be reduced and fuel cycle costs less than 0.7 mills/kwhre achieved at a conversion ratio of 0.9.

TABLE 2

1000-MWE MOLTEN SALT CONVERTER REACTOR PLANT FUEL CYCLE COST

<u>Material</u>	<u>Charges, mills/kwhre</u>			<u>Total</u>
	<u>Inventory</u>	<u>Replacement</u>	<u>Processing</u>	
Th ²³²	0.03	0.04		
Pa ²³³	0.01	-		
U ²³³	0.20		0.08	
U ²³⁵	<u>0.05</u>	<u>0.23</u>	<u> </u>	<u> </u>
TOTAL	0.29	0.27	0.08	0.64
Salt	0.06	0.08	-	<u>0.14</u>
Total Charges, mills/kwhre				0.8 (0.7*)

* With improved graphite.

Alternatively, the spent fuel may be processed in a central Thorex plant for recovery of both thorium and uranium. The capital cost of such a plant with appropriate head- and tail-end conversion steps was estimated³ at about \$37 million, with annual operating costs of \$3.7 million. This leads to an increase in the fuel cycle cost of only 0.03 mills/kwhre. The processing cost was also computed according to the recipe given in the Guide to Nuclear Power Reactor Evaluation.⁶ In this calculation, the daily operating charge was \$17,000, shipping cost is \$17/kg of heavy metal, and the turn-around-time was eight days. The resulting fuel cycle cost is 0.85 mills/kwhre. It is clear that, on any reasonable basis, the fuel cycle cost for the MSCR will certainly be less than 1.0 mill/kwhre, probably less than 0.85 mills/kwhre, and possibly as low as 0.7 mills/kwhre (with improved graphite).

MSCR Power Costs

These were obtained by combining fuel cycle costs with estimates of capital charges estimated from a design and cost study conducted jointly between ORNL and Sargent and Lundy, Engineers.^{4,5} Equipment was sized and specified in sufficient detail that costs might be estimated by usual procedures. Plant arrangement drawings were prepared from which costs of buildings, piping, services, etc., were estimated. Operation and maintenance costs were estimated according to standard procedure.⁶ A summary of the principle items is given.

TABLE 3

1000-MWE MOLTEN SALT CONVERTER REACTOR CONSTRUCTION COSTS

<u>Direct Construction Costs</u>	<u>Amount</u>
Structures and Improvements	\$ 5,998,000
Reactor Plant Equipment	51,324,000
Turbine-Generator Units	26,844,000
Accessory Electric Equipment	4,375,000
Miscellaneous Power Plant Equipment	<u>800,000</u>
Total Direct Construction Cost	\$89,341,000
<u>Indirect Cost</u>	
Contractor's Overhead and Profit (20% of direct labor cost)	2,333,000
General and Administrative Cost (6.3% of sub-total)	5,776,000
Miscellaneous Construction Cost (1% of sub-total)	<u>975,000</u>
Total Indirect Costs	\$ 9,084,000
<u>Engineering Design and Inspection Costs</u>	
Arch. Eng. Design and Inspection (11.1% of sub-total)	10,925,000
Nuclear Engineering (3.8% of sub-total)	<u>4,155,000</u>
Total Eng. Des. and Insp.	\$15,080,000

TABLE 3 (cont.)

Miscellaneous Charges

Start-up Costs (35% annual operating cost)	747,000
Land and Land Rights	360,000
Contingency (10% of subtotal)	11,461,000
Interest During Construction (9.4% of subtotal)	11,851,000
Intermediate Coolant Salt (including 1.5% interest during construction)	<u>10,952,000</u>
Total Miscellaneous Charges	\$35,371,000
Grand Total	\$148,876,000
Net Station Power	1038 Mwe
Unit Capital Cost	\$143/kwe

The capital cost, including the very expensive intermediate coolant salt, comes to only \$143/kwe. The fixed charges thus (at 14.46%) contribute 3.0 mills/kwhre to the power cost.

The uncertainty in this cost is hard to estimate, but conceivably might run as high as 15-20%, so that the fixed charges might range up to 3.5 mills/kwhre.

It is interesting to note that the direct construction cost (\$89 million) is the same as that estimated by Jackson and Moreland, Inc.¹³ for a 1000-Mwe fossile fuel power plant. The total cost, however, exceeded that of the fossil-fuel plant by \$30 million, of which only \$11 million was contributed by the cooling-salt. The excess of \$20 million resulted from the application of higher indirect-cost percentages and fees in the nuclear plant.

TABLE 4

1000-MWE MOLTEN SALT CONVERTER REACTOR OPERATING AND MAINTENANCE COST

Labor and Management	\$ 872,000
Materials and Supplies (nominal)	1,000,000
Central Office Gen. and Admin. Exp.	<u>262,000</u>
Total Annual Op. and Maint. Cost	\$2,134,000

Operation and maintenance thus contribute 0.3 mills/kwhre to a total power cost. In this estimation, materials and supplies were taken nominally at \$1,000,000, as prescribed in the "Guide."⁶ This may be low, and the operation and maintenance cost might well run as high as 0.5 mills/kwhre.

TABLE 5

1000-MWE MOLTEN SALT CONVERTER REACTOR POWER COST

<u>Item</u>	<u>Charge, mills/kwhre</u>
Fuel Cycle	0.7
Fixed Charges	3.0
Operating and Maintenance	<u>0.3</u>
TOTAL	4.0

Taking the upper bounds estimated above (fuel cost ~1.0, fixed charges ~ 3.5, operation and maintenance ~0.5) results in an upper limit on the cost of power of 5.0 mills/kwhre.

Advanced MSCR

The system evaluated above was based on current technology, and was conservatively designed in every respect. There are a number of obvious improvements that could be incorporated into a "second generation" design. If the design criteria were relaxed, metallic sodium could be substituted for the intermediate salt coolant (saving about \$10 million in capital costs). This would also permit the use of conventional once-through sodium-heated boilers and reduce the cost of the energy conversion system by about another \$10 million to ~\$125/kwe. By careful design and development the fuel volume might be reduced from 2500 ft³ to 1800 ft³. Separated Mo⁹² could be used to clad the graphite and so reduce absorption of xenon therein and also as a structural material by means of which a blanket of ThF₄ bearing salt could be added at the periphery of the core to reduce neutron leakage. The use of Fluoride Volatility coupled with the HF Solution Process¹² to remove rare earths would reduce the fission product poisoning to very low levels while permitting recycle carrier salt but not

thorium. Preliminary calculations show that these improvements (all within reach of modest development programs) would increase the conversion ratio above 1.02, and, with reduction in capital costs noted, would result in a power cost of 3.4 mills/kwhre.

Molten Salt Breeder Reactors

The nuclear capability of a thermal breeder (MSBR) was studied previously,⁷ and it was shown that two region two fluid systems are capable of conversion ratios up to 1.07 and doubling times as low as fifteen years. The fuel cycle costs were not well defined, but possibly are below 1 mill/kwhre for a doubling time ~25 years if a combination of fluorination and HF dissolution are used in the processing. Since two cores would probably be required to produce 1000 Mwe, the capital cost of the station may be greater than that of the MSCR, but the cost of power should lie between 4 and 5 mills/kwhre, on current bases. Development of on-site, reactor-integrated processing methods could lower the cost appreciably.

Fast molten salt breeders (MSFBR) have been investigated only recently. Preliminary results for an internally cooled two-region, two-fluid reactor using stainless steel or Inconel structure and a fissile and fertile stream carrier salt composed of the inexpensive fluorides of sodium and potassium, and processed by fluorination only, indicates that breeding ratios in excess of 1.1 are possible. Fuel cycle and capital costs have not been estimated; however, lower specific powers and higher processing costs may be offset by higher breeding credits.

Aqueous Reactors

Aqueous homogeneous reactors have been developed in the United States and abroad. A "solution-core" reactor, utilizing uranyl sulfate dissolved in D₂O was operated at ORNL;⁸ a "slurry-core" reactor is presently under study in Europe.^{9,10} Heavy water is unsurpassed as a moderator for thermal reactors, especially for those using thoirum, and Zircaloy can be used for internal structure in two-region reactors with only a small parasitic loss of neutrons.

Aqueous Slurry Converter Reactor

This one-region, one-fluid reactor is a scaled-up version of the KSTR,^{9,10} and requires only technology currently being developed. The fuel consists of a 350 g/liter slurry of ThO₂-UO₂ particles in D₂O, which is circulated through a 20-ft spherical core where 3640 Mw of heat is generated. The fuel enters at 500°F, exits at 572°F and 1400 psi. The flow rate is about 800 ft³/sec.

Preliminary results, not yet fully optimized with respect to either conversion ratio or fuel cycle costs, are given in Table 6. It was assumed that about 2/3 of all fission product gases escape from the particles and are removed by stripping steam. If all the xenon, etc., should be trapped inside the particles, or were readsorbed strongly, the conversion ratio would be ~0.95.

TABLE 6

NUCLEAR AND THERMAL PERFORMANCE OF 1000-MWE AQUEOUS SLURRY CONVERTER REACTOR

Thermal Capability	3640 Mwt
Thermal Efficiency	27.5%
Diameter of Spherical Core	20 ft
D/Th Atom Ratio	~ 50
Th:U Atom Ratio	~ 65
Volume of Circulating Fuel Stream	7,830 ft ³
Circulation Rate	825 ft ³ /sec
Processing Rate (Thorex)	$\left\{ \begin{array}{l} 15 \text{ ft}^3/\text{day}, \\ 150 \text{ kg Th/day} \end{array} \right.$
Power Density in Core (avg.)	30 w/cc
Power Density in Fuel Stream (avg.)	17 w/cc
Fertile Material Specific Power	46 Mwt/tonne
Fissile Material Specific Power	3 Mwt/kg
Fertile Material Exposure	24,000 Mwd/tonne
Mean Neutron Production	2.22
Conversion Ratio	0.98*

* Preliminary estimate. When fully optimized should be in excess of 1.0

ASCR Fuel Cycle Cost

From the standpoint of fuel costs, the ASCR is competitive with the MSCR. Thorium (as the oxide) was valued at \$19/kg of thorium, fissionables at \$12/gram, D₂O at \$28/lb (2% annual loss). The processing cost was estimated from a design and cost study of a 1000-kg Th/day Thorex plant in which both thorium and uranium were recovered and refabricated into a slurry by means of the "sol-gel" process. The capital cost was estimated at \$36 million, annual operating expense at \$3.6 million, and unit cost (with turn-around-time of 2 days) of \$40/kg of Th. Shipping costs were estimated at \$10/kg Th.

TABLE 7

1000-MWE AQUEOUS SLURRY CONVERTER REACTOR FUEL CYCLE COST*

<u>Material</u>	<u>Inventory</u>	<u>Charges, mills/kwhre</u>		
		<u>Replacement</u>	<u>Processing</u>	<u>Total</u>
Th ²³²	0.40	0.01		
Pa ²³³	0.02			
U ²³³	0.20	0.04	0.31	
U ²³⁵	<u>0.02</u>	<u> </u>	<u> </u>	<u> </u>
TOTAL	0.28	0.05	0.31	0.64
Heavy Water	0.27	0.04	-	<u>0.31</u>
Total Charges, mills/kwhre				0.95*

* Not fully optimized

Advanced ASCR

The loss in breeding ratio due to neutron captures in nonvolatile fission products was more than 0.09 at the processing rate selected (150 kg Th/day). This loss could be reduced substantially by processing at a more rapid rate, but the gain in breeding ratio would be offset by increased processing costs. However, the possibility exists that a large portion (perhaps 90%) of all fission products, could be removed very rapidly by adding finely divided activated charcoal to the fuel stream.¹⁰ When the fuel particles (ThO₂-UO₂) are sufficiently small, most of the fission fragments escape. The charcoal,

presenting a much larger surface than the oxide, preferentially adsorbs the fission products, whereupon removal of the charcoal also removes the fission products. In this way, breeding ratios as high as 1.05 are attainable at the same (Thorex) processing rate assumed above. Production credits lower the fuel cycle cost to ~ 0.8 mills/kwhre.

ASCR Power Costs

Capital investment for the ASCR has not been estimated. However, capital costs for a 1000-Mwe Aqueous Homogeneous Breeder Reactor (AHBR) utilizing three turbo-generators coupled to three reactors using uranyl sulfate dissolved in D₂O in the core and pebbles of ThO₂ in the blanket were estimated jointly by ORNL and Sargent and Lundy, Engineers,¹¹ at \$168/kwe (excluding investment in D₂O). The ASCR station has only a single reactor of much simpler construction (though larger). Perhaps as much as \$20/kwe could be saved from the AHBR costs. The contribution of the fixed charges is thus 3.1 mills/kwhre. Operation and maintenance costs should be no greater than in the MSCR, say 0.3 to 0.5 mills/kwhre. The cost of power thus lies in the range 4-5 mills/kwhe.

TABLE 8

1000-MWE AQUEOUS SLURRY CONVERTER REACTOR POWER COST

	<u>Mills/kwhre</u>
Fuel Cycle	0.8
Fixed Charges	3.1
Operation and Maintenance	<u>0.3</u>
Total Power Cost	4.2*

* Preliminary result, not fully optimized.

Aqueous Homogeneous Breeder Reactors

These were studied previously at ORNL.^{7,11} Uranyl sulfate dissolved in D₂O is circulated through cores about 4 feet in diameter and 12 feet long. Rare earth fission products are insoluble and may be removed by hydroclones. The blanket is filled with pellets of ThO₂ which are transported by fluidization,

and processed by Thorex. Three such reactors generate 1000 Mwe with a thermal efficiency of 27.5%. Fuel cycle costs range down to 0.9 mills/kwhre at doubling times of ten years. The capital cost, as mentioned above, was estimated at \$178/kwe.¹¹ Taking operation and maintenance costs at 0.7, the cost of power is 5.3 mills/kwhre, on current bases.

Conclusions

A near-term 1000-Mwe Molten Salt Converter Reactor is capable of producing power at a cost of less than 5 mills/kwhre, and perhaps as low as 4 mills/kwhre. This ability inheres in low capital costs (\$143/kwe), associated with use of a single highly efficient reactor-turbine complex, in the reasonably good conversion ratio obtainable (0.8 - 0.9), and in the simplicity of the fuel cycle using Fluoride Volatility. This simplicity in the fuel cycle is also a limitation in that the necessity of discarding the carrier salt and thorium along with fission products prohibits rapid elimination of fission products. By additional processing (HF Dissolution) and by introducing structural material (Mo^{92}) into the core to clad the moderator and provide a blanket, conversion ratios in excess of unity can be achieved. Second generation plants may have capital costs as low as \$125/kwe.

Molten salt breeder reactors show promise of achieving short doubling times, both in externally cooled thermal breeders (MSBR), and in internally cooled fast breeder (MSFBR). But two-region breeder reactors are necessarily smaller in size and power than one-region reactors, and therefore the capital cost of a 1000-Mwe station using several cores may not be as low as that of the MSCR. Processing for economic recovery of thorium remains to be developed.

Preliminary and incomplete estimates for an Aqueous Slurry Converter Reactor show that it is probably capable of power costs in the same range as the MSCR, i.e., 4 to 5 mills/kwhre, with conversion ratios approaching 1.0. Development of "charcoal" processing may permit conversion ratios up to 1.05 and doubling times less than 20 years in fully optimized systems. Two-region aqueous breeders (AHBR) have optimum doubling times of less than 10 years.

Molten salt reactors operate at high temperatures and low pressures; this advantage is offset somewhat by the necessity of maintaining the system at all times above 900°F, the liquidus temperature of the salt. The high temperature results in high thermal efficiency ($> 40\%$), which offset the lower conversion ratios. The aqueous reactors operate at high pressure (1400 psi) and low temperatures, with low thermal efficiencies ($> 30\%$), but have high conversion ratios and do not require preheating.

Both concepts appear to be economically competitive in near-term embodiments, and both show promise of development of breeders with short doubling times.

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Session II
Paper 11

LIQUID METAL BREEDER REACTOR (LIMB)

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Introduction

The ultimate goal of nuclear power is the development of economical breeder reactors. To attain this goal, reactor fuel cycle costs must be reduced drastically. This can only be accomplished by incorporating an integrated fluid fuel process. Moreover the process must be one that removes the minor constituents without changing the chemical state of the bulk. Such processes are currently being used to purify the more common metals (i.e., steels, copper, lead, bismuth, etc.).

Full advantage must be taken of the fluid fuel and maintenance concepts may have to be reviewed critically. It is conceivable that reactors may run until uneconomical without maintenance of radioactive parts. This can be accomplished by compartmentalization of fluid systems with provisions for failure without interrupting operationability.

This paper will describe the basic features of the Liquid Metal Breeder (LIMB) Reactor and give some preliminary evaluations of its potential with regard to breeding and economy. This concept incorporates a fluid fuel and breeder system with an integral process. A compartmentalized structure is proposed to minimize power costs.

Four basic configurations for liquid metal reactors are shown in Figure 1. Concept A employs three separate fluids. Concept B combines the coolant and fuel functions. Concept C combines the coolant with the blanket fluid, and Concept D incorporates the three functions into one stream.

The relative economic advantages of each concept can be realized by considering fuel investment and neutron flux level in the external heat exchanger. The latter leads to capital expenditures for additional shielding, for remote maintenance of the heat exchanger and pump, and for incorporating an intermediate coolant system which also degrades electrical power cycle efficiency. Concepts B and D have a large neutron flux and fuel holdup in the heat exchangers; therefore, the heat exchangers are as complex and expensive as the reactor core. These types would tend to be the most expensive. Concept C

Fig. 1. Basic Reactor Configurations.

reduces the neutron flux and investment of fuel in the heat exchanger to a level determined by the processing system. However, it is very likely that some neutron flux will always be present.

Concept A circulates no uranium in the heat exchanger and requires the lowest critical mass of the four concepts. Therefore, concept A appears to enjoy the lowest capital investment potential.

Concepts B, C, and D have been given detailed evaluation by Brookhaven, the Babcock and Wilcox Company, and many others involved in the Liquid Metal Fuel Reactor Programs supported by the Atomic Energy Commission.¹ However, Concept A, which is referred to as the "internally cooled" concept, has not been designed in sufficient detail to establish its feasibility. The reactor concept presented herein is based upon configuration A.

Basic Concept

The proposed reactor concept is shown in Figure 2. Unclad graphite containers for the three fluids are placed in a steel vessel. Coolant (lead) pumped through the vessel extracts heat from the core and blanket region and transports the heat to a water boiler. The pump and boiler are located outside the reactor neutron shield. Both the blanket (a dispersion of Th Bi_2 solid in a lead-bismuth liquid) and fuel (a uranium-bismuth solution) fluids are circulated to their respective processing vessels. A molten salt bridge between the two processing vessels introduces thorium to the blanket, moves uranium from the blanket to the fuel and extracts a large fraction of the fission products, predominately the rare earth elements. Fission products are removed either by their volatility or their insolubility in the uranium-bismuth solution or by chemical oxidation into the salt layer.

Fuel System

A solution of uranium in bismuth was chosen because uranium is soluble in bismuth and because dilute solutions are compatible with graphite containers to temperatures around $1,000^\circ\text{C}$. Figure 3 is a plot of the solubility of uranium in bismuth.² It is to be noted that the 0.5% uranium bismuth composition is a

Fig. 2. LIMB Reactor Concept.

Fig. 3. Solubility of Uranium and Thorium in Bismuth.

single phase above 480°C. This temperature is sufficiently low to accommodate start-up requirements and not too high since the fuel system will, in general, be at a higher temperature than the coolant which is planned to operate above 400°C.

The solubility of thorium is also shown in Figure 3.³ At 0.5% uranium solution temperature, 0.05% Th is soluble. Therefore, excess thorium can be separated by precipitation, and thus produce a fuel solution with a ratio of one part of thorium to 10 of uranium for circulation in the reactor core.

Studies have been completed on the reaction between uranium in bismuth solutions with graphite containers.⁴ Results indicate that no reaction occurs at temperatures below 1,000°C with concentrations around 0.5% uranium. There is also evidence that zirconium, which will be present as a fission product, will react preferentially to uranium with graphite at high temperatures.⁵ The reactions between the equilibrium fission products and uranium with graphite require further study. For the purposes of this preliminary design, the maximum graphite fuel interface temperature was limited to 1,000°C.

Blanket Fluid System

The solubility of thorium in molten lead bismuth alloys is even lower than that given for bismuth in Figure 3. To obtain a high concentration of thorium, the proposed blanket system will be a dispersion of a thorium bismuthide (solid particles) dispersed in molten lead-bismuth. The densities of these phases are very similar. Particles around 50 microns in diameter remain suspended for long periods of time in settled layers. These settled layers retain their fluidity and contain approximately 15% by weight thorium. This thorium concentration is sufficiently high to obtain high thermal neutron utilization.

Another feature of the thorium-lead-bismuth alloy is that the liquid phase shrinks upon freezing. Previous reactor designs proposed a bismuth liquid phase which expands upon freezing, thus causing concern in its application to large systems.

The choice of the particular thorium-lead-bismuth composition was based upon processing considerations.⁴ As thorium is converted, uranium-233 accumulates in the solid thorium bismuthide particles. The uranium can be extracted either by particle growth or by complete destruction of the particles. However, in both cases, retaining a useful particle form presented a problem.

Figure 4 is a typical isothermal ternary phase plot of the thorium-lead-bismuth system at temperatures below 600°C.⁶ The proposed blanket composition is indicated. The solid liquid equilibrium for the blanket fluid composition indicates that Th Bi_2 is in equilibrium with a lead-bismuth liquid containing approximately 75% lead. However, if the temperature is raised to around 1,000°C (Figure 5), the Th Bi_2 compound converts to $\text{Th}_4 \text{Bi}_5$, and the liquid phase then contains approximately 60% lead.³ Upon returning to lower temperature cycle accomplishes two process operations. During the conversion, a large portion of the uranium contained in the solid is redistributed into the liquid phase. Upon cooling, small Th Bi_2 particles are reformed by an exfoliation mechanism. During the thermal cycle, over 99% of the thorium remains in the solid form. This is the first step in the blanket process. Further details on the process will be given below.

Coolant System

The coolant chosen for the reactor design is lead. Lead has been circulated in steel systems for a very long period (over 13,600 hours in thermal convection loops) under a thermal gradient (400-550°C) with no signs of mass transfer.⁷ Furthermore, it has been reported that lead can be circulated up to 650°C with no corrosion problems.⁸ There has been no evidence of attack on graphite by lead.

Lead has a low thermal neutron cross-section and it does not become highly radioactive. In fact, the isotope that contributes practically all the radioactivity has no gammas and has a half life of 3.3 hours. The final decay product is stable bismuth. Therefore, the radioactivity of the lead in the boiler and pump can be considered nil. If a fuel element ruptures and fission products

Fig. 4. Th-Bi-Pb Phase Diagram at Temperatures Below 600°C.
(% by weight)

Fig. 5. Th-Bi-Pb Phase Diagram at 1000°C. (% by weight) (2)

escape into the coolant, they can be removed by trapping and chemical oxidation.

The lack of radioactivity or neutrons in the coolant makes it feasible to consider direct heat transfer to water or any other power cycle fluid without an intermediate loop. Since molten lead does not react chemically with water and shares compatibility with the same steels used for steam boilers, the heat exchanger design may not be complicated.

The thermal neutron cross-section of natural lead is 0.17 barns. Although the cross section is low enough to attain breeding, there are two other sources of lead with lower cross sections. In older uranium deposits, radiogenic lead (the decay product of natural uranium) occurs in large quantities. This lead has a cross section of 0.07 barns, less than half that of natural lead. There is a large enough resource to consider this lead for reactor application.

Another lead source is the separation of lead isotopes. Lead-208 has a cross section of 0.00043 barns and is 50% abundant in natural lead. Lead tetraethyl is a volatile compound of lead that could be used in a gaseous diffusion separation process. Of course, this source will be more expensive than natural lead. This cost must be counterbalanced by the value of the extra breeding gain.

Construction Materials

Graphite is the most important construction material. Its application in the internally cooled liquid metal reactor is similar to that in the high temperature gas cooled reactor (HTGR) currently being constructed. Impervious grades of reactor-grade graphite are available in the shapes and sizes needed for the LIMB Reactor.

The properties of graphite are well known. Probably the most important property is the thermal conductivity across the wall of a graphite tube through which the reactor power is transmitted to the coolant. In graphites available several years ago, the thermal conductivity across the tube wall was less than half that conducted longitudinally. Today, graphite tubes can be fabricated with isotropic properties and higher thermal conductivities. The effect of

radiation on the thermal conductivity and distortion at the anticipated reactor temperatures is expected to be small. Graphite is readily machined. High temperature adhesives for graphite are also available. Therefore, the shapes required should not present a problem.

The reactor vessel, piping, pumps, and heat exchangers will probably be fabricated of Cr-Mo steels which are commonly used for steam boilers at these temperatures. A great deal of development has already been accomplished on pumps for liquid metals.

Reactor Core Structure

Earlier attempts to design an internally cooled reactor¹⁰ encountered difficulty in the circulation of fuel throughout the reactor and in providing assurance of adequate fuel drainage in the event of a reactor shutdown. These problems were overcome in the design of the fuel element shown in Figure 6 by using a displacement concept.¹¹

The fuel element is closed bottom impervious graphite tube containing fuel solution (see Figure 6 "Sub-Critical Position"). A graphite plunger is poised above the fluid and actuated by a piston. With the plunger in this position, the reactor is subcritical. If a vacuum is created below the piston, the plunger moves downward and displaces the fuel into another configuration which is critical (critical position). A reservoir of fuel is created on top for processing purposes.

Small channels from the top of the plunger to the bottom provide for fuel circulation within the element by thermal convection.

Fission product gases are extracted from beneath the piston above the fuel reservoir by permitting some helium gas to leak by the piston into the vacuum system. Elsewhere, fission product gases are absorbed in a charcoal trap and the helium (which is used for a reactor cover gas) is recirculated.

Fuel elements, as described above, are clustered in an open hexagonal array. The coolant enters the bottom, rises around the elements, and then moves radially outward through a plenum at the top.

Fig. 6. LIMB Reactor Fuel Element.

Fluid fuel is extracted by gas pressurization to processing tanks above (shown in processing position, Figure 6). Temporarily, fission product gas removal is interrupted and the helium pressure below the piston is increased. Simultaneously, the pressure above the piston is increased to keep the plunger depressed. Thus, the fluids are forced upward through the dip tube in each system while the reactor continues to operate.

To turn off the reactor under emergency conditions, the helium gas pressure below all the pistons is increased causing the fuel to return to the bottom of the fuel element; thus returning the fuel to a subcritical position. In fact, should the compressors fail, the reactor will "fail safe" since graphite naturally floats on bismuth. For fine control, a modified fuel element with a finer control can be used as a positive reactivity control, or a liquid metal poison (using cadmium indium alloys) can be displaced into the core for a negative reactivity control.

An interesting feature of the fuel element design is the small movements required to cause large changes in the reactor's reactivity. In this design, the fuel level can move 5.5 fold that of the plunger. The total plunger movement is approximately 1 foot for operation of the fuel element. To show the sensitivity of the plunger movement, bare core nuclear calculations were made with the plungers assumed at various levels. The results are plotted in Figure 7.⁴ A plunger movement of 1 inch results in a large reactivity loss comparable to that used in safety devices for most current reactors.

Reactor Blanket Structure

The blanket above and below the reactor core is provided by openings in the plunger (Figure 6). When the fuel element is in the critical position these portions of the blanket are in their proper position. Passages between the upper and lower blanket are used to introduce blanket fluid into the core zone. This has been found necessary to optimize breeding and increase the critical size for larger power output. Blanket fluids in the fuel elements can be removed for processing by gas pressurization (processing position).

Fig. 7. LIMB Reactor Control.

The outer blanket and the major part of the reactor blanket consist of 5-inch thick plates having a slight radial taper (Figure 8). Blanket fluid circulates through a system of channels by means of a gas lift pump. The fluid flows upward through the channel next to the core and downward through the others. At the top, there is a settling basin where some excess liquid phase can be separated for processing. Periodically, a volume of clear liquid phase is extracted by gas pressurization to the blanket processing vessel. Coolant channels are provided in between the blanket elements.

Uranium that is bred in the blanket is roughly metered to the core by having the reactor divided into segments for processing as indicated in Figure 8. Eight pairs of processing tanks are located as shown.

Helium is proposed as a cover gas in the reactor vessel. It is maintained slightly below atmospheric pressure with a vacuum maintained between an outer and inner shell of the reactor vessel. The gas is compressed both for operating the fuel elements and for gas pressurization operations. Fission product gas contamination will be removed by charcoal traps placed in the line preceding the compressor.

Heat Transfer

The limitation in the ultimate economy of the LIMB reactor is in the maximum power density of the core. This power density is controlled by heat transfer through the graphite, fuel-graphite reaction temperatures and the neutron poisoning of the lead coolant.

As in all reactors, a uniform fuel loading would result in a high power density peak in the center of the reactor which would limit the power extracted. To increase the power output within the temperature limitations, the fuel must be redistributed with less fuel in the center or the quantity of blanket fluid must be increased in the center. This is easily designed into the fuel element described. The fuel annulus or blanket fluid channel dimensions can be varied from top to bottom and from fuel element to fuel element radially. Therefore, the reactor designer has the maximum of flexibility without large economic

Fig. 8. LIMB Reactor Blanket Elements.

penalties for complexity.

The fuel graphite reaction temperature does not appear to be very limiting. If further study reveals a problem, coatings of stable carbides may be used to overcome them. Changing the shape of the fuel channels can lower the local temperature appreciably. If channels are milled into the plunger for fuel passages, the plunger could be cooled more effectively thus reducing the graphite-fuel interface temperatures and the temperatures in the blanket fluid contained therein. If the latter problem becomes prominent, the blanket fluid could be contained in separate elements.

The poisoning effect of lead can be overcome by other isotopic lead sources, additions of bismuth or conversion to molten salt coolants.

A hexagonal shaped rod has been suggested for the form of the fuel rod but is not the only shape possible. Plates or larger clusters may be desirable to reduce the number of plunger controls and fuel processing lines.

The inherent advantage of the LIMB reactor design is its design flexibility. This has been realized by the three fluid approach and the unique fuel element design.

Chemical Processes

Four basic chemical mechanisms used for the LIMB processes are (1) chemical oxidation into a fused salt, (2) volatilization, (3) precipitation from the uranium-bismuth solution, and (4) dilution by displacement.

The chosen fused salt extraction is based upon complete oxidation or reduction in a batch operation. Table 1 is a compilation of the free energy of formation of chloride salts. The table indicates the relative stability of the chlorides, with the most stable heading the list. The fluoride salts give a similar picture, but generally have higher melting points.

Uranium and thorium are transported between the blanket and the core via the fused salt. They can be extracted into the salt by adding BiCl_3 or PbCl_2 to the salt phase or reduced into the metal by adding magnesium to the metal.

TABLE 1

FREE ENERGY OF FORMATION OF SALTS AT 500°K

Salt	$-\Delta F$ K cal/gm-atom of Cl	Salt	$-\Delta F$ K cal/gm-atom of Cl
CsCl	94.6	BeCl ₂	48.3
RbCl	93.9	AlCl ₃	48.1
KCl	93.1	MnCl ₂	47.6
BaCl ₂	92.8	ZnCl ₂	40.6
SrCl ₂	89.0	TlCl	40.5
LiCl	88.8	CdCl ₂	38.0
NaCl	87.4	CrCl ₃	34.7
CaCl ₂	86.4	GaCl ₃	34.3
LaCl ₃	76.0	InCl ₃	33.8
YCl ₃	69.5	PbCl ₂	33.9
PuCl ₃	67.4	FeCl ₂	33.2
MgCl ₂	66.8	SnCl ₂	32.6
ScCl ₃	64.3	NiCl ₂	27.8
UCl ₃	62.2	CuCl	25.7
ThCl ₄	61.8	AgCl	23.5
UCl ₄	53.9	BiCl ₃	22.2

During this operation, the rare earth fission products (represented by LaCl₂) are extracted into the salt and cannot be reduced by magnesium. Notice that PbCl₂ is more stable than BiCl₃; therefore, Pb may be introduced into the salt after contact with the blanket fluid. This may necessitate conditioning the salt before using it to remove fission products from the fuel. This can be done by contacting the salt with thorium-bismuth alloy. The thorium reduces the lead into the liquid metal and the thorium substitutes for the lead in salt. During these operations of transporting uranium and thorium, practically all the rare earths and some of the more active fission products, Ba, Sr, Rb, and Cs, are trapped in the fused salt. Periodically, a portion of the fused salt is

removed and replaced by fresh salt. Samarium-149, which accounts for a large fraction of fission product poisoning, is thus removed.

Some fission products are volatile and will be removed by a sweep gas at the top of the fuel element. Xenon-135 has a high neutron capture cross section and must be quickly removed. The removal rate is complicated by its precursor, iodine-135, which may be absorbed on surfaces in the fuel system. This problem requires further evaluation.

Several less important fission products can be permitted to buildup to their solubility limits and be removed by precipitation. Fortunately, these precipitates are lighter than bismuth and can be collected in the fuel reservoir on top of the fuel element. They then are transported to the fuel processing tank and later displaced over a weir in the processing vessel.

Excess thorium in the fuel can also be removed by precipitation. However, ThBi_2 , being more dense than bismuth, will sink, avoiding its removal with the non-oxidizable fission products.

Dilution by displacement may be necessary in removing fission products of minor importance having very high solubilities (for example, Pd and Rh). The operation would consist of first oxidizing the uranium and thorium into the salt and then adding bismuth to displace some of the fuel over a weir.

The precipitation and dilution processes are based upon solubilities. Some of the known solubility of fission products appear in Figure 9 as determined by Schwitzer and Weeks.¹² Zr, Nb, Ru, and Mo (not shown because they are low) are candidates for removal by precipitation while Pd and Rh may be removed by dilution.

The effect of fission product mixtures on their individual solubilities and that of uranium or thorium has not been thoroughly studied. It has been observed that zirconium significantly reduces the solubility of uranium.¹² Others increase or nullify the effects of others. However, the above data are sufficient to establish potentiality.

The driving force for the kinetics of these reactions and the efficiency of removal is the concentration of the fission product in the fuel. These will

Fig. 9. Solubility of Fission Products in Bismuth.

be assisted in the LIMB reactor design by the low volume of fuel used in the reactor. The rate of buildup is much larger than those considered by Brookhaven.¹³

Control of uranium concentration in the fuel will be maintained by a temperature regulated trap. Variation of uranium in the reactor core will be determined by chemical balance and observed changes in the reactor's reactivity. Since the rate of fuel burnup is high in the LIMB reactor, the reactivity will drop appreciably each day. The control system must be capable of accommodating these changes.

Bismuth in the fuel element is kept constant by the position of the dip tube used for removal of fuel from the element and the capacity of a cup in the fuel processing tank. Any excess overflows the cup. Should a leak develop in a fuel element, the fuel from that element cannot mix with the fuel of others. This is part of the compartmentalization scheme to eliminate maintenance. The leaky fuel element may be self-sealing when the excess lead, admitted to the element via the leak, is drawn into a vacuum line and frozen.

The movement of uranium from the solid thorium-bismuth compound to the liquid phase has been explained in the section discussing the blanket fluid. The remainder of the process is to separate the liquid phase of the thorium-bismuth lead dispersion and to oxidize dissolved thorium and uranium into the fused salt. As in the fuel system, oxidizable fission products will be trapped in the salt, volatile fission products will be swept out, and it is conceivable that the operations of precipitation and dilution could be carried out on the blanket. The latter two operations probably will not be justified.

Converter Process

At first, reactors will probably be operated as converters to produce uranium-233 from uranium-235. Since these isotopes have different nuclear properties, it probably would not be wise to mix them, and the fuel process would be entirely separate from the blanket process. From a practical viewpoint, this would prove a useful step toward the development of the more complex

process of the breeder.

As shown in Figure 10, fuel that is extracted from the reactor fuel element by gas pressurization would be introduced into a cup in the core process vessel. Uranium chloride and sufficient bismuth chloride would be added to the fused salt to remove all uranium and oxidizable fission products. After the uranium has been oxidized, a quantity of bismuth without magnesium will be introduced into the cup. This will cause displacement of bismuth contaminated with precipitated and soluble noble fission products over the cup weir. Magnesium-bismuth is then introduced in sufficient quantity to reduce the proper amount of uranium back into the bismuth. This may be sufficient for control of uranium concentration. If not, the cup's temperature may be regulated to the solution temperature. This will allow the excess to precipitate out before returning the fuel to the fuel element. In the return tube, a temperature controlled trap allows the fuel to pass, but freezes the salt. After equilibration of pressures in the fuel element and process tank, the trap is heated and gas pressure is admitted through a third line into the salt trap (not shown). This forces the salt back into the process tank and the fuel into the fuel element.

Periodically, some fused salt and the displaced bismuth containing noble fission products are removed to a uranium recovery vessel. In this vessel, the operations are repeated to remove the last traces of uranium into a separate volume of bismuth before the contaminated bismuth and salt are sealed in containers for waste disposal.

In the blanket element, uranium is transferred into the liquid phase by the thermal cycle treatment of the blanket dispersion described previously. This treatment may be accomplished in the reactor blanket by controlled thermal gradients or treated in a separate step. Liquid phase is removed into the process vessel above, which is compartmentalized, and contacts a salt containing either bismuth chloride or lead chloride. Uranium is thus oxidized into the salt. The concentration of uranium is permitted to reach a high level and is stored for future extraction into the fuel system of a new breeder reactor.

Fig. 10. Liquid Metal Fuel Converter Reactor (One Sector).

An alternative blanket process would employ the fluoride salts. The uranium could be removed by fluoridation to the volatile UF_6 compound.

Breeder Process

The proposed breeder process shown in Figure 11 is similar to that for the converter except that the salt from the blanket process is moved directly into the fuel process vessel. The concentration of thorium in the blanket salt may be the same as uranium or slightly higher. As mentioned above, some lead chloride may be present and more thorium may be added to condition the salt. The excess thorium is precipitated after the uranium and thorium has been reduced into the fuel bismuth. The thorium bismuthide is collected in the bottom of the cup. After the fuel solution has been returned to the fuel element, the thorium is oxidized again into the salt and thereby transported back to the blanket process tank. It is reduced into the blanket liquid phase and returned to the blanket.

Essentially, thorium and uranium pass over the salt bridge from blanket to fuel and only thorium returns.

Any excess of uranium bred in the blanket can be extracted with the contaminated fused salt into the waste treatment process and thereby recovered.

Detailed processing data has not been sufficiently developed at this time. This will be the subject for future study.

Start-up Procedures

All fluids used in the LIMB reactor design are solid at room temperature. Therefore, one of the major problems of start-up is to provide adequate heating. There are three general methods of increasing temperature: (1) radioisotope, (2) external heating sources, and (3) internal heating sources.

Polonium, an alpha emitting isotope, is generated by neutron capture in bismuth. Consequently, once the reactor is operated, this source of heat will keep the reactor fluids molten. To start the reactor, it is conceivable that a quantity of polonium may be introduced in the systems. However, this may lead

Fig. 11. Liquid Metal Breeder Reactor (One Sector).

to complicated loading procedures.

Probably the simplest procedure will use either external or internal heating or a combination of both. It will be necessary to provide a cooling system to the outside of the reactor to protect the radiation shield from excessive heat. This same system may be used to heat the reactor vessel initially to the melting point of lead (327°C). An auxiliary heater could then be operated to heat the circulating lead to bring the internals of the vessel up to the solution temperature of the fuel. Then the reactor will be turned on. The details of the procedure remain to be defined.

100 MW_H Reactor Design

The principle features of a LIMB reactor have been derived from a series of heat transfer, criticality and breeding ratio consideration. Table II lists the dimensions and nuclear parameters derived thus far.

A fuel element for this reactor would be 6 inches across the flat of the hexagon cross section and around 15 feet tall. The plunger will be shaped to provide a 1/4-inch fuel annulus. Blanket fluid can be distributed in several ways. One 1-inch diameter hole or two 3/4-inch holes could be used. A 1/8-inch coolant annulus between fuel elements will provide the necessary coolant volume.

Breeding Potential

As indicated in Table II the breeding ratio (exclusive of fission product poisons and protoactinium losses) is 1.04. This is a conservative estimate since the thorium neutron data did not include some important resonances. An optimistic estimate has been made assuming infinite dilution and the ratio became 1.09. Probably the true ratio is somewhere between.

These calculations assume equilibrium absorptions in the higher isotopes. A new reactor core had a conservative breeding ratio of 1.07 (probably 1.12 with the more optimistic thorium data). The higher isotopes will build up to equilibrium over a period of 3 to 6 years.

TABLE II
INTERIM LIMB REACTOR CALCULATIONS
(100 MW_H)

<u>Reactor Dimensions</u>		<u>Ft.</u>
Core Diameter (rt cylinder)		6.8
Blanket Thickness		2.25
Reflector		1.80
<u>Composition</u>	<u>Vol. %</u>	<u>Wt. %</u>
Core		
Coolant	4	
Pb		100
Blanket Fluid	9	
Th		15
Pb		41
Bi		44
U-233		0.0030
Fuel Fluid	13	
U-233		0.299
U-234		0.116
U-235		0.039
U-236		0.039
Total U		0.493
Bi		Balance
Moderator	74	
C		100
Blanket		
Blanket Fluid	66.7	
Th		15
Pb		41
Bi		44
U-233		0.030
Moderator	33.3	
C		100
Reflector		
C	100	100

Reactor Inventory

<u>Element</u>	<u>Core</u>	<u>Blanket</u>	<u>Wt. (kg)</u> <u>Reflector* (1 ft)</u>	<u>Total</u>
Bi	10549	67084	0	77633
C	8999	14580	31000	54850
Pb	5603	71953	0	77556
Th	962	24480	0	25442
U-233	24.2	5.2	0	29.4
U-234	9.5			9.5
U-235	3.2			3.2
U-236	3.2			3.2

* 1 ft. reflector assumed sufficient

TABLE II (cont.)

Nuclear Data

Neutron Balance

<u>Element</u>	<u>Core</u>	<u>Abs per U-233 + U-235 Abs</u>		<u>Total</u>
		<u>Blanket</u>	<u>Reflector</u>	
U-233	0.8866	0.0071	0	0.8937
U-234	0.1064	0	0	0.1064
U-235	0.1064	0	0	0.1064
U-236	0.0260	0	0	0.0260
Th	0.4861	0.4444	0	0.9305
Bi	0.0284	0.0049	0	0.0333
Pb	0.0591	0.0189	0	0.0780
C	0.0285	0.0013	0.004	0.0302
Leakage				<u>0.0013</u>
				2.21

Breeding Ratio

calc from abs (U-233, U-234, U-235, Th)
 calc from abs (U-233, Th)

1.03₇
 0.04₁

Specific Power (total reactor)

based on U-233 + U-235
 based on U-233

2780 kw/kg
 3120 kw/kg

The doubling time depends upon a better estimate of the breeding ratio than is available. Assuming a breeding ratio of 1.03 is possible, the doubling time is around 30 years.

Several calculations have been made assuming other lead sources. With radiogenic lead the breeding ratio can be increased at least 3 per cent which would halve the doubling time. A couple of per cent could be realized by using a lead-bismuth eutectic coolant. Utilization of fused salt and separated lead isotopes can render further improvements.

Another set of calculations have been completed to increase the size of the reactor by adding more blanket fluid to the core with the conclusion that larger sizes (for example 1000 MW_H) can be developed with essentially the same technology and very little change in breeding potential.

Economical Potential

No direct calculations of economics are possible until a reference design has been established. However, an examination of the estimated costs of small power units (40 mwe), recently completed by the AEC using known technology, can be used to indicate the potential of the LIMB reactor.

Some of the data presented by R. W. Ritzman are presented in Table III.¹⁴

The table is not a complete listing, but it extracts the prominent cost items and totals. In the table, a boiling water reactor (BWR), sodium-graphite reactor (SGR), and sodium fast reactor (SFR) are compared to a fossil plant. It was further anticipated in the paper that the costs could be reduced to 15.1, 13.2, and 12.8 mills per kwhr for the PWR, SGR, and SFR, respectively, by technological improvements. Most of the anticipated improvements are due to an anticipated reduction in fuel cycle costs which were 2.7, 2.5, and 1.6 mills per kwhr, respectively.

The LIMB reactor concept is aimed at reducing both capital and fuel cycle costs beyond that expected in advanced development of solid fuel element reactors. For example, the cost for the fuel investment, derived from the values given in Table III and the published cost of the uranium (as UF₆) is between

TABLE III

CURRENT STATUS OF POWER PLANTS
44 MWE GROSS ELECTRICAL GENERATING CAPACITY

Characteristics	<u>PWR</u>	<u>SGR</u>	<u>SFR</u>	<u>Fossil (coal)</u>
Total U loading kg	11,100	4,960	638	
U-235 enrichment w/d	3.95	2.81	93	
Reactor coolant exit temp °F	565	945	900	
Reactor coolant inlet temp °F	511	615	600	
System operating pressure psig	2,150	Atm	59	
Secondary coolant system	No	Yes	Yes	
Pressure containment required	Yes	No	Yes	
Capital				
Structures and improvement (\$1,000)	2,739	1,614	2,327	1,244
Reactor or boiler plant equipment (\$1,000)	8,510	7,358	6,497	3,505
Total capital cost (\$1,000)	23,940	20,000	19,820	12,800
Power Generating Costs *mills per kwhr				
Fixed charges	12.8	10.7	11.0	6.4
Operation and maintenance	1.7	1.6	1.7	1.2
Fuel Cycle				
Fabrication	1.2	.6	1.8	
Depletion	2.3	2.2	2.7	
Total	<u>4.3</u>	<u>4.4</u>	<u>5.5</u>	<u>3.8</u>
Total power generating cost	18.8	16.7	18.2	11.4

\$1.15 and \$7.67 million with the fast reactor costing the most. Compare this to 30 kg of fully enriched U-233 required for the LIMB reactor which costs less than \$450,000. This does not include fuel investment in the fuel cycle. The LIMB reactor promises further reductions there.

Since the operating pressures are low, no pressure containment would be required. Containment structures can easily add \$500,000 to \$1 million to the cost of a power plant.

Whereas the SGR and SFR require no containment, they use a secondary coolant system because of the sodium radioactivity in the primary loop. They also employ a more complicated water boiler to guard against the potential sodium-water reaction in the event of a leak. Moreover, the maximum temperature of the secondary coolant system is below that in the primary and leads to a low power cycle efficiency. The LIMB reactor enjoys the advantage of a high economy by eliminating the secondary loop and the expensive boiler while retaining maximum power cycle efficiency. The coolant temperatures available are high enough to produce steam qualities comparable to those in modern steam power plants.

All of the reactors evaluated in Table III employ solid fuels. Therefore, the capital equipment for removing fuel elements and handling radioactive fuel elements would represent a prominent expense. The LIMB reactor should not require as much expenditure for handling the relatively small volumes of fission product waste.

The largest cost advantage for the LIMB reactor will probably come through the reduced fuel cycle costs. Fabrication costs will be eliminated by the use of fluid fuel. Depletion charges are also eliminated by breeding. The simplified reprocessing cycle envisioned for the LIMB reactor would reduce some of the other factors that enter into the fuel cycle costs also. All of these should reduce the fuel cycle charges to less than 0.5 mills per kwhr.

On the other hand, the LIMB reactor will require extra capital for the integrated process. Further details are needed to tell whether these costs

are less than the reductions mentioned above.

It is an objective that the LIMB reactor be competitive with small fossil power plants so that the development of larger plants can be gained on practical working systems.

Larger Reactors

There are two ways to increase the power plant size. One way would be to add units, if each unit is economical. The second is to increase the quantity of blanket fluid in the core zone, which increases the core size and thus the heat transfer area. Either of these can lead to power plants having power outputs beyond 1000 MW_(h).

Conclusions

The essential features of the Liquid Metal Breeder (LIMB) Reactor have been described. The design utilized uranium-bismuth solution fuel, thorium bismuthide dispersion in lead-bismuth blanket fluid and lead coolant. The design has been developed sufficiently to receive preliminary evaluation.

The design incorporates an integral fuel and breeder process to minimize fuel cycle costs and a compartmentalization scheme to lower maintenance.

A reactor control using fuel displacement is proposed. Other features of the design are aimed at single pot construction with no internal maintenance.

Calculations have shown that a 100 Mw_n LIMB reactor is a potential breeder with natural lead coolant (breed ratio between 1.04 and 1.09). Lower cross section leads (which are also available) promise to increase the breeding ratio further. Doubling times from 30 years down to 15 years are possible. Further calculations have indicated that the basic design could be extended to large power sizes without loss of breeding potential.

The design is potentially economic at small power sizes since capital costs can be reduced by high power cycle efficiency, elimination of pressure vessel enclosure, direct power cycle heating, high specific power, and lower maintenance investment. Fuel cycles cost will be drastically lowered by an

integral fuel process and breeding. Preliminary evaluation of the power costs have been derived from estimates for solid fuel reactors in the same power range and appear competitive with fossil fuel power plants of the same size.

The features of the LIMB reactor are essential to attaining the goals of economic power breeder reactors.

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Session II
Paper 12

THE DRAGON CORE

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Introduction

The High Temperature Gas Cooled Reactor Experiment, in short, The Dragon Reactor, is being built to test the feasibility of a reactor operating at a high coolant temperature, a high power density and achieving a high burn-up. Consequently, graphite was chosen as a moderator and main structural material of the core. The fuel bodies are small to limit fuel temperatures as much as possible. A general layout of the pressure vessel is given in Figure 1.

A single fuel rod consists of a graphite sleeve of very low permeability which separates the main coolant from the purge flow and the fuel bodies. These are composed of coated particles embedded in a graphite matrix.

By this means an intimate mixture of fissile and fertile material with the moderator is achieved. The purge flow takes almost all volatile fission products away to the purification plant. To ease the load on this plant a fission product trap is built in at the bottom of every fuel rod. Seven of these rods are linked together at the top and the bottom to make up one fuel element, 37 of which form the Dragon Core.

The design of the Dragon Reactor Experiment is described elsewhere in detail, for example, by G. E. Lockett (1) from the engineering point of view and by L. R. Shepherd, P. Marien (2) from the research and development point of view. The discussion in this paper is restricted to calculations on the Dragon Core and to some preliminary results of burn-up calculations for a power reactor of the Dragon type.

The Dragon Core

Before going into more detail it is essential to give some overall specification of the Dragon core, as many problems one has to face for this reactor type are a direct consequence of these parameters. Some typical data are:

Thermal power output	20 MW
Average power density	14 MW/m ³
Coolant	20 atm, 350° - 750°C, helium
Loading	20 kg. 93% enriched uranium-235

Loading (cont.)	105 kg thorium
Atomic ratio graphite to uranium	2000
Core diameter	107 cm
Core height	160 cm

Owing to the high average power density only a small core is needed to produce the relatively modest thermal output of 20 MW. Neutron leakage out of the core is therefore high which makes the influence of the reflector very significant, an effect even more increased by the low graphite to uranium ratio in the core. These two effects make it possible to control the reactor by control rods in the reflector.

The high neutron leakage of this core restricts the life of one loading to about 200 to 300 days, depending on core composition, and consequently the high burn-up envisaged for a power station cannot be achieved. It was therefore found advantageous to have a core, its central region to be composed of fuel elements representing, in their isotope concentration, elements of a possible power station. The outer core region, on the other hand, serves as a driving region to keep the reactor critical. The outer elements were to be exchanged in turn after an approximate running time of 200 days (3). Detailed calculations showed that the power peaks at the core reflector boundary make a subdivision of the driving zone necessary. As already mentioned, the core is undermoderated and therefore the influence of the reflector is very pronounced, resulting in a strong spectrum shift in the neighbourhood of the core reflector boundary.

At beginning of life and after inserting fresh fuel in this region, fuel temperatures would rise between control rods far beyond the limits set by materials consideration. The need to flatten these peaks led to the proposal of a three zone core.

The central region, representing test elements for a power reactor, is reduced to seven elements. This gives greater freedom for flattening the power shape by varying the isotope concentration in the outer region of the core.

FIG 1 GA OF REACTOR

Suitably chosen recharge procedures can help in reducing the power peaks still further.

Owing to the hexagonal structure of the fuel elements, these central seven elements are encircled by a ring of twelve elements, forming the so-called intermediate zone. A third ring with eighteen elements comprises the outer zone. The table below shows the proposed fissile and fertile isotope concentration in the three zones.

Central Zone	7 elements	N = 15	U = 1.0
Intermediate Zone	12 elements	N = 2.6	U = 1.15
Outer Zone	18 elements	N = 3.3	U = 0.90

N = ratio of thorium to uranium concentration (local)

U = uranium concentration relative to central zone

Dragon = proposed fissile and fertile isotope concentration

The U-235 concentration is varied radially, mainly to flatten the power peaks at the core reflector boundary. It is further necessary to introduce some thorium into the two outer zones, to restrict the hot excess reactivity to about 10%. Calculations for this core show an initial relative power peak of about 1.6 between control rods. During burn-up the flux shape changes and at end of life of the first loading, after 300 days, we have to expect a maximum power shape factor of 1.45.

As mentioned, frequent recharges of the outer regions are necessary and some thought has been given to working out a reloading scheme which minimizes flux fluctuation. The proposed concept is in general to replace the intermediate zone by fresh fuel elements at any recharge. The spent fuel elements of this zone replace in turn twelve out of eighteen elements of the outer zone. The point here is that the amount of fissile material in the fuel elements of the intermediate zone at the end of their life in this zone is about the same as the initial amount of fissile material in the outer zone. Undesired core-reflector power peaks can therefore be avoided. With this scheme it is hoped

that the reactor can run at least for 800 days without the power shape factor exceeding 1.60.

One may think that in an inhomogeneous core as proposed, the power distribution has no direct bearing on fuel temperatures. However, before this question can be discussed it is necessary to say a few words about the nature of the fuel cartridges. They consist of coated particles embedded in a graphite matrix. In order to avoid an excessive burn-up of the coated particle, the uranium is diluted with either thorium dicarbide (in the ratio 1:15) or zirconium monocarbide (in the same ratio). The fuel bodies of the central zone will be made up of coated particles of the uranium-thorium brand only, whereas the fuel bodies for the two outer zones contain a mixture of either brand in the proper ratio. As the distribution of the fissile and fertile material in the cartridge greatly influences the fuel temperature, the coated particles are only dispersed in its outer region. The bigger the particles the smaller can be the annulus in which the necessary amount of fuel can be accommodated. By increasing the particle size from 200 to 400 μ , a temperature drop of 200°C can be gained.

Owing to the high dilution of the uranium the number of coated particles to be accommodated in the cartridge is about the same for the three zones of the reactor. The difference is only that zirconium forms a monocarbide and thorium a dicarbide. Therefore the temperature across the core follows closely the power density in spite of the inhomogeneous loading of fissile and fertile material. As there are not yet any experimental data available about the thermal conductivity for this type of graphite under irradiation at these high temperatures, no accurate predictions of the temperature in the core can be made. Calculations based on a thermal conductivity of 0.03 cal/cm sec °C lead to an average fuel temperature of 1300°C and a peak temperature of 1600°C.

Studies for a Power Reactor

As already mentioned the central zone provides an irradiation facility for the testing, under operational conditions, of fuel elements which might prove

suitable for use in a big reactor of the Dragon type. Therefore some calculations have been performed to give an indication as to the core composition of a land based power reactor of the Dragon type. A thermal output of 1000 MW was envisaged.

Two sets of calculations have been carried out, one by Brinkworth (4) of the U.K.A.E.A. and the other by Beliaev (5). Brinkworth assumed a constant power density and optimized the fuel costs for different ratings (MW/kg) and thorium to uranium concentrations, whereas Beliaev compared the attainable burn-up for power densities in the range between 5 and 15 Kw/liter, for different thorium to uranium ratio and different ratings.

Assuming a power density of 11.6 Kw/liter minimum fuel costs were achieved for a thorium to uranium ratio of about 10 and ratings of 1.0 MW/kg for batch loadings. In the case of a continuous charge and discharge a somewhat higher figure for the latter value was obtained, namely 1.15 MW/kg. It is, however, noteworthy to remark that the fuel costs do not change appreciably in a wide range around these optimum values. For instance, fuel costs are only 3% higher for a rating of 0.74 or 1.25 MW/kg. A continuous charge and discharge operation of the reactor offers a reduction in fuel costs of about 25% compared with batch loading, but this advantage may be offset by the difficulties in achieving a continuous reloading for this type of reactor. Furthermore fuel elements have to withstand an irradiation in the order of 1600 MWD/kg U-235 on average.

As it is very difficult at this stage to estimate properly the fuel costs, especially the fuel element fabrication and reprocessing costs, such a calculation is meant only to serve as a guidance and its results should be treated with great care.

In the second type of calculation the effect of changing the power density was taken into account, but fuel costs were not calculated, for the change in core size would change the capital costs as well.

Power Density	Burn-up	Rating	Thorium to Uranium
Kw/liter	MWD/kg	MW/kg	Ratio = N
5	1170	0.50	14
10	1060	0.84	9
15	1020	1.00	6

Maximum obtainable burn-up for batch-loading (5).

In the table above the maximum burn-up is given for three different power densities and the rating and N-value at which they occur. The burn-up achieved is somewhat higher in this calculation, the reason is presumably that spectrum changes during burn-up have not been taken properly into account. The program used was Fever in four groups, compared with the zero-dimensional ten group code used for the first mentioned calculation.

If one considers fuel costs, however, one will go to higher N-values than calculated for maximum burn-up, because the conversion factor increases, so reducing U-235 make-up costs. The maximum observed is so flat that the decrease in burn-up is not critical.

By comparing maximum burn-up for different power densities, the general tendency is shown again that even main parameters do not change the burn-up or the economy of the core appreciably. The influence of power density on maximum burn-up is small so that other factors, like the mechanical stability of the fuel element at high temperatures, pumping power, and costs for the pressure vessel and fabrication of the fuel elements will finally determine the power density.

As the Dragon type fuel element with its purge flow is easily adaptable to the removal of large quantities of fission products, some thought has been given to the feasibility of a fission product emitting fuel and its effect on core lifetime. To simulate a partial release of fission products a few burn-up calculations (6) have been carried out with a reduced fission product yield. The outcome is that a complete release of xenon 135 and samarium 149, 151 as well as a 20% release of the slow and non-saturating fission products increases the

burn-up only by 30%. According to a study of Pointud (7) on small particles, the assumed 20% reduction in the absorption cross section of the slow and non-saturating fission products seems to be the utmost one can hope for, namely a complete loss of krypton, zirconium, indium, iodine, cesium and xenon. Unless new evidence shows a higher volatility of various fission products than assumed the prospect of fission product emitting fuel does not seem to be very bright.

Summary

In the paper presented an account has been given of the considerations which led to the proposal of a three zone core for Dragon. This core allows the testing of fuel elements at the center under operating conditions and over long times. The outer region serves as a driving region, new fuel elements being inserted in the intermediate zone and spent elements removed from the outermost. Material problems, especially temperature and burn-up restrictions, played an important part in determining the core composition.

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Session III
Paper 13

RADIATION HAZARDS OF RECYCLED U²³³-THORIUM FUELS

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INTRODUCTION

The methods by which future power reactor fuels can be refabricated will depend upon the beta, gamma and neutron radiation intensities created by isotopes other than the fissile or fertile materials. Activities of gross or individual fission products can be reduced to very low levels by high-decontamination processes and thus be eliminated as serious radioactive hazards during fuel-element fabrication. However, the recycle of fuels through power reactors will increase parasitically produced isotope intensities much beyond those found for the naturally occurring elements. The increase in these radiation intensities can impose handling limitations for fuel element refabrication procedures.¹ These handling limitations on nuclear fuels may be imposed for one or more of the following reasons:

(1) Direct contact exposure to the hands may be high, (2) total body exposure at operating distances may be above set limits, and (3) internal exposure hazards due to air contamination may be created. The radioactivity contributing to each of these categories is: (1) for surface doses, beta particles, gamma rays and fast neutrons from (α, n) reactions and/or spontaneous fission; (2) for radiation at a distance, gamma rays and fast neutrons; (3) for air contamination, alpha-emitting dusts.

This paper attempts to enumerate each of these hazards for U^{233} -thorium fuels. The concern about isotopic contaminants is a relatively new one and has been accentuated by the desire to achieve high irradiation

levels and recycle of power reactor fuels.

Three methods of refabrication will be considered:

Direct refabrication. Refabrication by methods in which the hands are in direct contact 10-40 hr per week and exposures are limited to 100 mr/40 hr to the total body and 500 mr/40 hr to the skin of the hands.

Semiremote fabrication. Refabrication by methods which limit direct contact but in which only distance, structural metals or plastics are used for shielding. The facility may be enclosed in an air-tight or dry box, and can be directly maintained following removal of the work and minor decontamination. Probably semiremote handling should be limited to gamma intensities of less than 2.5 mr/hr at 1 m from the fuel.

Remote fabrication. Refabrication by methods which require that all operations be carried out behind heavy shields and under conditions for protection from alpha activity. If fission products can be removed, as by solvent extraction, and isotopic contaminants are the only sources of penetrating radiation, direct maintenance of facilities is possible after removal of fuel and minor decontamination. If high fission product activities are present, remote maintenance is also necessary.

ACTIVITY IN URANIUM-233

The chief source of radioactivity in U^{233} after Thorex processing of fuel from power reactors will be the decay products of U^{232} . This decay chain will contribute both very energetic gamma rays and neutrons from (α, n) reactions with any light elements associated with the uranium. The main production of U^{232} in a thorium reactor is initiated by an $(n, 2n)$

reaction on thorium:

Both the amount and the ratio of U^{232} to U^{233} produced increases with increasing neutron flux and irradiation time (See Figs. 1 and 2) and is highly dependent on the neutron energy distribution in the reactor, since only neutrons with energies above 6.37 Mev produce the $(n, 2n)$ reaction. For instance, the effective $(n, 2n)$ cross-section, based on thermal neutron flux, is of the order of 10^{-2} barn for a well-moderated reactor that has separate fuel and blanket regions, but, in reactors such as the Consolidated Edison Indian Point, that uses mixed $\text{ThO}_2\text{-UO}_2$ fuel and relatively poor neutron moderation, a cross-section of about 5×10^{-2} barn is expected. In this case about 1000 parts of U^{232} per million parts of U^{233} is expected in the first cycle after an 18,000 Mwd/tonne* irradiation, corresponding to 200 parts of U^{232} per million of total uranium. After several cycles the U^{232} will reach about 850 ppm, based on total uranium, giving about 2500 parts of U^{232} per million parts of U^{233} . Both during irradiation and after discharge U^{232} decays to Th^{228} and the remainder of the chain, which can be written as:

* tonne = metric ton (1000 Kg)

Fig. 1. Effect of irradiation level on U-232 concentration.

Fig. 2. Effect of irradiation level on U-232/U-233 ratio.

The alpha-produced neutron background is increased since many of the alpha emissions have sufficient energy to strip neutrons from light metal impurities. The gamma background is increased because of the high-energy gammas of Bi^{212} and Tl^{208} . A discussion of Th^{228} and the decay chain in recovered thorium is found in the section ACTIVITY IN THORIUM.

Gamma Activity

The major handling problem for any fuel is due to residual gammas or x-radiation. The source of this radiation could be the fissile or fertile isotopes and decay daughters, or residual fission products. The most significant gamma problems for any fuel are those associated with irradiated and decontaminated U^{233} and thorium. These gammas result from the decay daughters of the transmuted isotopes U^{232} and Th^{228} . After chemical separation the U^{232} will follow the U^{233} stream, and the Th^{228} will follow the thorium stream.

First, consider the U^{232} in U^{233} : For decay times of interest in fuel fabrication, Th^{228} with a half-life of 1.91 years controls the buildup of activity from U^{232} daughters, with the growth of gamma activity into freshly purified U^{233} containing U^{232} following closely the

amount of Th^{228} present. The gamma activities of primary concern are the 2.6-Mev gammas from Tl^{208} and the 0.8- to 2.2-Mev gammas from Bi^{212} . The buildup and decay of U^{232} and daughter product activities is shown in Table I. This table gives the radiation dose rate 1 m from a kilogram sphere of U^{233} as a function of time after final separation and U^{232} content. Table II lists the handling limitations or maximum allowable working time for U^{233} (without thorium) fuel elements. It is assumed that U^{233} will be refabricated semiremotelly and that the workers will be at least an average of 1 m away from the work at all times. This table lists working limits for the three conditions of (1) time for radiation intensity to reach 5 mr/hr, (2) working time to receive an average of 5 mr/hr over the working time, and (3) working time to receive an average of 2.5 mr/hr over the working time. The unfortunate situation concerning fuel element fabrication is that the most exacting detailed operations occur at the end of the fabrication period when the radiation levels are the highest.

In addition to the activity of the U^{232} decay chain, the gamma activity of U^{233} itself and of residual fission products must be considered. The penetrating radiation from U^{233} is γ rays in the 40- to 96-kev region and therefore is easily shielded. The residual fission product content of U^{233} can be decreased to almost any desired level by decontamination beyond that obtained in the Thorex process. However, a practical goal seems to be about $1 \times 10^6 \text{ dis-min}^{-1} \text{ g}^{-1} \text{ U}^{233}$ that produce 0.5- to 1.0-Mev γ rays. This is about the minimum residual fission product activity to be expected in the Thorex process product.

Table I. Radiation Intensities at 1 m from 1 kg of U^{233} Containing U^{232}

Time after separation (sec)	Dose rate per ppm U^{232} (mr/hr)	Time after separation (sec)	Dose rate per ppm U^{232} (mr/hr)
0	0	2×10^6	2.28×10^{-1}
1×10^4	3.2×10^{-7}	3×10^6	3.78×10^{-1}
3×10^4	1.52×10^{-5}	4×10^6	5.26×10^{-1}
1×10^5	5.7×10^{-4}	5×10^6	6.73×10^{-1}
2×10^5	3.37×10^{-3}	6×10^6	8.18×10^{-1}
3×10^5	8.55×10^{-3}	7×10^6	9.61×10^{-1}
4×10^5	1.57×10^{-2}	8×10^6	1.10
5×10^5	2.45×10^{-2}	9×10^6	1.24
6×10^5	3.46×10^{-2}	1×10^7	1.38
7×10^5	4.6×10^{-2}	2×10^7	2.68
8×10^5	5.8×10^{-2}	3×10^7	3.84
9×10^5	7.0×10^{-2}	4×10^7	4.85
1×10^6	8.35×10^{-2}	5×10^7	5.76
		6×10^7	6.55

Table II. U^{233} Handling Limitations
 Basis: 1 kg U^{233} per operation
 Dose measured 1 m from piece of U^{233}

U^{232} concentration (ppm)	U^{232} α pulse ratio (α_{22}/α_{23})	Maximum allowable handling time since final separation (days)			Necessary shielding (to 2 mr/hr) for 35 day aged U^{233} (cm)	
		To reach 5 mr/hr	To average 5 mr/hr	To average 2.5 mr/hr	(lead)	(concrete)
10	0.0218	45	108	76	1.89	11.4
20	0.0437	24	57	40	3.73	21.0
40	0.0875	15	31	22	5.47	29.7
60	0.131	11.5	23	16	6.47	34.7
80	0.175	9.9	18.5	13	7.18	37.9
100	0.218	8.5	15.6	11	7.71	40.6
200	0.437	8.0	10.5	7.4	9.40	48.3
400	0.875	4.2	7.2	5.1	11.0	56.1
600	1.31	3.5	5.7	4.0	12.0	60.5
800	1.75	2.9	5.0	3.5	12.6	63.6
1000	2.18	2.7	4.6	3.3	13.2	66.0
1500	3.28	2.3	3.7	2.6	14.1	70.5
2000	4.37	2.0	3.2	2.3	14.8	73.6
2500	5.46	1.7	3.1	2.2	15.3	75.9

Light shielding may be necessary if fabrication schedules of less than seven days are impossible or if U^{232} concentrations greater than 200 ppm are encountered. Table II also gives the required thickness of lead or concrete necessary to shield the fabrication facility. In these cases it is assumed that the worker's body be 1 m from the work with the center line of the shield placed 50 cm from the work. In all cases the decay time since separation is 3×10^6 sec (35 days) and the desired radiation level at 1 m is 2 mr/hr.

Neutron Activity

The expected permissible dose to the body is 100 mr per 40-hr week, and the permissible dose to the skin of the hands is 500 mr per 40-hr week. If (α, n) reactions were the only source of radiation from U^{233} then these limits should set the criterion for specifications. However, this is not the case; but these specifications can still be used for (α, n) reactions so that the neutron dose rate is insignificant compared to that from gamma rays. The dose to the hands is a complex problem when dealing with fast neutrons in that dose effects to the tissues of the hands must be compared to those of x-rays. If an x-ray dose of 500 mr is delivered to the skin of the hands, then the dose is 425 mr in the deeper tissues of the hands. However, the dose delivered to the tissues of the hands by fast neutrons is increased by 15% over that delivered to the skin. For these reasons the allowable skin dose for fast neutrons must be limited to 350 to 400 mr per 40-hr week in order to maintain the same tissue dose as will be contributed by x-rays delivering 500 mr per 40-hr week to the skin.

For the purpose of calculating the permissible neutron background in a piece of U^{233} metal, a dose rate of 1000 mr per 40-hr week at the surface of a kilogram sphere of metal and a direct-handling time factor of 0.4 was used. The kilogram sphere was chosen since the radiation intensity at the surface of a sphere would be greater than for any other shape containing 1 kg of metal. Also, a kilogram should be the maximum amount of fissionable material handled in any one element, either pure or as an alloy. The self-absorption of neutrons for any expected material should be nil.

The alpha-neutron emission rate may be expressed by an equation of the following type:

$$n = E(a + b\alpha + c\beta), \quad (1)$$

where E = concentration of light element, ppm,

n = neutron emission rate, neutrons $g^{-1} \text{ min}^{-1}$,

a = constant for each element which expresses the effect of U^{233} ,

b = constant for each element which expresses the effect of U^{232} ,

$\alpha = U^{232} \alpha$ emission ratio, $\left(\frac{dN_{\alpha}}{dt} \right)_{22} / \left(\frac{dN_{\alpha}}{dt} \right)_{23}$,

c = constant for each element which expresses the effect of Th^{228} and its equilibrium daughters,

$\beta = Th^{228} \alpha$ emission ratio $\left(\frac{dN_{\alpha}}{dt} \right)_{08} / \left(\frac{dN_{\alpha}}{dt} \right)_{23}$.

Table III lists the constants a, b and c for all the important light elements that may contaminate U^{233} . In order to set the maximum permissible concentration (MPC) for each light element, the neutron emission rate corresponding to the maximum permissible neutron dose and the appropriate value of α and β for a U^{232} concentration of 100 ppm were used. These constants are 0.25 for α and 0.025 for β 3-1/2 months after separation.

Table IV lists the MPC of each light element to give a neutron dose of 1000 mr per 40-hr week at the surface of a kilogram sphere if this were the only impurity present. The actual concentration would have to be much less than that listed if other impurities existed and if the dose from neutrons is to be kept below tolerance. For example, if there were 10 impurities and the neutron dose was to be maintained at 20% of the tolerance value, then the impurity concentration for each of the 10 should be a factor of 50 below the tabulated value.

If the alpha emission rates were higher than those corresponding to 100 ppm U^{232} in U^{233} aged 3-1/2 months, the impurity specifications would be altered accordingly.

Table III. Values of Constants a, b and c for each of the Important Light Elements which may contaminate U²³³

The constants are for the equation $n = E(a + b\alpha + c\beta)$

Light element	a	b	c
Li	0.366	0.50	4.00
Be	4.688	8.200	148.0
B	1.0714	2.3807	15.479
C	6.522×10^{-3}	1.45×10^{-2}	8.333×10^{-1}
N	$< 1 \times 10^{-6}$	$< 9.33 \times 10^{-4}$	$< 2.40 \times 10^{-2}$
O	2.804×10^{-3}	5.815×10^{-3}	1.138×10^{-1}
F	0.3158	0.7442	19.40
Na	2.678×10^{-2}	5.45×10^{-2}	4.584
Mg	2.069×10^{-2}	2.168×10^{-2}	14.567
Al	1.25×10^{-2}	4.276×10^{-2}	3.395
Si	3.0×10^{-3}	0.134	12.681
P	4.00×10^{-4}	1.348×10^{-3}	0.1894
S	3.409×10^{-5}	3.50×10^{-4}	1.2676
Cl	1.071×10^{-3}	1.857×10^{-2}	6.851
A	3.06×10^{-3}	3.023×10^{-2}	6.8065
K	3.921×10^{-4}	4.00×10^{-3}	1.623
Ca	0	0	1.000
Sc	4.76×10^{-5}	5×10^{-4}	0.9625
Ti	2.3×10^{-5}	3×10^{-4}	0.6977
V	0	0	0.5357
Cr	0	0	0.4054
Mn	0	0	0.303
Fe	0	0	0.1304
Co	0	0	0.125
Ni	0	0	4.166×10^{-2}

Table IV. Maximum Permissible Concentration of each Light Element (if it existed alone) in U²³³ Metal

Basis: Neutron dose of 1000 mr/per 40-hr week at the surface of a kilogram sphere of U²³³, a U²³² concentration of 100 ppm, and a time after processing of 3-1/2 months

Light element	MPC (ppm)	Light element	MPC (ppm)
Li	45	Cl	295
Be	4	A	125
B	10	K	810
C	6,050	Ca	2,100
N	45,000	Sc	1,240
O	26,400	Ti	7,250
F	20	V	14,000
Na	168	Cr	18,500
Mg	480	Mn	24,800
Al	240	Fe	57,500
Si	255	Co	60,000
P	4,550	Ni	180,000
S	5,900		

ACTIVITY IN THORIUM

The chief sources of radiation in thorium are the Th^{228} decay chain, $\text{Th}^{234}\text{-Pa}^{234}$ from neutron capture in Th^{233} , and residual Pa^{233} and fission products.^{2,3} These products contribute both beta and gamma activity as well as add to the air-contamination problems. The beta activity adds to the surface dose rates but is still insignificant compared with the gamma activity. The Th^{228} chain activity will be controlling since $\text{Th}^{234}\text{-Pa}^{234}$ activity can be decreased to insignificant levels by a decay time of 400 days, and that from fission products can probably be decreased to about $1 \times 10^8 \text{ dis min}^{-1} \text{ kg}^{-1}$ of thorium by the Thorex process. Thus the major source of activity in recovered, recycled thorium becomes the Th^{228} decay chain. (Neutron activities are minor in recovered thorium.) Th^{228} is formed by decay of parasitically produced U^{232} , with decay occurring both during irradiation and during the decay period following discharge. Since part of the Th^{228} is formed during the decay period, it is possible to reduce the total Th^{228} concentration by processing after as short a decay period as possible. Short decay cannot eliminate the problem, however. Continuous recycle of thorium through reactors, decay, processing and refabrication will increase the Th^{228} concentration over that formed during the first cycle. The value of the steady state concentration depends upon the exact combinations of recycle conditions used, but practical considerations indicate that this value is approximately three times the one-cycle concentration. The concentration of Th^{228} following infinite recycle can be estimated by the following equation:

$$\frac{N_{08}^{\infty c}}{N_{08}^{1c}} = \frac{1}{\left\{ 1 - \exp \left[- \lambda_{08} (T_R + T_C + T_P) \right] \right\}}, \quad (2)$$

where $N_{08}^{\infty c}$ = Th^{228} concentration after an infinite number of cycles,

N_{08}^{1c} = Th^{228} concentration after the first cycle,

λ_{08} = radioactive decay constant for Th^{228} ,

T_R = reactor irradiation time,

T_C = pre-Thorex decay time,

T_P = post-Thorex decay time.

An analysis of the health hazards involved in the handling of thorium after it leaves the Thorex plant indicates that the most critical operations are the machining of metal and those involving the handling of dry solids, such as ThO_2 . Thorium activity specifications, whether for salt, metal or oxide, should be based on the total external gamma radiation and on the alpha, beta and gamma internal-radiological hazards associated with all steps between chemical separation and final fuel element fabrication. Handling and operating techniques must be carefully controlled in order to limit dust contamination, waste-stream activity levels, fume evolution from metal furnaces, and unnecessary handling time.

In order to increase allowable irradiation levels it becomes necessary to handle thorium which has activity levels much greater than 10 times that of natural thorium. If radiation intensities ≥ 10 times natural thorium are encountered it will be necessary to fabricate thorium elements behind several centimeters of lead or concrete shielding. The

other alternative would be the holding back the thorium stream from the Thorex process for approximately 12 years in order to allow decay of Th^{228} . Table V lists the radiation intensities, required shielding or Th^{228} decay times for several Th^{228} activity levels in recovered thorium. The concentration and activity of Th^{228} in recovered thorium at the time of reactor discharge can be found from Fig. 3. The Th^{228} concentration after any pre-processing decay period may then be found from the following equation:

$$N(08) = N_D(22) \lambda_{22} \frac{\exp(-\lambda_{22} T_C) - \exp(-\lambda_{08} T_C)}{\lambda_{08} - \lambda_{22}} + N_D(08) \exp(-\lambda_{08} T_C), \quad (3)$$

where $N(08)$ = Th^{228} concentration, atoms/atom of Th^{232} ,

$N_D(22)$ = U^{232} concentration at discharge, atoms/atom of Th^{232} ,

$\lambda_{22}, \lambda_{08}$ = radioactive decay constants for U^{232} and Th^{228} , respectively.

Table V. Thorium Handling Limitations

Basis: Thorium billet, 10 cm diam x 10 cm long
Dose measured on surface and 1 m from billet

Th ²²⁸ activity ^a (dps/kg Th)	Th ²²⁸ concentration (ppm) in Th	Radiation intensities (mr/hr)		Necessary shielding for thorium for 2 mr/hr 1 m from billet, cm		Decay time to reduce Th ²²⁸ act. to that of natural Th (years)
		At surface	At 1 m	(lead)	(concrete)	
4.1 x 10 ⁶	1.35 x 10 ⁻⁴	163	1.2	0	0	0
2.05 x 10 ⁷	6.75 x 10 ⁻⁴	815	6	2.86	18.9	4.43
4.10 x 10 ⁷	1.35 x 10 ⁻³	1,630	12	4.53	27.1	6.33
8.20 x 10 ⁷	2.70 x 10 ⁻³	3,260	24	6.20	34.7	8.25
2.05 x 10 ⁸	6.75 x 10 ⁻³	8,150	60	8.40	44.9	10.8
4.10 x 10 ⁸	1.35 x 10 ⁻²	16,300	120	10.0	52.3	12.7
8.20 x 10 ⁸	2.70 x 10 ⁻²	32,600	240	11.6	60.5	14.6
2.05 x 10 ⁹	6.75 x 10 ⁻²	81,500	600	13.8	71.0	17.2
4.10 x 10 ⁹	1.35 x 10 ⁻¹	163,000	1200	15.4	79.0	19.0

^a Th²²⁸ activity in natural thorium in complete equilibrium with decay daughters is 4.1 x 10⁶ α dps/kg.

Fig. 3. Effect of irradiation level on Th-228 concentration.

CALCULATED ACTIVITY LEVEL FOR TYPICAL FUEL-FABRICATION SITUATION

The total activity from the various sources in recycled thorium and U^{233} makes it desirable to use shielding and remote operation in preparing the fuel material and fabricating fuel elements for the thorium fuel cycle. For calculational purposes, a typical process situation may be visualized as a sphere of thorium oxide-uranium oxide with a density of 4.5 g/cc and containing 33 kg of thorium and 1 kg of U^{233} . The contribution of the U^{232} decay products and unirradiated thorium to total penetrating radiation at 10-cm distance from this sphere as a function of decay time after processing is shown in Fig. 4. Three cases are considered: (1) complete removal of all U^{232} decay products at zero time, (2) complete removal of all decay products except 1% of the Th^{228} which will have grown in during two months' storage and shipping, and (3) removal of 90% of the Th^{228} but none of the other decay products produced by two months' decay. Case 2 is representative of a TBP solvent extraction removal of the decay products, and Case 3 a cation exchange removal of Th^{228} . The values were calculated for U^{233} containing only 50 ppm of U^{232} (material currently on hand at ORNL), unirradiated thorium which contains only a third of the equilibrium concentration of Th^{228} in normal thorium, and no residual fission product activity. Even for this very conservative situation, about 5 cm of lead (Fig. 5) would be required to decrease the radiation level to 1 mr/hr at 10 cm five days after isolation of the U^{233} , and it is difficult to visualize fuel preparation and fabrication being completed in less than 5 days.

Fig. 4. Radiation from recycled ThO₂-UO₂ as a function of time after processing. Case 1, removal of 100% of U-232 daughters at time zero; Case 2, removal of 99% of U-232 daughters; Case 3, removal of 90% of Th-228 only.

Fig. 5. Lead shielding requirements as a function of time after processing. Case 1, removal of 100% of U-232 daughters at time zero; Case 2, removal of 99% of U-232 daughters; Case 3, removal of 90% of Th-228 only.

On the other hand, recycled power reactor U^{233} -thorium fuels would require shielding after only one to two days buildup even if 100% daughter removal could be achieved. If 1% of the daughter products remain in the fuel, shielding would be required from the outset of fabrication. Also if recycled thorium which has not been decayed to Th^{228} background levels is used, it will not be necessary to decontaminate the uranium product by more than a factor of 10 since the Th^{228} activity which builds up in the recycled thorium during irradiation and a normal preprocessing decay period will control the shielding requirements. These effects are shown in Figs. 6 through 8. The assumptions used in these cases are as follows:

1. Fuel rods that are 3-1/2 feet long and that contain 1 kg of thorium each as a 3% UO_2 -97% ThO_2 mixture.
2. The uranium has a U^{232} concentration of 500 ppm.
3. The thorium has a Th^{228} activity equivalent to 500 times that of normal thorium for the thorium recycle cases and 1/3 that of normal thorium for the cases where purified thorium is used.

Comparisons were made for 99 and 100% removal of U^{232} daughters, with no thorium recycle, and 99% removal of U^{232} daughters, with and without final thorium decontamination for the thorium recycle cases. Calculations were made for surface dose rates from a single fuel rod and a 38-rod cluster and for the necessary ordinary concrete shielding for a 38-rod cluster (or its equivalent) to reduce the radiation intensity at the outside of the shield to 0.25 millirad/hr.

Fig. 6. Surface dose rates from fuel rods.

Fig. 7. Surface dose rates from 38 rod cluster.

Fig. 8. Shield requirements for 38 rod cluster.

CONCLUSIONS

The buildup of isotopic contaminants during successive irradiations can greatly affect the handling procedures associated with the recycle of nuclear power reactor fuels. Because of high irradiation and many recycles, the levels of alpha, gamma, or neutron activity may govern the procedures that must be followed during all steps of the fuel cycle. The buildup of activities in U^{233} or thorium systems follows definite patterns, and these activities cannot be reduced to allowable exposure levels unless excessive decay periods are used. Since these activities cannot be reduced, the only alternative procedures would be refabrication by remote or semiremote methods. These alternatives and the reasons for using them are discussed below.

The use of U^{233} -thorium fuels requires semiremote or remote handling and/or definitely established schedules with complete decontamination for each scrap recycle. Reactor fuel elements containing U^{233} can be fabricated semiremotelly provided that complete fabrication can be accomplished in one or two weeks or less. If the U^{233} contains greater than 200 ppm of U^{232} , then a shielded refabrication facility is necessary. Also, the U^{233} metal must be free of light-element contamination in order to reduce the alpha-produced neutron background. Thorium can be handled directly during some recycle steps and semiremotelly during others. In many cases it may be justifiable to handle natural thorium during the refabrication of reactor fuel elements and to hold back the irradiated thorium for approximately 12 years to allow decay of Th^{228} to natural thorium backgrounds, and the practicality of this procedure will depend on the actual cost of thorium and the inventory charge. Since recycled

power-reactor thorium will have radiation intensities greater than 10 times that of natural thorium it must also be refabricated in a shielded facility. Also, it appears that economic irradiation levels in thorium must be greater than 5000 g/tonne and thus the very active recycled thorium must be fabricated behind shielding.

If a shielded fuel-handling facility is to be used it may not be necessary to use purified thorium for the fabrication of mixed-oxide fuel elements because the shield thickness will be increased by only 20 to 30 cm by recycling the thorium. On the other hand, those conversion and refabrication operations that use only thorium may be handled more economically by using low-activity thorium without shielding. This would be especially true if the reactor used separate fuel elements of U^{233} and thorium. Even if mixed fuels are used it would still be possible to carry on the shielded operations after blending. A thorough economic study will be necessary before a firm statement can be made about the relative merits of complete thorium recycle (no excessive decay period), compared with a refabrication operation that uses purified thorium, with the spent thorium being allowed to decay for about twelve years.

In an actual fuel-cycle-operations analysis, in addition to the activity that builds in from U^{232} decay, it will be necessary to consider the following:

1. residual Th^{228} and/or daughter activity in the recycled uranium fraction,
2. residual Th^{228} activity in the thorium fraction,
3. fission product contamination in both the recycled uranium and the thorium fractions, and

4. equipment and cells which are contaminated by a small amount of longer-aged uranium or thorium.

Calculated radiation intensities for a realistic situation to be encountered in the thorium fuel cycle for power reactors as a function of time (Table VI), again with conservative assumptions, indicate that about 8 cm of lead is required for safe handling.⁴ For the calculations the U^{232} content in the U^{233} was assumed to be 200 ppm, the minimum expected for recycled power reactor fuels. The residual Th^{228} content of the thorium was assumed to be the equilibrium amount in normal thorium that could be attained only after decay storage of 10 to 18 years. The contamination of equipment with older U^{232} -containing material was assumed to be only 1% of the equipment capacity, assuming a complete cleanup every two months, and the amount of residual fission products was based on two complete cycles of Thorex processing of irradiated fuel that had been decayed 400 days before processing.

Table VI. Gamma Activity of a Sphere Containing 33 kg of Thorium and 1 kg of U^{233} as Oxide

Density: 4.5 g/cc
 U^{233} containing 200 ppm of U^{232}

Time Since Final U Separation (days)	Radiation Intensity at 10 cm (millirads/hr)				
	U^{232} Daughters ^a	Residual Th Activity ^b	Equipment Contamination ^c	Fission Products ^d	Total
1	15	20	15	5	55
3	30	20	15	5	70
7	90	20	15	5	130
12	200	20	15	5	240
20	380	20	15	5	420
30	640	20	15	5	680

^aBased on 99% removal of U^{232} decay products at zero time.

^bBased on Th that contains an equilibrium concentration of Th^{228} .

^cResidual contamination of process equipment assumed to be 1% of equipment inventory and aged an average of 2 months.

^dFission products based on 1×10^8 dis min⁻¹ kg⁻¹ of Th, plus 1×10^9 dis min⁻¹ kg⁻¹ U^{233} (0.5- to 1.0-Mev gamma rays).

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PCUT, A PROGRAM FOR RECYCLE OF POWER REACTOR FUEL

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PCUT
A Program for Recycle of Power Reactor Fuel

1. INTRODUCTION

The use of thorium-uranium fuel elements and the development of techniques for reprocessing and fabricating them are important steps toward economic nuclear power. Several reactors throughout the world now use thorium-uranium fuel elements, and there are chemical plants capable of separating fission products from the fuel. But a meaningful demonstration of the economics of the thorium fuel cycle requires a plant which will not only reclaim the fissionable material but reconstitute the fuel elements.

The potential of the thorium cycle for obtaining low nuclear fuel cost has been shown to result from the excellent nuclear characteristics of U-233. Obviously, the U-233 formed must be returned to the reactor in order that this advantage be realized. The economics of this recycle will be discussed at the end of this paper.

The Comitato Nazionale Per l'Energia Nucleare (CNEN) and the Allis-Chalmers Manufacturing Company have undertaken a joint program to develop and demonstrate the thorium fuel cycle for central station power reactors. One of the principal undertakings in the program is the design, construction, and operation of a pilot plant for reprocessing and fabricating reactor fuels containing thorium and uranium. The plant described in this paper will extract usable fuel material from the spent fuel elements of a thorium-uranium reactor, reconstitute the extracted material in a suitable form, and assemble new fuel elements for use in the same reactor.

This project has been incorporated as a key effort in the Italian atomic energy program. The facility has been designed to permit future conversion to process thorium loadings of the SENN Reactor now under construction near the Garigliano River in Italy. Thus, Italy would have the facilities for the complete thorium cycle, including reactor and reprocessing plant.

2. DESIGN BASIS

The recovery and reuse of fissionable material from spent fuel elements involves several chemical and mechanical processes which are made more difficult because of the high radioactivity of the spent fuel. Remote handling is therefore required in all the processing steps, not only because of the fission-product activity but because of the radioactivity associated with uranium-232 and thorium-228. Each step in the chemical process must be designed to preclude the possibility of criticality and both the mechanical and chemical processes must be carried out remotely from behind shielding walls.

The fuel assembly for which the plant is now designed (it can be converted later to handle SENN fuel) is that of the Elk River Reactor in Minnesota. This assembly (Fig. 1) is 81-5/8 in. long, approximately 3-1/2 in. square, and weighs about 86 lb. It consists of 25 stainless-steel tubes filled with ceramic pellets of uranium oxide and thorium oxide; grid castings at each end to hold the tubes in a 5 x 5 array; top and bottom end fittings that support and position the assembly in the reactor core; and clamps to maintain the correct spacing between rods over the length of the assembly.

Fig. 1. Elk River Reactor Fuel Assembly.

The plant has been designed for an instantaneous capacity of 15 kg of thorium-uranium oxides per day. Enrichments up to 10 per cent in U-233 can be handled safely. Minor additions to the plant, principally in the dissolving and recycle areas, will permit reprocessing at an instantaneous capacity of 30 kg of thorium-uranium per day.

Spent fuel elements from the Elk River Reactor are expected to be discharged at a rate of 1/3 core every 8 months. These elements can be reprocessed and refabricated in 50 operating days.

Spent fuel elements from the SENN Reactor (if loaded with a thorium core) could be processed in 290 operating days/year assuming a burnup of 17,000 - 18,000 Mwd/Mt.

3. REPROCESSING AND REFABRICATION PROCEDURES

The processing sequence consists of four major phases: disassembly, recovery of the fuel material, reconstitution of the recovered fuel material, and assembly of a new element. The processing sequence is represented schematically in Fig. 2.

3.1 DISASSEMBLY

The spent fuel elements are received in shielded shipping casks and unloaded underwater. The fuel elements are transferred to an isolated section of the canal where a remotely operated disassembly machine (1)* cuts off all structural fittings (which contain no fuel) but leaves all fuel-bearing rods intact so as not to expose the fuel

(1)*Paranthesical numbers refer to the numbered steps in Fig. 2

Fig. 2. Reprocessing Sequence.

material. The rods are loaded into a shielded magazine and carried from the canal to a chopping mechanism above the chemical processing cell.

3.2 RECOVERY OF FUEL MATERIAL

The chopping mechanism cuts the rods into short segments (2) that fall into a dissolver tank where the fuel material is dissolved (3) in a concentrated nitric acid solution, leaving the empty segments of the stainless-steel tubing. The resulting nitric acid solution containing fission products and the nitrates of thorium and uranium is adjusted so that its concentration is suitable for the next step. The properly adjusted solution is then pumped into a mixer-settler device (4) where the thorium and uranium are separated from the fission products by solvent extraction.

The aqueous product solution from the mixer-settlers is concentrated and then adjusted to ensure the proper thorium-uranium ratio.

Formic acid and urea are added to the adjusted solution, then the mixture is heated to 60°C and passed through a bed of alumina pellets containing 5 weight per cent platinum catalyst. This reduces the uranium valence state from +6 to +4 and permits precipitation (5) of both uranium and thorium with oxalic acid. The resulting slurry of thorium and uranium oxalates is centrifuged (6) to remove the supernatant liquid. The thorium-uranium oxalate solids are then passed through a calcining furnace where the volatile materials are driven off and uranium and thorium oxides are formed.

These oxides of uranium and thorium are the end product of the fuel recovery phase.

In the next phase, this material is formed into pellets for use in the fuel elements.

3.3 RECONSTITUTION OF RECOVERED FUEL MATERIAL

The dry mixed oxides of uranium and thorium are passed through a "Mikro-Pulvizer" to break up any aggregate bodies formed during the calcining step. The resulting oxide powders are blended (8) with water, an organic binder, and an extrusion aid in a Muller-Mixer prior to loading the resulting "clay" into an extrusion press. There the blend is extruded (9) in 91 cm. lengths, which are air dried (10) and cut to pellet length (11). The "green" pellets are then sintered (12) at temperatures up to 1700°C to produce pellets of the required high density.

The sintered pellets will be ground to the specified diameter by use of a centerless grinder. Pneumatic gauging attachments on the machine will permit continuous measurement of dimensions and continuous weighing of the finished pellets. Density calculations will be obtained from a computer using these measurements as a continuous input.

3.4 ASSEMBLY OF A NEW ELEMENT

The finished pellets (13) are loaded into new fuel tubes (14) under a vacuum and the tubing is sealed by welding in a helium atmosphere (15). The completed fuel rods are heated in a vacuum chamber which is connected to a helium leak detector.

The helium in the fuel rods ensures a positive test of the integrity of the rods. Bundles of 25 rods are assembled and fitted with spacer clamps (16), after which the end pieces are pressed into position (17). Specially designed snap rings lock the rod bundles to the end pieces and obviate further remote welding, which is complicated and difficult.

4. MACHINE DESIGN

Examples of some of the machines which have been designed for use in the PCUT plant are shown in Figs. 3 through 7.

4.1 DISASSEMBLY MACHINE

The disassembly machine shown in Fig. 3 operates in the pool under 20 ft of water.

The fuel assembly is clamped in place and moved forward to the circular milling cutters which are positioned to cut off the end fittings of the assembly. The assembly is then moved forward to the milling cutters which cut the intermediate straps holding the fuel rods together. Spacers inserted between the fuel pins prevent accidental cutting of the fuel cladding during this operation. In this way the fuel assembly is separated into individual fuel rods which are placed in storage cans by extension tool manipulators.

The fuel rods are carried to the next operation in shielded transfer casks.

4.2 CHOPPING MACHINE

The chopping mechanism shown in Fig. 4 is in the floor of the corridor above the hot cell. The transfer cask containing the fuel rods is moved into the corridor and placed over the chopping mechanism. The fuel rods are dropped one by one, from

Fig. 3. Disassembly Machine.

Fig. 5. Pellet Loading Machine.

Fig. 4. Chopping Machine.

Fig. 6. Helium Leak and Weld Tester.

the magazine of the cask into the chopping mechanism. The chopping blade is actuated by a hydraulic unit which moves the blade in both directions. The chopped pieces fall through the pipe into the dissolver in the hot cell. Air leaks into the dissolver through the pipe at a velocity of 20 fps. A ball valve seals this pipe when the dissolver is operating.

4.3 PELLET LOADING MACHINE

Figure 5 is an assembly drawing of the pellet loading machine, located in the warm cell. The machine is designed (1) to accept a fuel tube with one end plug partially inserted, (2) to fill the tube with fuel pellets, (3) to insert a second end plug with spring spacer, (4) to evacuate the fuel tube and back fill with helium, and (5) to complete the insertion of both end caps, thus trapping the helium in the tube. The machine is operated and loaded manually, with remote through-the-wall manipulators and valve controls in a panel outside the warm cell: the operation is observed through a shielding window.

4.4 HELIUM LEAK AND WELD TESTER

After the end fittings have been welded into the fuel pins, the fuel pins may be tested in groups of from one to twenty-five contained in a quiver or assembled in a complete fuel element assembly. Figure 6 is an assembly drawing of the helium leak and weld tester.

While in the furnace the fuel pins will lie on a tray which slides into and out of the furnace as the seal retainer is opened and closed by the lower pneumatic cylinder.

The fuel pins will be placed on the tray, while the tray and seal retainer are in the open position, by means of a remotely controlled crane or manipulator. The seal retainer will be held closed by the upper pneumatic cylinder and also by atmospheric pressure when the furnace has been evacuated.

The operating temperature of the furnace is $500\text{ F} \pm 50\text{ F}$ and the pressure is 1×10^{-3} mm of mercury. When these conditions have been achieved a helium leak detector outside the warm cell will be used to detect leaks in the fuel pins.

4.5 FUEL-ELEMENT ASSEMBLY MACHINE

The fuel-element assembly machine (Fig. 7) holds the 5 separate components (sub-assemblies) in proper alignment with each other and slides them together until the snap ring fasteners lock into place. The five subassemblies are the top end fitting, bottom end fitting, 2 spacer grids, and the bundle of 25 fuel tubes. This assembly technique was developed to eliminate any welding or bolting operations in the cell. The 25 fuel pins are properly spaced and held in a "quiver" which fits into the assembly machine. This quiver is removed after 14 inches of the assembly stroke has been completed. The assembling force of 1400 lb is exerted by a pneumatic cylinder arrangement. The complexity of the machine lies chiefly in the holding and aligning devices from which the completed assembly must be removed.

5. DESIGN OF REPROCESSING AND REFABRICATION CELLS

The operations described above are carried out in two shielded cells: a hot cell for operations with material of high activity and, a warm cell for operations involving lower levels of activity.

Fig. 7. Fuel-Element Assembly Machine.

5.1 HOT CELL (Fig. 8)

The hot cell in the upper right of Fig. 8 contains and shields the high activity level chemical process equipment. The space for active process equipment is 35 ft long, 11 1/2 ft wide, and about 14 ft high.

The hot-cell equipment is mounted on eleven racks; two spare racks have been included to permit future modification and expansion of the process system. Each rack is a plug-in unit similar to an electronic plug-in chassis. All feed lines, instrumentation, and control lines and interconnections between racks are made through three shielding plugs on the rack which fit into and seal the north wall of the cell. Models of the dissolving rack and one of the solvent extraction racks are shown in Figs. 9 and 10, respectively. After hot feed has begun to flow during plant operation, the hot cell becomes and remains an exclusion area. To service or change the equipment on any rack the rack must be removed by remote handling devices to the decontamination cell adjoining the hot cell.

The rack-transfer mechanism consists of a translating carriage and push-pull device. This arrangement was selected because of the expected infrequency of rack removal. It permits any rack to be remotely transferred from its operating position in the hot cell to the decontamination cell and replaced with another rack. Pipe connections to the feed lines, sample lines, instrumentation, etc., are made and broken from the piping corridor in a low radiation environment.

A rack is removed in four steps:

- (1) All equipment on the rack to be removed is emptied of process solutions and the equipment and lines are cleaned as thoroughly as possible by flushing with

Fig. 8. Hot Cell and Warm Cell.

Fig. 9. Model of Dissolver Rack.

Fig. 10. Model of Solvent Extraction Rack.

water and acid solutions. This is expected to reduce the activity level by a factor of 100 or more.

(2) The tubing and other connections to the rack in the north wall are broken manually with special tools and, if necessary, with the additional portable shielding for personnel.

(3) The carriage of the rack removal equipment is advanced to the rack position and locked in place. The pushing mechanism is put in place and the rack is advanced onto the carriage and disconnected.

(4) The carriage and rack are then transferred to the door of the decontamination cell and introduced into the cell by a push-pull rod operating through the north wall.

The rack is returned to the operating position by reversing this procedure.

5.2 DECONTAMINATION CELL

The decontamination cell is 12 1/2 ft long, about 14 ft wide, and slightly less than 17 ft high; it is equipped with wash-down facilities. To reduce the amount of low-level liquid waste, the wash-down system is of the recirculating type, i.e., the decontamination solution can be pumped from the sump and re-used. The decontamination cell has one shielding window, one pair of heavy-duty manipulators, and special wall plugs duplicating the north-wall plug system in the hot cell. There

are two doors in the decontamination cell; one to the decontamination area and one to the hot cell. The inner door is operated by a hydraulic assist mechanism; its opening is large enough to accommodate a full-sized rack (the minimum opening is approximately 3 1/2 ft wide and 13 1/2 ft high).

The ceiling of the decontamination cell has removable shielding plugs for handling material vertically in the cell and for removal and introduction of material and equipment from the service corridor on the first floor.

5.3 WARM CELL

The warm cell is a shielded enclosure which permits remote handling of the low-activity chemical processing equipment, and of the mechanical equipment necessary for fuel-pellet production and fuel-element assembly.

The warm cell is shown in the center of Fig. 8; it is 13 ft wide, 56 ft long, and 16 1/2 ft high. The warm cell is equipped with glass shielding windows, a pair of manipulators for each of nine windows, and a single manipulator for the tenth window. The equipment also includes a General Mills No. 100 mechanical arm and a 3-ton hoist of the General Mills type, which are used primarily to assist in servicing the machines and transferring material.

In addition to openings in the cell wall required for manipulators and machinery operators, there are removable roof plugs opening to the service corridor to permit the passage of machinery and equipment, including the cell cranes. Clearance around the cell in the cell operating area is about 14 ft, to allow for the removal of the manipulators.

A transfer lock near the east end of the warm cell is used to raise the refabricated fuel elements into the transfer flask in the corridor over the warm cell. Non-radioactive materials are also introduced into the cell through the transfer lock.

During construction and startup operations, that is, before active material is in the cell, personnel may enter and leave the cell through an opening in the east wall. Before hot operation begins, this opening will be semi-permanently closed. Other openings in the warm cell include a small transfer drawer with which small objects may be placed into or removed from the cell, and a number of wall plugs for instrumentation leads, utilities lines, and mechanical linkages.

Equipment in the warm cell is fastened to base plates with locating pins and quick-disconnect clamps, and is easily removable. When a piece of equipment must be repaired or replaced, the quick-disconnect clamps are removed with an impact wrench fastened to a cell crane and guided by manipulators. The item to be removed is first enclosed in a polyethylene bag to prevent contamination of the corridor, then lifted by the cell crane and moved beneath one of the cell covers. The equipment is lifted out of the cell with the corridor crane and placed in the decontamination cell. In the decontamination cell, the polyethylene bag is removed and decontamination is begun with manipulators and external sprays. When the activity level of the equipment is acceptable for personnel entry, the equipment will be repaired or replaced and returned to service.

6. WASTE HANDLING

6.1 GASEOUS WASTES

Gaseous wastes will be discharged through two off-gas headers: the dissolver off-gas header for gases of high fission-product activity, and the vessel off-gas header for gases of lower fission-product activity. Since the equipment in the dissolver, feed-adjustment, and high-level waste evaporator systems has the highest potential fission-product activity, it will be vented through the dissolver off-gas header. All other radiochemical process equipment will be vented through the vessel off-gas header.

The vessel off-gas header contains a condenser to remove water vapor; the condenser will be maintained at a pressure of 2-1/2 to 3 in. of water below atmospheric. The dissolver off-gas header will be maintained at a pressure of 60 to 80 in. of water below atmospheric. The two headers join downstream of the pressure reducing stations and empty into a gaseous waste header maintained at a lower pressure by a high-capacity vacuum pump. The gaseous wastes are passed through a caustic scrubber where ruthenium, iodine, and oxides of nitrogen are removed together with particulate matter which can be scrubbed out of the air stream. The scrubber vent gas will be heated slightly to prevent condensation, then sent to a filter for further removal of particulate matter. Before the off-gas is discharged to the stack it will be monitored to ensure that no harmful quantities of radioactivity are discharged to the atmosphere.

6.2 LIQUID WASTES

Liquid wastes will be segregated into four classes: (1) concentrated high-level wastes, (2) low-level acid wastes, (3) low-level neutralized wastes, and (4) process wastes with

Fig. 11. Plot Plan of Waste Storage Area.

very low activity levels. The disposition of the first three types is shown in Fig.11 which is a plan of the waste storage area.

Wastes in class 1 will be stored in stainless-steel tanks housed in underground concrete vaults, and must be cooled to dissipate the fission-product decay heat. Wastes in class 2 that are generated in the feed adjustment steps contain rather large quantities of nitric acid, which it may be desirable to recover later. These will also be stored in stainless-steel tanks placed in an underground concrete vault. Wastes in class 3 are those which either contain neutralized irrecoverable acids or are basic. These wastes will be concentrated and stored in carbon-steel tanks in an underground concrete vault. Wastes in class 4 will be sent to a retention basin for discharge to the environment.

6.3 RETENTION BASINS

Each of the two retention basins have a capacity (25,000 cu ft) sufficient to hold one day's output of cold wastes prior to discharge to the river. Wastes entering the retention basins are continuously monitored for activity so that the plant can be shut down immediately if active materials appear in this waste stream. This will avoid gross contamination of the cold wastes in the retention basins. Samples of the retained wastes will be taken and analyzed prior to discharge to the river. Discharged wastes will not exceed the maximum permissible concentration listed in Table 1 of NBS Handbook 69.

7. BUILDING

The processing building is shown in Fig. 12. The low structure in the foreground is the office wing which houses the offices, library, locker rooms, lavatories, a utility and compressor room, and a laboratory room. The taller structure is the main process building. The

Fig. 12. Reprocessing Building.

stack can be seen in the background. The waste building and other auxiliary structures are behind the building.

7.1 DESIGN CONSIDERATIONS

A plan of the ground floor of the process building is shown in Fig. 13.

The building layout reflects five principal requirements:

- (1) Underwater loading and unloading of the shipping cask and disassembly of fuel elements.
- (2) The transfer of materials and equipment into and out of the pool, decontamination cell, hot cell, and warm cell, either with or without shielded containers according to the activity of the material being handled. This necessitates a service corridor extending over these areas.
- (3) The use of the rack concept and through-the-wall connections for the high level chemical process system.
- (4) Through-the-wall manipulation from both side faces of the warm cell.
- (5) Future expansion of the production capacity of the pilot plant.

The building also ensures that work flows smoothly from a higher to a lower radiation level throughout the processing and fabrication cycle. The pipe access area has a relatively low level of radiation to permit easy interconnection between the process equipment and three supporting facilities: the sampling system, the transmitter equipment for instrumentation

Fig. 13. Ground Floor Plan of Reprocessing Building.

signals, and the chemical makeup area, all of which are conveniently located on the floor above.

The control room is beneath the transmitter equipment room and adjoins the pipe-access area. The cells, the pipe access area, the control room, the cell operating area, and the decontamination area are integral and isolated from the rest of the building.

The hot area of the building is always entered from the cold area through the change room; exit from the hot area is always, except for controlled emergency exits, through the change area.

7.2 SUPPORTING AREAS AND FACILITIES

The ground floor of the main building has a machine shop, receiving area, hot change room, laboratories, electrical switchgear room, and a manipulator and instrument repair shop in support of the main operating areas.

The first floor of the main building (Fig. 14) houses the cold makeup area, transmitter area, sample area, hot analytical facility and filter room.

With these facilities, the PCUT plant constitutes a self-sufficient complex capable of performing all operations necessary to reprocess and refabricate fuel assemblies.

7.3 HEATING AND VENTILATION

The plant is ventilated by three separate systems: one services the areas where hot phases of the process are carried out, one the potentially contaminated (warm) areas of the processing building, and the third the cold area or office wing.

Fig. 14. First Floor Plan of Reprocessing Building.

The hot system supplies 16,000 cfm of air through roughing filters and steam coils. This air is distributed through three flow paths as follows:

- (1) 8000 cfm to the corridor area and warm cell.
- (2) 2400 cfm to the decontamination area and hot cell.
- (3) 5700 cfm to the receiving and service areas.

Pressure differentials are maintained so that the flow of air is always from the colder to the hotter areas. Room pressures range from negative pressures of 20–25 mm water for the hot and warm cell to positive pressures of 0–25 mm water for the machine shop.

Some of the air is exhausted directly to the filter and stack system; the remainder (7400 cfm) is exhausted through the hot cell and warm cell which are maintained at the lowest pressure level. All the exhausted air of this system (17,100 cfm) is discharged through an absolute filter system to a 200-ft stack.

The warm system supplies 30,000 cfm of air through roughing filters and steam coils to the control room, cell operating areas and the various support areas.

Pressure differentials are maintained so that the flow of air is always from the cold areas to the potentially hot or warm areas. Room pressures range from negative pressures of 5–7 mm water for the hot analytical facility room to positive pressures of 0–2.5 mm water for the control room.

Air from this system is discharged through high efficiency filters to a short exhaust port on the roof.

Quick closing dampers on the inlet ducts of both systems and on the outlet duct of the warm system prevent the release of excessive activity to the atmosphere. These shutoff dampers, together with visible and audible evacuation alarms, are actuated by (1) high activity levels on monitors on the exhaust duct of the warm system and (2) reversal of normal pressure differentials between the hot and cold areas of the plant.

The cold system services the office wing of the building and supplies filtered and tempered air to the various office areas. Air from this system is discharged through roof ventilators.

8. DEVELOPMENT PROGRAM

8.1 EXTRUSION DEVELOPMENT

An extrusion development program has been completed at the Greendale laboratories of Allis-Chalmers which demonstrated the feasibility of extruding fuel pellets, which can be sintered to greater than 93 per cent of theoretical maximum density. The sintered density and diameter are sufficiently reproducible to ensure a low recycle ratio, and the sintered straightness is good enough to permit surface grinding to meet fuel pellet diametral tolerances. These results have been obtained without adding bentonite to the extrusion clay. An extension of the extrusion work is still in progress at the Ceramic Technologies Laboratories of the Materials Division of CNEN. These studies are providing further verification of the Greendale work and are aimed at additional reproducibility and surface grinding studies.

8.2 ITALIAN APPLIED RESEARCH

Two processes for the coprecipitation of uranium and thorium have been developed by the scientists of the Materials Division of CNEN in the course of their work on behalf of the PCUT program. These are discussed below.

8.2.1 NH₃-Oxalate Coprecipitation Process

The first process successfully used for the coprecipitation of uranium and thorium from nitrate solutions employed both oxalic acid and ammonia as precipitating agents. A 10-per cent stoichiometric defect of oxalic acid was used to precipitate most of the thorium as the oxalate. Ammonia gas was then added to adjust the pH of the final slurry to between 5.9 and 6.2, which precipitates the balance of the thorium as thorium hydroxide and the uranium as ammonium diuranate.

Losses to the supernate using this process are low once equilibrium is established in the continuous precipitator. Uranium losses during startup were high due to the solubility of U⁺⁶ oxalate and a uranyl-ammonia oxalate complex ion formation. Although the startup losses were not prohibitively high, further work on this process was discontinued after development of the catalytic reduction and oxalate coprecipitation process.

8.2.2 Uranium Reduction to U⁺⁴ and Oxalate Coprecipitation

The U⁺⁶ oxalate is slightly soluble in nitric acid solutions, while the U⁺⁴ oxalate is insoluble. Therefore, in order to quantitatively coprecipitate uranium and thorium from nitrate solutions with oxalic acid alone, the uranium must be in the +4 valence state. Development work during the PCUT program has demonstrated that this reduction can be accomplished

conveniently by catalytic hydrogenation (see Fig. 15). In a continuous plant, uranyl nitrate solutions can be catalytically hydrogenated in two ways: (1) by employing gaseous hydrogen under a pressure of 5–30 atm or (2) by evolving the hydrogen in the solution itself by decomposition of formic acid previously added to the solution. For simplicity and safety the latter method was chosen for use in the plant.

8.3 FUTURE WORK

Fuel from the first core of the Elk River reactor will be recycled to the reactor after reprocessing and refabrication in the PCUT facility; therefore, it is desirable to perform an irradiation proof-test using an assembly fabricated by the PCUT reference process. This test, conducted in a boiling water reactor, will confirm the adequacy of the fuel design and the process for refabrication of the fuel.

Like the first core loading of the Elk River reactor, the test elements in the test assembly will be clad in stainless steel. However, neutron economy is a prime requisite for reactors operating on the thorium cycle; therefore, several of the rods in the test assembly will be clad with Zircaloy to provide the basis for a refabrication process based upon Zircaloy cladding.

The irradiation tests will be designed for burnup of approximately 10,000 Mwd/MT with test specimens examined at intermediate burnup levels of 5000 and 7500 Mwd/MT. The tests will yield the following information:

- (1) Both absolute quantities and calculated percentages of release of the fission gases generated.

Fig. 15. Reduction and Precipitation Flowsheet.

(2) Dimensional behavior as determined by before-and-after measurements of the extruded and sintered fuel bodies and the fuel rods.

(3) Mechanical condition of the fuel after irradiation.

(4) A comparison with pellets by using pelletized fuel in the experiment as a standard.

A fuel assembly containing extruded and sintered urania-enriched thoria fuel will be irradiated in the VBWR. The mixed oxide powder, the extrusions, the fuel rods, and the fuel assembly will be manufactured in the fuel laboratory of the Greendale laboratories of Allis-Chalmers. This irradiation program is scheduled for completion in October of 1964.

9. CONSTRUCTION STATUS

Detailed design of the PCUT has been essentially completed by Allis-Chalmers and its subcontractor, the Blaw-Know Company. The remaining detailed design work which was considered to be best performed in Italy is in progress. Procurement has started in the United States and Italy for certain long delivery items. A civil contractor has been chosen by CNEN and a site near the town of Policoro in the south of Italy is being prepared. Startup is scheduled for July of 1964.

10. APPLICATION OF THE PCUT PLANT CONCEPT TO LARGER BOILING-WATER REACTORS

Preliminary studies have been made of a scaled-up version of the PCUT plant which would be capable of reprocessing the spent fuel from one or two 300-Mwe boiling-water nuclear power plants on the same site as the reprocessing plant. The fuel cycle costs of such an integrated station with the thorium cycle were shown to be lower than that of a similar reactor operating on low enrichment uranium with the spent fuel returned to the AEC.

10.1 PLANT AND PROCESS ECONOMICS

The net electrical capacity is an important consideration in the economics of the integrated station, and especially in its effect on the unit costs of the fuel processing and refabrication facility. The tendency in the past has been to think in terms of large central reprocessing plants because unit processing costs are conventionally reduced as capacity increases. However, this is true only if there is a market for the reprocessing service, and if all the fuel reprocessed is the same. Note, for example, that a reprocessing plant with a capacity of 1 ton/day, which is quite small compared to weapons-material reprocessing plants, could process the fuel from 25 reactors the size of Dresden. This reveals a rather severe market limitation on the scale of reprocessing plants. What is needed is a small plant requiring relatively small capital investment, in which fuel can be processed at a cost low enough to result in competitive nuclear power. How, then will it be possible to offset the lower unit processing costs offered by large scale plants so as to achieve the desired economy in our integrated station?

The answer is that in the integrated reprocessing station (1) some reprocessing costs associated with central uranium plants are eliminated, (2) some are reduced, and (3) some are independent of plant capacity.

10.1.1 Eliminated Costs

The small integrated plant essentially eliminates all shipping costs as well as the costs of conversion of UF_6 to UNH_3 , the conversion of UNH_3 to UF_6 , and the conversion of plutonium nitrate to metal. The U. S. Atomic Energy Commission will furnish to industry uranium in the form of UF_6 only and the credits for returned fissionable material are based on uranium as UF_6 or on plutonium as metal.

10.1.2 Reduced Costs

In addition to the costs eliminated completely, the processing steps remaining are simplified so that the effect of low capacity is less important. For instance, rather than three cycles of solvent extraction to obtain full fission-product decontamination, only one cycle is used. The resulting increase in the fission-product radioactivity that must be handled during the fuel manufacturing steps does not increase equipment or operating costs because remote fabrication is required in any case due to the activity associated with the heavy-metal isotopes in spent fuel, such as U-232 and its decay products in the thorium cycle. Thus the presence of a comparable fission-product background is no penalty. Figure 16 shows the principal nuclear reactions associated with the thorium cycle and illustrates the presence of these heavy-metal isotopes.

PRIMARY NUCLEAR REACTIONS

FORMATION OF URANIUM-232

DECAY OF URANIUM-232

Fig. 16. Principal Nuclear Reactions Associated with the Thorium Cycle.

The design of the plant to serve a single reactor also results in a significant saving. Clearly, a large central plant, even a 1 ton/day plant, would have to be designed for several different types of fuel. It is probable that if it were sized for 25 reactors it would have to handle 25 different fuel assemblies. This requires a multiplicity of head-end and dissolving facilities, which, because of the high activity, are the most expensive.

A more subtle but nonetheless important cost saving in the small plant results from the lower rate of return required of the invested capital. Since the plant has a guaranteed market for the life of the reactor, the capital investment in the processing plant need only be returned at the rate of the reactor itself, rather than at a rate of approximately twice this, which would be reasonable for an independent central processing plant.

Finally, according to recent estimates the utilities and services which must be provided account for in the neighborhood of 25 per cent of the cost of processing in a 1000-kg/day plant. In a small plant, erected on its own site, these services would represent an even larger fraction of the total. However, in an integrated station consisting of even one 300-Mwe reactor, the incremental costs for utilities (roads, fences, parking lot, personnel, shipping and receiving, health physics, guards, radiation monitoring, etc.) are very low. These services are provided at a unit cost determined by the total investment on the station site and not by the cost of the processing facility alone.

10.1.3 Cost Independent of Plant Capacity

The major cost of the reprocessing cycle is not the chemical processing itself, but the refabrication of the fuel assemblies. Where the cost of chemical processing in a

1 ton/day plant might be \$17/kg, the cost of fabrication of the fuel assemblies might be \$100/kg. But this cost is not strongly influenced by the capacity. The fabrication of the fuel assemblies is a piece-work job requiring jigs and fixtures and trained personnel, and the fabrication capacity of a plant can only be doubled by doubling the equipment and personnel. Moreover, with zirconium-clad fuel, a large share of the fabrication cost is the cost of the cladding itself.

It should be emphasized that the construction of a facility of whatever capacity, that processes the fuel chemically but does not refabricate the recovered fissionable materials into useful fuel assemblies, would be to concentrate on only a small portion of the total problem. Such an approach does little to remove the present uncertainties from the fuel cycle.

10.2 NUCLEAR CONSIDERATIONS

The foregoing economic argument is independent of the choice of fuel material, and the power plant and reprocessing station are designed for operation with either thorium-uranium or low enrichment uranium fuel. The various combinations of uranium and thorium systems entailing recycle of one or more core constituents and the uranium system without recycle are compared functionally in Fig. 17. However, it is believed that the attractive nuclear characteristics of the thorium-uranium cycle dictate its preference in the integrated station.

The economic advantages of thorium-bearing fuels result from the nuclear difference between the thorium-uranium and the uranium-plutonium systems and depend upon a realistic evaluation of unsubsidized fuel-cycle costs.

URANIUM with Pu RECYCLE

URANIUM with U and Pu RECYCLE

URANIUM without RECYCLE

THORIUM with RECYCLE

Fig. 17. Nuclear Fuel Supply Systems.

According to the present rules, the fissionable material in the spent fuel from either system can be returned to the AEC for a credit. However, since there is no important use for this material other than as a reactor fuel, the development of a viable nuclear power industry must be based on reclamation of fissionable material for use in reactors. In a true reactor economy, the important question is not the dollar value of the bred material, but the nuclear value of the material and the costs of its recovery and reuse in the same or a similar reactor. In short, the AEC's quoted prices for returned spent fuel should be considered as a temporary measure that will not be important when fuel is recycled.

Thus, the early development of economical reactor-fuel reprocessing techniques is essential to any nuclear power development program; and in a nuclear power economy based on reprocessed fuels and thermal reactors, the thorium-uranium system, with its unique ability to produce U-233, enjoys a considerable advantage over the uranium-plutonium system.

Since the number of neutrons generated per absorption in U-233 is 10 per cent higher than in U-235, and about 20 per cent higher than in PU-239 (Fig. 18), it can be shown that a thorium cycle, in which a significant proportion of fissions occurred in U-233, could result in a two-fold savings in burnup costs and thus in a significant reduction in the net cost of power. In a carefully designed reactor operating on the thorium cycle, eventually approximately 80 per cent of the fissions will occur in U-233.

Fig. 18. Eta vs Energy for U-233, U-235, and Pu-239.

The recycle streams in an equilibrium thorium system are shown in Fig. 19. Note that the makeup material is largely thorium; in fact, the net fuel requirement is about 80 per cent thorium and only 20 per cent U-235. Plutonium can be used as the fissionable-material makeup instead of the U-235 shown in Fig. 17 without significantly effecting the economics of the system. This marked reduction in uranium or plutonium makeup requirement, and hence in burnup cost, is the reason that the thorium cycle is preferred for the integrated station.

11. CONCLUSION

The plant design which has been described departs in three ways from that of existing radiochemical plants. First, since the full-scale plant will be only 3 to 5 times as large as the PCUT pilot plant, it is possible to rely on geometric criticality control in both the pilot plant and the full-scale plant. The small size of the full-scale plant also permits a maintenance and service technique based on rack-mounted units with quick-disconnect couplings.

The second major departure from conventional radiochemical processing technology is the integration of fuel recovery and refabrication operations. If the fuel is to be recycled, the advantage of this integration seems obvious. Separation of these functions would only be sensible if a large-capacity plant were required.

The third departure from conventional design results from the less severe requirements for fission-product decontamination of the process materials. In either the plutonium or the thorium cycle, remote fabrication is required owing to alpha activity. In the

Fig. 19. Equilibrium Recycle Streams in the Thorium Cycle.

thorium cycle, additional protection against gammas from U-232 is necessary. Thus, since remote fabrication is necessary in any case, there is no need to remove all fission products from the fuel material. This permits a considerable simplification in the process and plant design.

In existing plants spent fuel material would be put through three solvent extraction cycles to remove nearly all fission-product activity and fresh fuel would be fabricated by direct manipulation in glove boxes. In the PCUT plant, only one solvent extraction cycle is used, and the fresh fuel is fabricated in a shielded warm cell. Even if the warm cell were shown to be more expensive to construct than a series of glove boxes, the use of one extraction cycle rather than three would permit an enormous simplification and economy in the design and operation of the plant. If, as is suspected, the cost difference between a warm cell and a glove box line is not significant, the advantage of a single solvent extraction cycle is obvious.

The construction and operation of the PCUT pilot plant will be the clearest demonstration of the advantages of both the thorium fuel cycle, and small-plant reprocessing techniques. CNEN and Allis-Chalmers are pursuing this project in the belief that it will be an important contribution to the achievement of competitive nuclear power.

Session III
Paper 15

THE THORIUM FUEL CYCLE DEVELOPMENT FACILITY CONCEPTUAL DESIGN

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THE THORIUM FUEL CYCLE DEVELOPMENT FACILITY CONCEPTUAL DESIGN

By

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A conceptual design for a Thorium Fuel Cycle Development Facility (TFCDF) has been completed by Giffels and Rossetti, Inc., of Detroit, Michigan, with criteria and project direction being provided by Oak Ridge National Laboratory. Final design and construction has not yet been funded.

The TFCDF is designed to provide a versatile, integrated facility for development of all phases of the thorium fuel cycle. The fuel types that were considered in the development of criteria were oxide and carbide; however, other fuels such as alloys, dispersions, and beryllides could be accommodated. The two fuel elements that were considered for the establishment of criteria were the ones to be used in the Consolidated Edison Thorium Reactor and the High Temperature Gas-Cooled Reactor, thus providing consideration of the most difficult cases. Because this facility is to be used for development and not for production, capacity figures are not especially significant, as the capacity will be a function of the complexity of the process and the design of the production equipment. It is thought that 35 kg/day could rather easily be processed and refabricated in a facility of this size.

The facility is to be capable of processing and refabrication of fuel assemblies having maximum lengths of 12 ft and which have decayed for 90 days. Shielding is to be sufficient to permit refabrication of fuel which has undergone little or no decontamination. Normal source size will be limited to 35 kg irradiated to 25,000

Mwd/tonne; however, larger sources could be handled without overexposure of personnel to radiation. The desirability of a heavily shielded fuel cycle facility for either experimental or production purposes derives from two factors. The first point is that the material to be refabricated will to an appreciable degree be radioactive and will require confinement in a closed, sealed, and shielded space; in addition, operations on a significant scale will most probably be carried out by automatic equipment or by use of manipulators. The second point is that no doubt some saving can be made in capital expenditure for, and operating cost of, re-processing equipment by a reduction in decontamination requirement. Instead of using a high decontamination, multi-cycle process, some simpler single cycle process yielding relatively low decontamination factors could be substituted. Because both capital cost of the shielded space and operating cost for the fabrication equipment will obviously not be strongly influenced by reasonable shield thickness, it is apparent that a heavily shielded facility can quite possibly yield an overall fuel cycle cost lower than can a facility with shielding adequate only for the U^{232} decay products at short times after complete decontamination.

To accomplish the objectives, four operating cells and two service cells will be required. The first floor plan of the building is shown in Fig. 1. The four operating cells are arranged in a line with one of the service cells, which is to be used for decontamination and as a radiation lock, teeing off from the line at the point where the two large central cells join. Another service cell, to be used for storage of contaminated equipment, is located at the basement level and joins the Decontamination Cell via a hatch in the Decontamination Cell floor. Excepting the Storage

Fig. 1. First floor plan-thorium fuel cycle development facility.

Cell, each cell is to have the equivalent of 5-1/2 ft of normal concrete up to the 12-ft level and 4-1/2 ft for the remaining portions. The Storage Cell will have 1-1/2 ft of normal concrete shielding. The four operating cells are to be used for chemical processing, mechanical operations incident to irradiated fuel recovery and to reconstitution of fissile and fertile materials into forms suitable for use in fuel element manufacture, fabrication operations through the point at which fissile and fertile material is contained in fuel elements, and final fabrication operations such as inspection and assembly.

All operating cells will have a common roof line; however, the floor level will vary to provide different inside cell heights (Fig. 2). The Chemical Cell will be 30 ft deep, the Mechanical Processing Cell 18 ft, the Contaminated Fabrication Cell 18 ft with a 6-ft-deep pit provided in one 16 x 20-ft area, and the Clean Fabrication Cell will be 24 ft deep. An area concept somewhat akin to that used in the Sandia Engineering Reactor Facility¹ is being used here. The individual cells, or areas, are rather large, varying in size from 16 x 20 ft for the Chemical and Clean Fabrication Cells to 41 x 20 ft for the Contaminated Fabrication Cell. This arrangement will permit easy integration of equipment and will allow replacement and transfer of equipment with a minimum of difficulty.

Five of the six cells either are, or can be, maintained entirely by remote devices (Fig. 3). The Clean Fabrication Cell is the exception because it is to receive fuels only after they are encapsulated in tubes or other containers. In this cell the

¹ J. L. Cole, "Hot Area Concept for Radiation Test Facilities," Proceedings of Eighth Conference on Hot Laboratories and Equipment.

Fig. 2. Elevation of operating cells.

Fig. 3. Cell maintenance method.

installation and repair of equipment will be accomplished by contact methods. Either remote or contact maintenance may be used in the Chemical Cell. A doorway and shielding is to be provided such that it can be either isolated from or joined with the Mechanical Processing Cell. If the door is open and the shielding removed, the overhead crane and mechanical arm bridges can enter the Chemical Cell and large objects can be transferred in and out.

The lifeline of the cell complex is the transportation system. This consists of a pair of overhead bridge cranes which can travel over essentially all the area in the Glove Maintenance Room, Decontamination, Contaminated Fabrication, Mechanical Processing, and Chemical Cells (Fig. 4). A special transfer bridge system is to be provided in the Decontamination Cell which can move in three planes and which will provide for easy movement of a hoist from one area to another and will also allow removal of the operating cell bridges to the Glove Maintenance Room for repair. All moving parts of the crane system located in the operating cells can be removed by remote means for maintenance. The special transfer bridge system located in the Decontamination Cell may require contact maintenance. This should not be a great disadvantage because maintenance requirements should be low and this cell will not house large sources or items of process equipment other than on a transient basis. Cranes are also provided for the Clean Fabrication Cell and the Storage Cell. The Clean Fabrication Cell bridge and hoist can be lifted from the cell into the cell roof area for maintenance. The Storage Cell hoist can be removed into the Decontamination Cell and Glove Maintenance Room for repair.

Three bridge-mounted mechanical arms will be provided for the cell complex.

Fig. 4. Cell bridge crane system.

Two of these will operate in the Contaminated Fabrication, Mechanical Processing, Chemical, and Decontamination Cells. The third unit will operate in the Clean Fabrication Cell. All units will be mounted for ready removal to a maintenance area.

The operating cells and the Decontamination Cell are laid out on a modular pattern of approximately 8 x 10 ft. Figure 5 is a view of a typical space within the shielded area.

With some exceptions, each module is provided with a window liner, holes for master-slave manipulators, five 1-in. stainless steel pipes leading to the service area, ten bent-tube service access sleeves and three stepped plugs for passage of replaceable service lines, two 1500-watt iodine-quartz lamps, plus a number of precisely located foundation pads in the floor for mounting of equipment. At alternate modules, stations are provided for waste collection, hot off-gases, and future periscope installation. Windows and manipulators will be provided for approximately half the window liners and manipulator holes and the remaining ones will be plugged because it appears that there will be no need for this number of windows and manipulators in the initial phases of operation. The floors, walls, and ceilings of the Chemical, Mechanical Processing, and Contaminated Fabrication Cells are to be lined with stainless steel.

The remotely maintained portion of the cell complex is to be exceptionally well sealed in order to adequately confine radioactive materials and to allow for future conversion to an inert atmosphere. All openings, whether they are for viewing windows, doors, or service access, will be tightly sealed. This seal is to be maintained at all times. In order to maintain a constant seal, somewhat special designs are being used for windows, service access sleeves, manipulators, and other devices.

Fig. 5. Typical cell module.

The window will consist of two major assemblies (Fig. 6): a seal glass removable from inside the cell, and a shielding window removable from the nonradioactive side. The window will be a composite unit consisting of approximately 6 in. of glass and 60 in. of zinc bromide solution. Normally there will be two, or possibly three, gas seals present to ensure zero leakage of gas between the radioactive and nonradioactive sides of the window. Only one of these seals is a part of the inner seal glass assembly. Hence, either the inner or outer assembly can be removed without breaking the seal on the cell.

The service access sleeves will be of two types: the bent-tube and the stepped plug (Figs. 7 and 8). The bent-tube unit is to carry replaceable service lines from the third floor or cell roof area to the cell modules, while the stepped plugs lead from the first floor operating area to the cell space. Both of these devices are so contrived that the part which is subject to becoming contaminated is fitted with a seal and is drawn into the cell when it is to be replaced. The outer portions of the units are pulled back into the operating area at this time and new assemblies, consisting of both inner and outer portions, are inserted into the hole. As the new assembly is inserted, the old inner subassembly is either pushed or pulled into the cell.

The master-slave manipulators for the remotely maintained cells are to be sealed. They are to be equal to the Model A manipulator manufactured by Central Research Laboratories.

The cell system has a number of points of access (Fig. 9); they are:

1. Through air lock and glove maintenance room.
2. Solid sample withdrawal port on roof of cell.

Fig. 6. Composite window concept.

Fig. 7. Bent tube service access.

Fig. 8. Push-thru stepped service access plug.

Fig. 9. Points of cell access.

3. Liquid sample withdrawal from Chemical Cell at second floor level.
4. Entry points for small objects at operating floor level.
5. Transfer ports in roof.
6. Transfer ports in intercell walls.
7. Tunnel from Fuel Storage Basin to Decontamination Cell.

The air lock can accept objects up to 6-1/2 ft in any dimension. Objects weighing up to 50 tons may be lowered onto a transfer car in the air lock and transferred into the Decontamination Cell via the Glove Maintenance Room.

The building will provide space for operating areas, service equipment, offices, change rooms, small development laboratories, and an equipment receiving area. A 50-ton crane with 5-ton auxiliary will provide transportation for heavy objects from the receiving area to the crane bay and into the Fuel Storage Basin. A 3-ton elevator will carry casks and other small objects between the first and third floors.

Air will enter the building through the offices and first floor operating areas and will pass sequentially through areas of higher potential contamination. Backflow dampers will be provided between building areas of different contamination potential. More effective anti-backflow devices and high-efficiency filters will be provided in the air ducts leading from the building into the cells. Temperature control will be maintained in the various personnel-occupied areas by means of unit heaters and coolers equipped with roughing and high-efficiency filters. Temperature gain in the cells will be limited by varying the air flow. A portion of the building ventilation air is discharged directly to the atmosphere via high-efficiency filters and the remainder is drawn into the cells. Cell exhaust air is filtered by two roughing filters

and two high-efficiency filters in series. Provisions are to be made for future installation of charcoal absorbers for iodine.

Liquid wastes leaving the building will be monitored in temporary storage tanks, from which they will be routed either to the environment or to the appropriate ORNL plant waste treatment system. No permanent storage for radioactive waste is provided by this project.

The cost of this facility is estimated to be $\sim \$6 \times 10^6$ exclusive of process equipment but inclusive of manipulators, remote cranes, viewing windows, design, and inspection.

Session III
Paper 16

THE OAK RIDGE NATIONAL LABORATORY KILOROD FACILITY

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THE OAK RIDGE NATIONAL LABORATORY KILOROD FACILITY

ABSTRACT

The Oak Ridge National Laboratory (ORNL) Kilorod Facility was designed to provide space and equipment for performing chemical processing and fabrication operations involving U^{233} and thorium. Existing facilities were extensively modified and revised to provide an improved system for solvent extraction. An existing cell was used as secondary containment for shielded cubicles which contain feed preparation and fabrication operations. The facility provides equipment for solvent extraction, for preparation of U^{233} -thorium oxide by the sol-gel technique, for loading the oxide in tubes by vibratory compaction, and for closure and inspection of the loaded fuel tubes.

The facility was designed specifically for fabrication of fuel rods, approximately 1/2 in. in diameter and 46 in. long, having Zircaloy-2 cladding and each containing 890 g of (3 wt % U^{233} -97 wt % Th) oxide, but it has sufficient flexibility to allow general development work on a pilot plant scale.

Construction of the facility is complete, and the process equipment is now being installed.

I. INTRODUCTION

Construction is now complete on the ORNL Kilorod Facility which provides space for performing chemical processing and fabrication operations involving U^{233} and thorium. Equipment for accomplishing the various operations has been designed and constructed and is now being installed in the facility. The Kilorod Facility is to be an integral part of the ORNL fuel cycle program and will enable an extension of thorium fuel cycle technology by providing valuable processing and fabrication experience as well as data on radiation attending the handling of U^{233} .

Although the facility has sufficient flexibility to accommodate a variety of work, it was specifically designed to handle the chemical processing, fuel preparation, and fabrication steps for making fuel rods that are to be used in criticality, zero power experiments at Brookhaven National Laboratory (BNL). Approximately 900 rods, each containing 890 g of (3 wt % U^{233} —97 wt % Th) oxide, and 200 rods, each containing 310 g of the same oxide, are to be fabricated. The facility is designed to process approximately 10 rods per day.

This paper, which describes the development of the facility, is divided into three main sections. These consist of a discussion of solvent extraction, solids preparation and rod fabrication, and the calculations and predictions for the radiation dose rates to be encountered in the process.

II. SOLVENT EXTRACTION

The solvent extraction purification process to be used for the removal of U^{232} decay products and ionic contaminants consists of feed preparation, one cycle of solvent extraction using 2.5% di-secondary butyl phenyl phosphonate (DSBPP) in diethyl benzene as the extractant followed by product concentration by evaporation. Existing solvent extraction equipment has been modified to provide an improved system.

The uranium supplied to the facility will consist of uranyl nitrate solutions of varying concentrations and massive metal fragments (Fig. 1). Dissolution of the fragments will be accomplished in a boiling mixture of 1.4 M thorium nitrate solution containing 4 moles of free nitric acid per liter. A total mass of 4 kg of U^{233} metal will be charged to the batch dissolver vessel during one dissolution cycle. Criticality control in the geometrically unsafe tank will be assured by (1) the presence of thorium which will give a U^{233}/Th ratio of 0.025 and (2) maintaining the volume in the dissolver vessel such that the eversafe concentration of U^{233} in light water

Fig. 1. Kilorod Feed Preparation Flowsheet.

may never be exceeded. The dissolution of each 4-kg batch will be done at 108°C and is expected to be complete after 24 hr. The resulting solution will then be adjusted to terminal feed conditions by dilution with water. The procedure employing uranyl nitrate solution as a feed material will consist of the blending of this solution, in small increments, with existing 400 g/liter thorium nitrate solution.

The flowsheet selected (Fig. 2) for the uranium purification program utilizes a battery of three pulse columns placed in series. Each run, made on a three-week cycle, will provide 5 kg of purified U^{233} which has been decontaminated from both the U^{232} decay product γ activity and the thorium in the feed solution by a factor of 10^4 . This separation factor represents a factor of 4 greater than that expected from a similar system employing tributyl phosphate (TBP) as the extractant.

Feed from the adjustment tank is pumped into the top section of a 38-ft by 5-in.-diam pulse column. The extractant containing 2.5% DSBPP in a diethyl benzene diluent will extract the uranium into the organic phase. The extract is then scrubbed in a second column with a 0.8 M aluminum nitrate solution which is acid deficient ($-0.4 \text{ M } H^+$) to remove entrained thorium and ionic contamination. The aqueous raffinate from the scrub column is then diverted into the top of the extraction column and is eventually routed to storage. The scrubbed organic then cascades to a strip column wherein the uranium is removed from the organic phase with water containing a trace amount of nitric acid (0.005 M). The uranium product solution, containing 10 g/liter U^{233} is then transferred through a static diluent wash column for the removal of trace quantities of organic prior to solution buildown. Final concentration to 100 g/liter is accomplished in a critically safe evaporator vessel. The tail-end product is then withdrawn from the evaporator product storage tank as required

Fig. 2. Kilorod U²³³ Purification Flowsheet.

by the sol-gel process. Spent solvent leaving the process is collected batchwise, treated with 0.2 M Na_2CO_3 , and reused.

The majority of the vessels to be used for chemical processing are not of critically safe geometry; consequently, several important operational and equipment modifications have been made. The total mass of uranium within the facility will not exceed 5 ± 0.5 kg. Solutions will be maintained below the U^{233} ever-safe value of < 10 g/liter by flowrate adjustments for aqueous streams and chemical saturation of organic streams. The only stream which will exceed this value will be the tail-end product stream (100 g/liter), which will be boiled down in a critically safe evaporator consisting of a 5-in.-diam pipe surrounded by a 6-in.-diam steam jacket.

In addition to mass and concentration control, the feed extraction column and raffinate catch tanks will contain sufficient thorium to yield a U^{233}/Th ratio of 0.025. The thorium also serves as an extraction salting agent.

As a final safety device, Pyrex glass rings containing 4% B have been placed in critical process vessels. Nuclear hazards exist in the expanded 8 to 16-in. sections of the pulse column disengaging sections and in large-diameter vessels. These sections and vessels were packed with rings and an x-ray procedure was developed to ascertain periodically the location and condition of the rings.

III. SOLIDS PREPARATION AND ROD FABRICATION

The oxide preparation and rod fabrication steps will be accomplished in shielded, alpha-tight cubicles which are shown in Fig. 3. The cubicles are installed in a 20-ft long $\times$ 19-ft wide $\times$ 27-ft high chemical processing cell (Cell 4) which is being used for secondary containment of radioactivity which might escape from the cubicles. Operation will be accomplished by gloved hands or manipulator tongs.

Fig. 3. Solids Preparation and Rod Fabrication Facility.

Solids Preparation

The oxide will be prepared by the sol-gel technique.¹ The sol-gel preparation equipment is housed in a sealed carbon steel cubicle approximately 9 ft long $\times$ 7 ft wide $\times$ 7 ft high, having 8 windows, 10 glove ports, and 3 transfer ports. This cubicle is located on the third floor of Cell 4. Shielding is provided on the sides by 8 in. of barytes concrete or 4 1/2 in. of steel and on the floor by a 4 1/2-in.-thick steel slab. The top and back of the sol-gel cubicle adjoin a 4-ft-thick concrete slab. Means are provided in the cubicle whereby the furnace, blending pump, and other vulnerable parts may be maintained either through glove ports or by direct entry using a plastic tunnel airtight.

The process to be carried out in this cubicle consists of preparation of a thorium sol by addition of thorium powder to water in a blend tank, sorption of uranyl nitrate by the sol, drying of the sol to form a gel, which is calcined to form hard oxide particles of uniform composition and near theoretical density.

A description of the equipment and operations involved in achieving this product follows.

Blend Tank. The blend tank, shown in Fig. 4, is of slab-type construction, 1 3/4 in. thick $\times$ 40 in. wide at the top, and has a capacity of 31 liters. A centrifugal pump is provided to produce a mixing action in the tank by recirculating solution from the bottom of the tank to a side inlet. Thorium powder is admitted through an inlet at the top and uranyl nitrate is introduced through a tube at the top of the vessel. Sight glasses are provided on one side for observation of the qualitative condition of the material in the tank.

Uranyl Nitrate Measuring Tank. The measuring tank consists of a constant diameter 2-in. glass pipe approximately 5 ft long. Measurement of liquid level is by visual means through a shielded window in the cubicle and is aided by

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Fig. 4. Solids Preparation Cubicle, North and West Sides.

use of a cathetometer. Fluid is transferred into this vessel from the solvent extraction area by means of a small blowcase system and is transferred out by using the vessel as its own blowcase.

Tray Drier. This unit, shown in Fig. 5, consists of eight shallow trays installed inside a box through which warm air is slowly passed. The trays are made of stainless steel and are 1 in. deep by 24 in. square. Four trays will hold one batch of sol. Filling of the trays is accomplished by adding sol to the top tray only; when the level reaches the prescribed point in the top tray, it overflows through a downspout into the tray below and so on down until the entire charge from the blend tank has been emptied into the drier. Two days are allowed for drying each batch. The exit air is drawn through a cooler, where it is dehumidified, and then is discharged into the building vessel off-gas system.

Dry-Gel Transfer from Drier to Calciner. A lift table is provided that is positioned in front of the drier and to one side of the tray dumper. The table elevation can be varied to match the elevation of any tray in the drier as well as the elevation of an opening in the side of the tray dumper. The tray dumper consists of (1) a device to receive, hold, and invert one tray at a time, (2) a housing to prevent spread of dust when the tray is emptied, and (3) a funnel-like chamber at the bottom to direct the tray contents into a calcining crucible which is in contact with a bottom opening. (See Fig. 6.) One crucible can hold the dried contents of two trays or 1/2 batch. The crucibles are moved manually along a stationary table to a point in front of the calciner where they are placed on a small dolly and inserted into the calciner cavity.

Calciner. The calciner is a modification of a standard, metal resistor-type furnace. The modifications provide for water jacketing to prevent excessive heating of the cubicle, intermittent air cooling to provide a faster cooling

Fig. 5. Tray Drier for the Sol-Gel Process.

Fig. 6. Solids Preparation Cubicle, West and South Sides.

cycle, and a modified door suited to operations that must be made at arm's length and with the aid of tongs, etc. It has a $5\frac{1}{2} \times 7\frac{5}{8} \times 14\frac{1}{2}$ -in. cavity. The air cooling is accomplished by means of metal tubes which pass near the heated cavity. The resistors can be removed and replaced via gloved access without violating the cubicle containment.

Final Transfer and Weighing. The cooled crucible is removed from the calciner by the small lift dolly and placed on a weigh cell. After the weight is determined, the contents are dumped by means of the device shown in Fig. 6 into a storage hopper and pipe which lead to the particle sizing equipment below. The crucible dumper consists of a rubber-gasketed flange which fits against the crucible top, a flexible boot that extends between the entry flange and the tube leading to the equipment below, and a clamping and tilting device to hold the crucible during the dumping operations. The dumper is equipped with a screen which precludes the charging to the particle sizing equipment of particles having any two dimensions greater than $\frac{1}{2}$ in.

Rod Fabrication

The design of most of the fabrication equipment has been greatly influenced by the configuration of the BNL fuel rod which is shown in Fig. 7. As indicated, 890 g of (3 wt % U^{233} -97 wt % Th) oxide are contained in a Zircaloy-2 tube. The U^{233} to be used contains nominally 40 ppm U^{232} . The cone-shaped bottom fitting serves to locate the rods in the critical lattice and the top end fitting supports the rods in the lattice and provides a lifting lug by which the rods may be handled. The compression spring and ceramic spacer, shown in the void volume at the top of the fuel column, prevents fuel redistribution if the rods are inverted in handling. In addition to these 46-in. long rods, 18-in. long fuel rods otherwise identical in design will be fabricated.

Fig. '7. Design Features of the Brookhaven National Laboratory Fuel Rod.

The procedures employed to fabricate these fuel rods include (1) sizing the $\text{UO}_2\text{-ThO}_2$ received from the solids preparation facility into an optimum particle-size distribution for vibratory compaction; (2) vibratory compaction; (3) welding of the final end closure; (4) fuel rod decontamination; and (5) fuel rod inspection.

The optimum size distribution for $\text{UO}_2\text{-ThO}_2$ produced by the sol-gel process consists of a mixture of three size fractions: a coarse fraction, a fine fraction, and an intermediate fraction. As seen in the flow diagram, Fig. 8, these fractions are produced from the as-received oxide by a system of crushing, classifying, and ball milling. Following comminution and classification of the bulk fuel into the three working fractions, quantities of each fraction appropriate to one fuel rod loading will be apportioned and blended together.

In the vibratory compaction operation, the blended aliquot of fuel is loaded into a fuel tube, which contains one end plug, and vibrated to the specified density. This loaded fuel tube is transferred to a welding fixture where the final end closure weld is made and visually inspected.

At this juncture, the loaded and sealed fuel rod is decontaminated by ultrasonic cleaning in water and smeared to check the level of surface contamination. The integrity of the end-closure weld is evaluated by helium leak checking, and the density of the fuel is determined with a gamma-absorption scanning device. Finally, the hanger fitting is attached prior to loading into a shipping cask.

The cubicles for performing the rod fabrication occupy the first and second levels of Cell 4 (see Fig. 3). Located on one corner of the first level and extending through to the top of the second level is the 4-x 7-ft powder preparation shaft. Directly adjacent to this shaft on the first level are three fabrication cubicles that extend along two walls. The first of these

Fig. 8. Rod Fabrication Flow Diagram.

cubicles is used for vibratory compaction and welding, the second for decontamination, and the third for inspection. A glove repair area is located on the second level adjacent to the powder preparation shaft and directly above the vibratory compaction-welding cubicle and the decontamination cubicle.

The shielding on the tops, sides, and fronts of the rod fabrication cubicles is 4 1/2-in. steel, and the backs and floors of the cubicles adjoin thick concrete slab. The cubicles have a total of 20 windows. Thirty-one ports are provided which allow outfitting with either gloves or manipulator tongs and allow interchange of gloves and tongs without loss of containment of radioactive material. Plans are to operate the rod fabrication facility with 9 tongs and 2 gloved ports. The 20 remaining ports will be used for maintenance.

Powder Preparation Shaft

The powder preparation equipment was designed to afford maximum dust confinement and to utilize gravity feed for transporting the fuel from one equipment unit to the next. All of the equipment in the powder preparation shaft, which is shown in Fig. 9, is remotely controlled, either electrically or by flexible shafts. Minor repairs to the equipment can be made in place through glove access ports. For major repairs, the equipment is mounted on movable racks in the front half of the shaft, and the offending piece of equipment can be removed by pushing the equipment rack to the rear and lifting the piece with a hoist to the glove maintenance area.

Located on the top rack of the shaft is the jaw crusher and ball mill. The jaw crusher is a standard laboratory-size crusher, modified for dust containment. Directly above the jaw crusher is a feeder valve which is used

F g. 9. Powder Preparation Shaft.

to control the rate of feed to the jaw crusher. The ball mill utilizes an alumina grinding jar and a single roll mill incorporated in a device that can be filled, perform the grinding function, and be discharged while maintaining a seal from the cubicle atmosphere.

The classifier is located directly below the jaw crusher and ball mill, and continuously classifies the feed material into dispensing hoppers. The rate of feed to the classifier is controlled either by the feeder valve controlling the feed to the jaw crusher, or by another feeder valve from the ball mill. Six transparent glass storage hoppers, three for the working fractions and three for recycle fractions, are located around the base of the classifier. The three recycle hoppers are connected directly to a recycle manifold. The recycle manifold empties into a recycle hopper which is mounted on a vertical track running the height of the shaft. This recycle hopper is used to convey material to the jaw crusher or the ball mill for reprocessing.

Directly below the classifier is a remote weigher consisting of one scale and three individually controlled feed mechanisms for weighing out exact quantities of each of the working fractions. As each fraction is weighed, it is dumped directly into the blender located below the weigher. The blender is a twin-shell blender that was modified to facilitate loading and discharging.

Vibratory-Compaction Apparatus

The vibratory-compaction apparatus, shown in Fig. 10, consists of two main components, a tube filling assembly and a chuck assembly. The tube filling assembly is located in the equipment shaft at the upper right corner of the vibratory-compaction welder cubicle but is separated from it by a nylon iris valve. The fuel tube is inserted through the iris and into the filler mechanism.

Fig. 10. Vibratory-Compaction Apparatus.

The tube filling assembly consists of a hopper into which blended fuel is received, a "Syntron" vibratory feeder, a funnel for directing the fuel into the tube without spread of dust, and a follower rod for applying a static load to the fuel column during vibration.

The vibratory chuck assembly consists of an anvil to which the chuck is attached and through which the vibrational energy is transmitted and a "Branford" variable impact vibrator. The chuck and the anvil are placed inside the cubicle; and, to allow convenient servicing, the vibrator is located outside the cubicle. The vibrator is sealed from the cubicle by a neoprene diaphragm.

End-Cap Welding Machine

The vertical end-cap welding machine (Fig. 11) is comprised of two units: an elevator mechanism for inserting the rod into the welding chamber and the welding chamber. The welding chamber assembly consists of a mechanical press for inserting the top-end plug, a means for rotating the rod for welding, and a welding torch. In addition, the chamber will embody a vacuum system for evacuating the fuel tube as well as a helium-inlet system for backfilling the tubes.

Decontamination Equipment

A one-kilowatt ultrasonic cleaner is used to decontaminate the completed fuel rods one at a time. The cleaner is equipped with a remotely actuated cover which embodies a mechanism for holding and rotating the rod during cleaning, rinsing, and drying.

Helium-Leak Checking System

The welded and decontaminated rod will be checked for leak-tightness with a mass spectrometer helium-leak detector. The system includes a chamber into

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Fig. 11. End-Cap Welding Machine.

which the end of a fuel rod is sealed, a standard leak, the leak detector, and a roughing vacuum pump. Particle filters are used to isolate the rod vacuum chamber from the pumping and detection station.

Density Scanner

The density in each rod is determined by means of a gamma-adsorption device which is shown in Fig. 12. It consists of a one-curie Co^{60} gamma source incorporated in a lead pig and a detecting crystal with its associated power supply, amplifier, and recorder. A trolley is provided to drive the fuel rod through the collimated gamma beam at a constant rate.

Shipping Cask

The shipping cask, which is designed to hold 132 rods, is loaded in the horizontal position in the facility and discharged vertically at BNL. For loading, the cask is held on a dolly in the horizontal position and secured to the cubicle door with turnbuckles. The lattice structure which is provided in the cask to position the rods is partially inserted into the loading cubicle to facilitate loading by tongs. After loading, the lattice is retracted into the cask; the top is secured, and the cask is removed by means of an overhead crane. During production, two casks are to be shuttled between the facility and BNL.

IV. RADIATION DOSE PREDICTIONS

The importance of obtaining meaningful radiation data at each process stage was recognized in the early planning of the Kilorod Program. Such data will indicate the level of radiation that might be expected from other arrangements of the same operations and from handling U^{233} with other concentrations of U^{232} . The experimental data will assist in determining the amount of shielding or remote operation that is actually necessary at each step in preparing $\text{ThO}_2\text{-U}^{233}\text{O}_2$ fuel material by the sol-gel process and mechanically loading fuel pins with such material.

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Fig. 12. Gamma Absorptiometer.

Prior to the planning of the radiation monitoring in the Kilorod Facility, calculations were made of the gamma dose rates to be expected at the various process steps using a shielding code developed by E. D. Arnold and B. F. Maskewitz² of ORNL. At each point, the geometry best representative of the actual one, was used. The material density, shielding of the ThO₂, and shielding by equipment and containers were considered in the calculations. In all cases the dose point was taken at 5 cm from the surface of the equipment containing the source, as shown in Fig. 13.

Since the code permitted use of up to twelve source strengths, the gamma energies listed in Table 1 were used with the indicated yields in calculating curves of source strengths vs time after uranyl nitrate hexahydrate (UNH) cleanup. In these calculations data by Arnold³ for buildup and decay factors for members of the U²³² decay chain were used.

Several basic assumptions affecting the calculations follow.

1. Uranium-232 concentration in the uranium is 38 ppm.
2. The U²³³ to be used does not contain fission products.
3. Uranium-232 daughters are completely removed by solvent extraction just prior to a two-week operating cycle.
4. Uranyl nitrate hexahydrate feed material not used during the two-week cycle is returned to solvent extraction.
5. Ten 10-kg sol-gel batches are run during the two weeks.

From the calculated dose rates, after assuming reasonable times for operator exposure at each operation, values for the expected cumulative dose to one man, if he carried out all the operations in the line, were obtained. For the Kilorod Facility only hand and arm exposure is expected during normal operation. This exposure will be minimized by the use of manipulator tongs in the rod fabrication portion of the facility. The results of the calculations, both dose rates and cumulative doses, are summarized in Figs. 14 and 15.

Fig. 13. Dose Points for Calculations, Sol-Gel Process.

Table 1. Radiation Sources for Calculations

Isotope	Gamma Energy (Mev)	Yield (gamma/disintegration)
Pb-212	0.250	0.40
Tl-208	0.510	0.25
	0.582	0.80
	0.859	0.15
	2.62	1.00
Bi-212	0.720	0.19
	0.830	0.19
	1.03	0.06
	1.34	0.05
	1.61	0.07
	1.81	0.07
	2.2	0.035

Fig. 14. Sol-Gel Process Dose Rates.

Fig. 15. Rod Fabrication Dose Rates.

The anticipated dose rates for the sol-gel line is shown in Fig. 14. The shaded bars are for the first of the ten sol-gel batches from a UNH lot, and the upper, unshaded bar is for the tenth sol-gel batch from the same UNH lot. The figures at the top of each bar give the time after UNH cleanup for completion of the operation, which is named just below the bars. The left ordinate gives the dose rate in millirem per hour.

Superimposed on the bar graph are cumulative dose curves for the two sol-gel batches. Assuming that the cumulative dose for the other batches is a linear function of time, the dose from each of these is indicated on the right ordinate. The sum of the expected dose from the ten batches is approximately 1200 mrem. This dose, received over a two-week period, is well within the accepted limit of 1500 mrem per week to the hands and arms, or to the head and neck.

A similar graph for the operations in rod fabrication is shown in Fig. 15. For normal operations in the Kilorod Facility, manipulators will be used. However, times for gloved-hand manipulation were assumed, and the cumulative doses shown in Fig. 15 are for such operations. For these, the exposure times are quite short, and the total dose from handling all of the ten batches is only about 90 mrem over the two weeks.

Even when the dose rates are scaled up to account for higher concentrations of U^{232} , the results indicate that the production of $ThO_2-U^{233}O_2$ (containing 3 wt % U^{233}) by the sol-gel process and the subsequent fabrication can be performed without heavy shielding if the UNH is well decontaminated just before use and if there are no extensive delays in the operations or accumulations of material in equipment. It is notable that one of the primary objectives in operating the facility will be to determine the effect of these

latter uncertainties that were not considered in the calculations. During the initial operation of the Kilorod Facility, extensive monitoring with instruments and film packs will be used to obtain actual data on dose rates and cumulative doses to operators.

V. SUMMARY

In summary, the ORNL Kilorod Facility is an integrated pilot plant for carrying out the recycle of highly decontaminated U^{233} containing a low concentration of U^{232} . The construction of the facility is complete, and equipment is now being installed. Commencement of hot operation of the facility is now scheduled for early 1963.

Operation of the facility will place thorium fuel cycle technology in a much improved position in a number of areas.

1. One of the most discussed and debated facets of U^{233} recycle technology is the radiation problem arising from the U^{232} . The Kilorod Facility will provide heretofore unavailable radiation data especially as affected by material holdup in equipment and by processing delays.
2. Heretofore, fuel recycle costs have generally been extrapolated from the costs of contact processing techniques. Since the error in estimating recycle costs is probably directly proportional to the range over which extrapolation must be done, it is obvious that operation of the Kilorod Facility will enable a more accurate evaluation of such costs.
3. In designing facilities and equipment to accomplish a task that has never before been done, there is always doubt as to the features that should be included and the philosophy of operation that should be used.

To a great extent, the facilities, equipment, and procedures are selected by personal judgment and intuition. Operation of the Kilorod Facility will test the validity of the design features and philosophy selected for it. The experience will be invaluable in determining the manner in which future facilities and equipment should be designed and operated.

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Session III
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AQUEOUS PROCESSING OF THORIUM FUELS

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1. INTRODUCTION

Work is continuing at Oak Ridge National Laboratory to develop aqueous methods for processing thorium fuels. An extensive survey of ORNL work in this field (ORNL-3219, Part I) was presented at the CNEN Symposium on Thorium Fuel Cycle at Rome in 1961.¹ This survey included aqueous decladding methods, core dissolution and solvent extraction studies, corrosion data, and design criteria. The present paper (Part II) presents recent work on (1) mechanical decladding, shearing, and core-leaching procedures, (2) dissolution of graphite- and carbide-type fuels, (3) advanced solvent extraction methods, and, (4) for continuity, a brief review of previous work.

Objectives of the program are to develop more economical processing methods and to derive the data required to evaluate alternative recycle systems, for example, short-cooled processing (where protactinium is a problem) versus long-cooled processing (where protactinium has disappeared) and also recovery and reuse of thorium vs the exclusive use of fresh, unirradiated thorium in the fuel recycle system. Primary effort has been placed on stainless-steel-clad $\text{ThO}_2\text{-UO}_2$ fuels of the Consolidated Edison type (CETR) and graphite-bearing fuels similar to those proposed for the High Temperature Graphite (HTGR) and Pebble Bed Reactors, with a minor effort on aluminum-clad (Borax IV) or zirconium-clad fuels. The shear-leach (also called, "chop-leach") processing development work was carried out on an engineering scale with a 250-ton shear, using tubular stainless steel assemblies filled with UO_2 , $\text{ThO}_2\text{-UO}_2$, or ceramic cores to simulate actual fuel. SRE core 1 spent fuel was used in the mechanical decladding development program. Cladding

dissolution studies with unirradiated $\text{ThO}_2\text{-UO}_2$ fuels were performed on an engineering scale, but the core dissolution and extraction studies were made only on a laboratory scale with small irradiated fuel pins or tracer levels of activity.

2. MECHANICAL PROCESSING

Mechanical decladding^{2,3,4} and shear-leach^{7,12} methods for processing stainless-steel-clad uranium-thorium metal or oxide fuels were successfully developed and tested on a small pilot-plant scale. Mechanical decladding was used to remove the stainless steel cladding from irradiated NaK bonded, 2.7% -enriched uranium metal Sodium Reactor Experiment Fuel (SRE, Core 1). A similar method could be used to declad the SRE Core 2 fuel (7.8% Th-U). An engineering-scale shear-leach complex consisting of a 250-ton shear and a countercurrent leacher was successfully tested with prototype assemblies consisting of stainless-steel-clad porcelain, UO_2 , and $\text{ThO}_2\text{-UO}_2$. Nuclear Fuel Services will probably use a similar system but with a batch leacher in a commercial fuel processing plant.⁵ A conceptual study for installation of a shear-leach complex at the Idaho Chemical Processing Plant was completed.⁶

Advantages of mechanical processing include: (1) Lower waste-disposal costs than for aqueous decladding. In a comparative cost estimate, waste costs were eight times lower for mechanically decladding² SRE Core 1 fuel and 20 times lower for shearing and leaching⁷ Merchant Ship Savannah fuel, compared with dissolution of the stainless steel cladding in sulfuric acid (Sulfex Process). (2) Reduction of explosion hazard⁹ by removing liquid-metal bonds prior to aqueous fuel dissolution. (3) Shattering of UO_2 or $\text{ThO}_2\text{-UO}_2$ fuel cores during shearing increases the amount of core which can be dissolved per unit of time because of greater surface area.

2.1 Mechanical Decladding of SRE Fuel

Twenty-six SRE-Core 1 irradiated fuel clusters were successfully declad at ORNL in a specially designed² equipment complex (Fig. 1) using the steps shown in Fig. 2. The SRE Core 1 fuel consists of clusters, 105.5 in. long, of seven elements or rods

Fig. 1. Mechanical processing equipment for decladding SRE Core I fuel (interior view, Cell A) ORNL segmenting facility.

Fig. 2. Mechanical decladding of SRE fuel.

containing 2.7% enriched uranium slugs in thin-walled (0.010 in.) type 304 stainless steel tubular cladding, 92-5/16-in. long and 0.790 in. outer diameter. The active fuel length is 72 in., consisting of 12 slugs, 0.750 in. in diameter and 6.0 in. long, of unalloyed uranium thermally bonded to the clad by a 0.010-in. NaK eutectic annulus. At the end of the column is a helium-filled space, approximately 18 in. high, which allows for expansion of the NaK bond and serves as a reservoir for fission gases. The fuel was irradiated to an average exposure of 675 Mwd/tonne and decayed about two years. The fuel was subjected to an undesirably high temperature during a reactor incident in which organic pump coolant leaked into the sodium core coolant.^{8,10} Undesirable fuel characteristics (pitted, swollen, elongated and bent fuel slugs, and partially solidified NaK) were attributed to the incident. The unexpected hardness of the stainless steel may have resulted from work hardening. These characteristics complicated the decladding operation.

About 1.8 metric tonnes of fuel consisting of 175 tubular fuel rods were mechanically declad, steam cleaned, recanned, and placed in dry storage at rates of 2 to 9.2 kg U/hr, with negligible loss of uranium and plutonium. Hydraulic expansion of the cladding and expulsion of the slugs, the primary method of decladding, was effective on 16% of the rods. Slugs from 77% were dislodged by a mechanical screw, the secondary processing method, and 7% had to be processed by a third method using an auxiliary roller-cutter unit followed by peeling of the clad from each fuel slug with a remotely operated manipulator. The primary and secondary methods could not adequately cope with the damaged fuel. Decladding by remote manipulation was successfully used with the damaged fuel, but it is much too time consuming to be practical.

Other stainless-steel-clad, liquid-bonded fuels, such as the SRE Core 2 (7.8% Th-U),⁸ can be declad mechanically if the fuel is not damaged and if the cladding remains ductile. Either hydraulic expansion or the mechanical screw methods are applicable. SRE Core 3, containing UC, could be processed similarly if the carbon content of the core remains less than stoichiometric.¹¹ A greater than stoichiometric amount of carbon in the fuel causes embrittlement of the cladding.

2.2 Shear-Leach

The experimental shear-leach complex (Figs. 3 and 4) was designed to process subassemblies of the type used in the Yankee, Nuclear Merchant Ship "Savannah," Commonwealth Edison, Pressurized Water Reactor (blanket), Consolidated Edison (CETR), or Rural Cooperative reactors or any subassembly whose cross section does not exceed 6.36×6.36 in. ORNL prototype assemblies, stainless-steel-clad ceramic "dummies," ThO_2 , or UO_2 , were used in development work (Fig. 5). The 250-ton shear, (Fig. 4) conveyor feeder, and inclined rotary leacher were successfully tested with unirradiated prototype fuel. Interlocking of the components by a fail-safe electrical system for proper operation was highly successful.

After a fuel assembly is placed in the feed envelope of the shear, the mechanical events that follow may be initiated automatically or manually. Prototype assemblies filled with UO_2 were sheared and leached at rates of up to 12 kg of UO_2 /hr. The cost of the shear was \$185,000, and the conveyor feeder and leacher were \$40,000 each. Tests in which stainless-steel-clad UO_2 - ThO_2 fuel prototype assemblies were sheared into 1/2 and 1 in. lengths were satisfactory, and combined shear-leach tests on unirradiated stainless-steel-clad ThO_2 and Zircaloy-2-clad UO_2 is scheduled for early 1963. Irradiated fuel will not be processed.

Shear. — The life of the stepped, moving shear blade (Fig. 6) is estimated at 10,000 cuts of a 36-tube ORNL Mark I assembly filled with porcelain dummies, UO_2 , or UO_2 - ThO_2 . A Squarekeen* No. 3 blade was chipped on the main tooth after 5982 cuts on porcelain-filled ORNL Mark I prototype assemblies. One side of a blade would be used to make 5000 cuts, then turned to the other side for an additional 5000 cuts. Damaged blades could be recovered by grinding the first two steps of the blade to remove the worn edges. The useful life of a single blade is probably sufficient to shear one typical reactor core into 1-in. lengths.

Inner and outer "gags" (Fig. 7) were developed to hold an assembly while it is being sheared. Currently, the shortest terminal piece of fuel assembly that can be held and sheared satisfactorily is 1.5 in. long, the width of the inner gag. A 1-in.-wide

*Composition weight percentage: C-0.53, Mn-0.31, Si-0.87, Cr-5.00, Mo-1.28, W-1.23, S-0.01, P-0.02; hardness, RC-54 to 56; cost \$250.00.

Fig. 3. Shear and leach complex.

Fig. 4. ORNL 250 ton shear assembly.

MATERIAL OF CONSTRUCTION TYPE 304 STAINLESS STEEL		
AVERAGE WEIGHT/ASSEMBLY		
STAINLESS STEEL TUBES AND FERRULES*	19.42 kg	
UO ₂	58.65 kg	
UO ₂ -ThO ₂	53.50 kg	* EXCLUDING END ADAPTERS
ThO ₂	40.50 kg	
PORCELAIN	14.40 kg	

FERRULES BRAZED TO TUBES WITH			
NICO BRAZE-50		OR KANIGAN BRAZE	
NICKEL	74 %	NICKEL	90 %
PHOSPHORUS	10 ± 1 %	PHOSPHORUS	10 %
CHROMIUM	13 ± 2 %

Fig. 5. ORNL Mark I Prototype Fuel Element.

Fig. 6. Stepped shear blade for ORNL 250 ton shear.

Fig. 7. Gag for ORNL 250 ton shear.

gag will be tried. Except for this terminal-length limitation, discrete sheared lengths of 1/2 to 2 in. are obtainable. Shearing of fuel into 1/4-in. lengths is not desirable because the clad is severely flattened, trapping pieces of core (Fig. 8). The shortest practical length is probably about 1/2 in.

Brazed fuel assemblies having ferrules as spacers between fuel tubes are easily sheared. Unbrazed assemblies having tube sheets (Fig. 5) as spacers can be sheared as easily as brazed fuel. Near the tube sheets, however, undesirable chunks of fuel held together by the sheet itself are produced. These chunks cannot be handled in a continuous countercurrent leacher because they cannot be completely submerged in the counterflowing acid. Also, the chunks may block the flow of solids in a continuous leacher in which dimensions are minimized because of criticality considerations.

A batch leacher may be required for fuels containing tube sheets. The size distribution of particulate composites composed of cladding, core and braze metal which were dislodged during the shearing of (a) porcelain, (b) UO_2 , and (c) $\text{UO}_2\text{-ThO}_2$ -filled, ORNL stainless-steel-jacketed prototype fuel into 1/4, 1/2, 1, and 1-1/2-in. lengths are presented in Fig. 9. Curves of the particle-size distribution of each component are available.¹² Generally, sheared UO_2 -filled and $\text{UO}_2\text{-ThO}_2$ -filled assemblies produce equal quantities of particles. The amount of UO_2 and stainless steel dislodged increases as the length of sheared pieces is decreased (Table 1).

The cladding of two porcelain-filled Mark 1 assemblies was carburized prior to shearing to simulate hardening and embrittlement of fuel cladding from neutron bombardment in a reactor. Carburization had two effects: (1) More core and clad were dislodged, Table 2 and Fig. 10, than from an untreated assembly. (2) The tonnage required was only about half that required for an uncarburized assembly. In tests by Goode, using a small single-tube shear, the amount of particles dislodged when shearing single tubes of stainless steel or Zircaloy-2 filled with UO_2 pellets irradiated to approximately 16,000 Mwd/ton U did not differ significantly from the amount produced from unirradiated specimens¹³ ($\sim 6\% < 10$ mesh for 1 in. of length) although the irradiated fuel pellets were shattered ($0.1\% < 10$ mesh) during the irradiation period prior to shearing. Measurements of the amount of particles contributed individually by the clad and core were not made.

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Table 1. Distribution of UO₂ and Stainless Steel Particles from a Sheared ORNL Mark 1 Fuel Assembly

ORNL Mark 1 assembly: square bundle, 3.625 x 3.625 in., of 36 type 304 stainless steel tubes, 1/2 in. OD x 72 in. long x 35 mil wall, assembled with 1/4 in.-OD x 1-in.-long Kanigen or Nicro brazed spacer ferrules at ~12-in. spacing. Tubes filled with UO₂ pellets, 0.420 in. OD x 0.625 in. long.

Sheared Length (in.)	UO ₂ (Wt %) ^a			
	Dislodged			Retained in Clad
	<44 μ	44-1,000 μ	1,000-9,520 μ	
0.5	22.4	57.6	4.5	15.5
1.0	7.35	25.6	2.4	64.6
1.5	4.5	12.0	1.2	82.3
	Stainless Steel (Wt %) ^b			
	Dislodged			Retained
0.5	0.023	0.38	7.6	92.0
1.0	0.007	0.12	2.1	97.8
1.5	0.003	0.057	2.6	97.4

Wt % computations: (a) $\frac{\text{Weight (g) of UO}_2 \text{ dislodged}}{\text{Weight (g) of UO}_2 \text{ in fuel assembly}} \times 100$

(b) $\frac{\text{Weight (g) of stainless steel dislodged}}{\text{Weight (g) of stainless steel in fuel assembly}} \times 100$

Table 2. Distribution of Particles from UO₂, Porcelain, and Carburized Porcelain-Filled ORNL Mark 1 Fuel Assemblies Sheared into 1-in. Lengths

ORNL Mark 1 assembly: square bundle (3.625 x 3.625 in.) of 36 type 304 stainless steel tubes 1/2 in. OD x 72 in. long x 35 mil wall, assembled with 1/4 in.-OD x 1-in.-long Kanigen or Nicro brazed spacer ferrules at ~12 in. spacing. Tubes filled with 0.420-in.-OD x 3-in.-long porcelain sections or UO₂ sections, 0.420 in. OD x 0.625 in.

	Core Material (Wt %) ^a			
	Dislodged			Retained in Clad
Core Material	<44 μ	44-1,000 μ	1,000-9,520 μ	
UO ₂ (Ductile clad)	7.4	25.6	2.4	64.6
Porcelain (Ductile clad)	3.0	16.2	4.3	76.5
Porcelain (Carburized 0.8% max, clad)	3.5	24.0	16.0	56.5
UO ₂ (Ductile clad)	Stainless Steel (Wt %) ^b			
	Dislodged			Retained
UO ₂ (Ductile clad)	0.007	0.12	2.1	97.8
Porcelain (Ductile clad)	0.03	0.108	2.5	97.4
Porcelain (Carburized clad)	0.0165	0.115	5.2	94.7

Wt % computations: (a) $\frac{\text{Weight (g) of core material dislodged}}{\text{Weight (g) of core material in fuel assembly}} \times 100$

(b) $\frac{\text{Weight (g) of stainless steel dislodged}}{\text{Weight (g) of stainless steel in fuel assembly}} \times 100$

1/4-inch
Sections

1/2-inch
Sections

1-inch
Sections

Fig. 8. Comparison of stainless steel tubing when shearing a porcelain-filled ORNL Mark I prototype fuel assembly into 1/4-, 1/2-, and 1-inch sections using a stepped blade and ORNL 250 ton shear. Dislodged porcelain fines are not shown.

$$\text{Weight percentage} = \frac{\text{Weight of all particles dislodged (g)}}{\text{Weight of assembly (g)}} \times 100$$

Fig. 9. Distribution of total particles smaller than 9520 μ dislodged from the shearing of porcelain, UO_2 , or $\text{UO}_2\text{-ThO}_2$ -filled ORNL Mark I fuel into 1/4-, 1/2-, 1-, and 1-1/2-in. lengths.

Conditions: (1) Horizontally-actuated ORNL 250-ton shear; stepped blade operated at 1.22 in./sec; 4.5 cuts/min. (2) Description of fuel assembly sheared: square bundle (3.625 x 3.625 in.) of 36 tubes, type 304 stainless steel 1/2 in. in OD x 72 in. long x 35 mils thick, with 1/4-in.-OD x 1-in.-long 304 stainless steel Kanigen or Nicro-brazed spacer ferrules at a spacing of about 12-in. The tubes were filled with either UO_2 or $\text{UO}_2\text{-ThO}_2$ pellets, 0.420 in. x 0.625 in. long or porcelain, 0.420 in OD x 3 in. long.

Fig. 10. Comparison of single cut made on carburized ($2.6\% C_{\max}$) and ductile stainless-steel-clad, porcelain-filled ORNL Mark 1 prototype fuel assemblies.

A bellows-sealed flapper valve¹⁴ (Fig. 11) was developed for use in the feed chutes or discharge ports of the chop-leach complex. The valve was designed to pass solids downward in the open position without constriction of the chute. When the valve is closed the flapper disk seals against rising leacher fumes by seating against an inverted fixed seat. The inverted position prevents trapping of solids and fouling of the seal. The useful life of the valve, based on one cycle per hour, was estimated from tests¹⁴ to be about four years.

Leaching. — In the shear-leach complex, sheared fuel is leached counter-currently with boiling nitric acid in an inclined, rotary spiral leacher. The leacher consists of an inner cylinder into which is welded an internal spiral containing vertical-slot-type weirs (Fig. 3). Solids and liquid are elevated countercurrent to boiling acid flowing through the weirs. Leaching takes place in the lower four stages of the spiral, and washing of the leached clad occurs in four upper stages.

To ensure submergence of sheared fuel under the acid dissolvent, the slip angle for 1.5-, 2.25-, and 3.0-liter batches each of empty type 304L stainless steel tubing (1-in. long), solid stainless steel rod (1/2-in. in diameter x 1 in. long), and stainless-steel-jacketed, porcelain-filled Mark 1 elements sheared into 1-in. lengths were measured at leacher elevations of 10, 20, and 30°. There was little difference in the slip angle of equal volumes of empty cladding, solid stainless steel rods, and porcelain-filled Mark 1 elements. The angle of slip increased with batch volume and less significantly with leacher elevation. At a leacher elevation of 15°, the slip angle increased from about 28 to 32° when the batch volume increased from 1.5 to 3 liters. The optimum leacher batch size is 2.25 liters of sheared Mark 1 prototype, which is equivalent to 8 in. of length.

The slip angle is defined as the counterclockwise angle of rotation of the leacher (looking into the feed end of the leacher) sufficient to bring an originally horizontal batch to the point of slippage (Fig. 12). Slippage first occurs when approximately half of the batch is above the liquid level. To ensure submergence of chopped fuel as it is advanced each flight, the leacher is rotated 360° plus the slip angle (~28° for a 2.25-liter batch) then reversed by the amount of the slip angle.

Fig. 11. Exploded view of bellows sealed flapper valve.

Fig. 12. Cross-section of leacher from feed end showing slip angle.

Leaching of unirradiated UO_2 -filled ORNL Mark 1 prototype fuel sheared into 1/2, 1, and 1-1/2-in. lengths was accomplished successfully, with negligible loss of uranium. A typical curve of uranium loading (g/liter) vs dissolution time (min) is presented in Figure 13 for 7 M HNO_3 fed at a rate of 4 g-moles HNO_3 /g-mole UO_2 . At this acid strength and ratio, apparent steady state was attained at about the fifth hour. For all sheared lengths tried, a growing inventory of UO_2 was recorded (Figure 14). Increasing the acid-to- UO_2 ratio from 4 to 6 eliminated the UO_2 inventory after the third hour. Mixed ThO_2 - UO_2 leach tests will be made in 1963. An increased residence time will be required to dissolve this fuel. Since both irradiated and unirradiated fragmented fuel (8-20 mesh) was >99% dissolved in 5 hr in batch tests^{15, 1} (Sec 3.1.5), a residence time of 10-15 hr should be adequate for the continuous leacher.

3. AQUEOUS DISSOLUTION METHODS

3.1 Ceramic Cores Clad in Stainless Steel, Aluminum, or Zirconium

These fuel claddings can be dissolved in a suitable reagent prior to dissolution of the oxide core in boiling 13 M HNO_3 --0.04 M HF.¹⁵⁻²⁸ Two head-end processes for Thorex solvent extraction, Darex and Sulfex, were developed on a laboratory and small engineering scale for dissolution of CETR fuel. In the Sulfex process^{15-18,20,22,23} the stainless steel cladding is dissolved in boiling 4 to 6 M sulfuric acid, whereas the cladding is dissolved in dilute aqua regia in the Darex process.^{15-17,19,21-23} Hot-cell experiments^{15,22} show that the Sulfex process will probably be satisfactory for highly irradiated elements but that losses of uranium to the decladding solution are excessive with the Darex system. The BORAX-IV core was processed²⁸ at the Idaho Chemical Processing Plant (ICPP) with a process²⁷ that involved dissolution of the aluminum cladding in NaOH - NaNO_3 , dissolution of the lead bond in dilute nitric acid, and dissolution of the ThO_2 - UO_2 core in 13 M HNO_3 --0.04 M NaF .

3.1.1 Dissolution of Stainless Steel Cladding in Sulfuric Acid

In the Sulfex process for CETR fuel^{15-18,20,22,23} (Fig. 15), the 30-mil stainless steel cladding is dissolved in three times the stoichiometric amount of boiling 4 to 6 M

Fig. 13. Uranium loading as a function of dissolution time for a 4 stage rotary leacher.

Fig. 14. Uranium inventory in rotary leacher versus dissolution time.

Fig. 15. Decladding and dissolution of Consolidated Edison reactor fuel by the Sulfex-Thorex process.

H_2SO_4 in 1 to 3 hr. About 1.1 moles of hydrogen off-gas are evolved when 55 g (1 mole) of stainless steel is dissolved. The stainless steel cladding is often passive due to either a protective oxide film or traces of nitric acid in the solution. Brazed elements, however, are usually not passive. If passivation occurs, it is most conveniently broken by contacting the element with steel wool.

Losses of uranium to the decladding solution from high-density (greater than 95% of theoretical) fuel specimens were generally less than 0.3% and were not greatly affected by burnup over the range of 620 to 20,000 Mwd per ton of core.^{15,22} The increase in loss with burnup is attributed to the larger surface area present as the result of shattering of the highly irradiated fuel specimens. These results indicate that the Sulfex process will be suitable for the decladding of highly irradiated $\text{ThO}_2\text{-UO}_2$ reactor fuels.

3.1.2 Darex Decladding

In the Darex process for CETR fuel^{15-17,19,21-23} (Fig. 16), the stainless steel cladding is dissolved in sufficient boiling 5 M HNO_3 --2 M HCl to yield a solution containing about 50 g of stainless steel per liter. The off-gas contains 20% NO_2 , 35% NOCl , 35% N_2 , and traces of N_2O , NO , HCl , Cl_2 , and H_2 . Dissolution of a 30-mil-thick cladding requires about 2 hr.

The uranium loss to the Darex decladding solutions was excessively high from highly irradiated CETR fuel specimens;^{15,22} the loss increased from 0.15 to 5% as the burnup increased from 0 to 20,000 Mwd per ton of core. Fragmentation of the fuel pellets undoubtedly contributed to the high losses, but the losses were higher than expected from fragmentation alone. If the Darex process is used, the uranium and thorium can be recovered in the Acid Thorex solvent extraction system (see Sec 4.).

3.1.3 Aluminum Dissolution

Aluminum cladding from $\text{ThO}_2\text{-UO}_2$ fuels such as the BORAX-IV is readily dissolved²⁷ in NaOH-NaNO_3 solutions, with a uranium loss of less than 0.2%. The BORAX-IV fuel, which contained a lead bond between the $\text{ThO}_2\text{-UO}_2$ fuel and the

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Fig. 16. Decladding and dissolution of Consolidated Edison reactor fuel by the Darex-Thorex process.

aluminum cladding, was processed at ICPP²⁸ by the method developed at ORNL.²⁷ The aluminum cladding was dissolved in caustic, and the lead bond was dissolved in dilute nitric acid prior to dissolution of the core in 13 M HNO₃-0.04 M HF.

3.1.4 Zirconium Dissolution

Preliminary experiments¹ with unirradiated ThO₂-UO_{2.7} fuel specimens (4.2% UO_{2.7}, 83% of theoretical density) indicated that the zirconium cladding could be dissolved in boiling 6 M NH₄F--1 M NH₄NO₃ (Zirflex process²⁴⁻²⁶), with attendant uranium and thorium losses of less than 0.4%. Losses would undoubtedly be even lower with higher-density UO_{2.0} fuel pellets.

3.1.5 ThO₂-UO₂ Core Dissolution

Thorium metal, thorium oxide, and ThO₂-UO₂ mixtures dissolve in boiling nitric acid containing small amounts of hydrofluoric acid as catalyst.^{1,17,29} Dissolution of high-density fuel pellets (greater than 90% of theoretical) in the optimum reagent, 13 M HNO₃--0.04 M HF, is relatively slow, however. In three times the stoichiometric amount of this reagent, 25 to 40 hr are required to dissolve completely typical 0.26-in.-diam CETR fuel pellets.

The rate of dissolution of ThO₂-UO₂ mixtures containing up to 10% UO₂ depends on the nitric acid concentration, the hydrofluoric acid concentration, the thorium concentration in solution, and the density and state of subdivision of the mixture. When other variables are constant, the rate is maximum when the nitric acid and hydrofluoric acid concentrations are 13 and about 0.06 M, respectively. The instantaneous dissolution rate decreases by a factor of about 5 as the thorium concentration in solution increases from 0 to 0.9 M. Rates of dissolution of ThO₂--4.4% UO₂ pellets (density, 95% of theoretical) in solutions containing 0.04 M NaF were correlated by:

$$R = 0.627 \left(\frac{M}{10} \right)^3 - 0.336 \left(\frac{M}{10} \right)^4 - 0.12 \left(\frac{M}{10} \right)^3 M_{Th},$$

where R is reaction rate, mg g⁻¹ min⁻¹; M is nitric acid concentration in the dissolvent, molarity; and M_{Th} is thorium concentration in the dissolvent, molarity. The dissolution

rate of ThO_2 --5% UO_2 pellets decreases with increasing pellet density; the initial rate in boiling 13 M HNO_3 --0.04 M NaF --0.1 M $\text{Al}(\text{NO}_3)_3$ decreased from 18 to about 1 $\text{mg min}^{-1} \text{cm}^{-2}$ as the pellet density increased from 60 to 95% of theoretical. The rates of dissolution of ThO_2 and ThO_2 -- UO_2 pellets containing up to 10% UO_2 were practically the same when the other conditions, such as pellet density, were constant.²³

Fused ThO_2 , as expected, dissolved more slowly than material of lower density. For example, in 5-hr experiments with -4 to +8 mesh samples, only about 30% of the fused ThO_2 sample dissolved in a 200% excess of boiling 13 M HNO_3 --0.04 M NaF --0.1 M $\text{Al}(\text{NO}_3)_3$, compared with 88% of a sample of 95.8% ThO_2 -- UO_2 .³⁶ which was 93% of theoretical density.²³ Both unirradiated and irradiated (15,000-20,000 Mwd/T) 8- to 20-mesh fuel samples were greater than 99% dissolved in a 5-hr reaction with a 200% excess of boiling 13 M HNO_3 --0.01 M NaF --0.1 M $\text{Al}(\text{NO}_3)_3$. The small residue was dissolved in a second digestion with fresh reagent.¹⁵ Soluble neutron poisons, H_3BO_3 or $\text{Cd}(\text{NO}_3)_2$, can be added to the dissolvent in concentrations up to 0.1 and 0.075 M , respectively, without affecting the rate of dissolution.

3.2 Graphite-Base Fuel Elements

Advanced graphite-base reactor fuel elements will probably contain 150 to 400 μ -diam UC_2 -- ThC_2 fuel particles coated with 25 to 60 μ of pyrolytic carbon dispersed throughout a graphite matrix. Representative fuels are the HTGR and the PBR. Several aqueous methods for processing graphite-base fuels have been investigated.³⁰⁻³³ For elements containing coated fuel particles, however, only two methods appear applicable. These are: burning in oxygen followed by dissolution of the ThO_2 -- U_3O_8 ash in boiling 13 M HNO_3 --0.04 M F , or fine grinding, probably to 200 mesh to ensure rupture of all the fuel particles, followed by acid leaching to recover the uranium and thorium. At present, the combustion-dissolution approach appears more attractive since both fine grinding and separation of the leach liquor from the residual fines by filtration or centrifugation are difficult. An extensive study has been made of the reactions of thorium and uranium carbides and graphite with H_2O , HCl , H_2SO_4 , or HNO_3 .^{34,35}

3.2.1 Combustion-Dissolution

Combustion (in oxygen at temperatures above 700°C) of graphite-base fuels followed by dissolution of the oxide ash leads to quantitative recovery of uranium and thorium from fuels containing carbon-coated fuel particles^{32,33} (Table 3). This method may also be applicable to fuels containing BeO-coated particles, using procedures developed for the dissolution of sintered BeO;³⁶ however, alumina-coated fuels probably cannot be processed by an aqueous method because of the chemical inertness of sintered Al₂O₃. The Al₂O₃-coated particles remain virtually intact after burning and would have to be crushed to allow recovery of the uranium and thorium by an aqueous dissolution process.

Considerably more effort will be required to develop fully the combustion-dissolution method. Particular attention will be given to methods for treating the radioactive off-gas, to design of the burner (preferably one in which both burning and dissolution can be conducted), and to the evaluation of materials of construction suitable for the burner.

Table 3. Uranium and Thorium Recovery from Graphite-Base Fuels by the Combustion-Dissolution Process

Conditions: Fuel burned in oxygen at 700-900°C; ash digested for 6 to 10 hr in boiling reagent

Fuel	Fuel Comp. (%)		Leachant	Recoveries (%)	
	Uranium	Thorium		Uranium	Thorium
Uncoated UC ₂ -ThC ₂	1.7	8.0	13 M HNO ₃ -- 0.04 M HF-- 0.1 M Al(NO ₃) ₃	100	100
Pyrolytic carbon-coated UC ₂ -ThC ₂	9.9	33.0	13 M HNO ₃ -- 0.04 M HF-- 0.1 M Al(NO ₃) ₃	100	100
Al ₂ O ₃ -coated UO ₂	8.0	0.0	10 M HNO ₃	9.9	---

3.2.2 Fine Grinding Followed by Acid Leaching

After a fuel that contains carbon-, BeO-, or Al₂O₃-coated fuel particles is ground fine enough (about 200 mesh) to ensure rupture of the particles, the uranium and thorium can be recovered^{32,33} by leaching with either nitric acid or a mixture of nitric and hydrofluoric acids (Table 4). Digestion for 6 to 8 hr with the boiling reagent is required to effect high recoveries. It is probable that hydrofluoric acid will be required in the reagent to ensure adequate recoveries, although there are too few data to allow a final conclusion.

Table 4. Uranium and Thorium Recovery from Graphite-Base Fuels by the Grind-Leach Process

Conditions: Fuel ground to 200 mesh and leached for 6 to 8 hr with boiling reagent

Fuel	Fuel Comp. (%)		Leachant	Recoveries (%)	
	Uranium	Thorium		Uranium	Thorium
Al ₂ O ₃ -coated UO ₂	8.0	0.0	15.8 <u>M</u> HNO ₃	99	--
Pyrolytic carbon-coated UC ₂ -ThC ₂	9.7	33.8	15.8 <u>M</u> HNO ₃	~99	99.9
Pyrolytic carbon-coated UC ₂ -ThC ₂	9.6	33.5	13 <u>M</u> HNO ₃ -- 0.04 <u>M</u> HF-- 0.1 <u>M</u> Al(NO ₃) ₃	99.4	99.9

Two major problems remain to be solved with the grind-leach process. First, the feasibility of grinding coated-particle fuels to the desired fineness on a large engineering scale must be demonstrated. Second, suitable equipment must be designed for separation of the solids from the acidic leach slurries by centrifugation or filtration.

3.2.3 Reactions of Thorium and Uranium Carbides with Water and Nitric Acid

Reactions of thorium and uranium carbides in various aqueous reagents are being studied to provide basic process data.^{34,35} Hydrolysis of uranium and thorium carbides in water at 80°C results in the formation of the respective solid hydrous oxides and mixtures of hydrogen and hydrocarbons. The nature of the hydrocarbon products depends on the carbide being hydrolyzed. The two monocarbides, ThC and UC, yield a gas consisting of 83% methane and 13% hydrogen on hydrolysis. All the carbide

carbon is converted to gaseous products (Table 5). In contrast, hydrolysis of the higher carbides, U_2C_3 , ThC_2 , UC_2 , results in much less gas evolution. However, the gas contains 30-40% C_2 - C_8 hydrocarbons and 50-80% hydrogen. Furthermore, 50-80% of the carbide carbon remains as nonvolatile carbon compounds. Hydrolysis of the respective carbides yields about the same gaseous products in 6 N HCl and 6 M H_2SO_4 as in water. On the other hand, reaction of UC with 4 M HNO_3 gives completely different results. The off-gas is comprised mainly of NO and CO_2 and contains no hydrogen or hydrocarbon gases (Table 6). In addition, 30-50% of the carbide carbon remains in solution as a mixture of oxalic, benzene polycarboxylic, and higher-molecular-weight organic acids. No insoluble wax is formed. The soluble acids should not constitute a process hazard, however, since they are not nitrated. Similar reactions are expected between other uranium and thorium carbides with nitric acid, but quantitative studies have not been completed. Initial tests show that no solid or waxy residues are formed.

The most reactive carbides are UC , ThC , and ThC_2 , and they hydrolyze completely in a few hours at 80°C , whereas about 24 hr are required for U_2C_3 and UC_2 at the same temperature (Fig. 17). Specific reaction rates cannot be obtained because samples (3-4 g each) disintegrate to powder within approximately 30 min. But in any event the rate of reaction of massive pieces is not dangerously fast under any conditions, even at the boiling point. At room temperature, as expected, the rates of reaction are much lower. For example, complete hydrolysis of 3- to 4-g samples of UC and ThC requires about a week at 25°C .³⁴

The data given above indicate that the best method for processing sodium-bonded UC or UC-ThC fuels clad in a metal such as stainless steel is shearing followed by steaming or reaction with liquid water to destroy the bond and hydrolyze the carbide core. With stoichiometric or substoichiometric carbides, all the carbide carbon will be evolved, and the hydrous oxide residue from the steaming operation will dissolve readily in nitric acid, yielding a solution free from organics. However, if the fuel contains higher carbides, waxes will remain from the steaming operation. These waxes react with nitric acid to yield as-yet-unidentified organic products. These organic products could be a mixture of acids similar to that obtained from the UC-HNO_3 reaction; in this case, there should be no problem presented to further processing.

Fig. 17. Relative rates of hydrolysis at 80°C of 3 to 4 g samples of uranium and thorium carbides in water.

Table 5. Hydrolysis of Thorium and Uranium Carbides in Water at 80°C

	Type of Carbide				
	UC	ThC	U ₂ C ₃	UC ₂	ThC ₂
Volume of gas evolved, ml (STP) per gram of carbide	96	92	61	44	65
Composition of off-gas, vol %					
Hydrogen	13	13	58	45	78
Methane	84	82	2.5	15	1.5
Saturated C ₂ -C ₈ hydrocarbons	2.4	3.5	32	31	8.1
Unsaturated hydrocarbons	0.3	1.3	7.7	9.0	12.4
Nonvolatile carbon compounds, % of original carbon	0	2	48	67	77

Table 6. Reaction of UC with 4 M HNO₃

Product	% of Total Carbon in Product	Product Composition
Off-gas	50-70	77% NO; 19% CO ₂ ; 4% N ₂ O; trace CO; no hydrogen or hydro- carbons.
Soluble organic acids	30-50	20-30% mellitic acid; 5-10% oxalic acid; remainder, benzene and poly- nuclear polycarboxylic acids; product is not nitrated.

The reaction of graphite with nitric acid was also studied briefly because of its importance in processes involving the nitric acid leaching of powdered graphite-base fuels. Reaction is very slow: With finely powdered graphite, only 60-80% of the carbon reacted in 500 hr with boiling 16 N HNO₃. Less than 2% reacted in 24 hr, with up to 20% of the reacted carbon remaining in solution as a mixture of benzene and

higher-molecular-weight polycarboxylic acids. As in the case of the UC-HNO₃ reaction, the products were not nitrated and should not constitute a hazard to the process.

4. SOLVENT EXTRACTION

"Acid" solvent extraction processes have been developed for the extraction of uranium-233 (Acid Interim 23 process)³⁷ or co-extraction of uranium and thorium (Acid Thorex process)³⁸ from nitric acid solutions with tributyl phosphate (TBP) or di-sec-butyl phenyl phosphonate (DSBPP). These processes are designed for systems where criticality is a major problem, and they differ from previous flowsheets³⁹ in that nitric acid is used as the salting agent, rather than aluminum. Decontamination and uranium or thorium recovery with the "Acid" processes are equal to those of the older methods. Advantages include a large reduction in evaporated waste volumes because of elimination of aluminum and, in the case of the Acid Thorex process, a reduction of stage heights in extraction columns by factors of 2 to 4.⁴⁰

4.1 Acid Thorex Process

In the Acid Thorex process, both uranium and thorium are extracted from the fission-product-bearing nitric acid solution (Fig. 18). Protactinium-233, present at short cooling times, is not extracted. Aluminum is present (0.1 M) as a complexing agent for fluoride, added in the previous dissolution step, and is therefore not effective as a salting agent. The volume of the evaporated waste is a tenth that from the Interim 23 process. Decontamination factors obtained were 1000, 5000, 1000, and 10⁵, respectively, for ruthenium, zirconium-niobium, protactinium, and rare earths. Uranium and thorium losses were 0.01 and 0.3%, respectively. A high (30%) TBP concentration is required to extract both uranium and thorium, and, consequently, an acid-deficient feed is used to counteract the increased tendency for extraction of fission products. When an acid feed was used, decontamination was reduced by a factor greater than 10.⁴¹ The high decontamination achieved with the acid-deficient feed is attributed to the slow conversion of the ruthenium, zirconium-niobium, and protactinium from highly inextractable species present in acid-deficient systems to the highly extractable species formed in the acid sections of the column.

Fig. 18. Acid Thorex process.

In laboratory countercurrent experiments, the fission products contacted the aqueous phase for approximately 20 min. In pulse columns this time would be reduced to about 8 min. The two scrub solutions shown in the flowsheet combine to form a 1 M HNO_3 scrub. They are added separately, however, with the low-acid scrub at the top of the column to minimize extraction of acid with the organic product. Thus, the thorium and uranium may be costripped in a single column with minimum aqueous volume and number of stages. If the thorium and uranium are recovered separately in partitioning and strip columns, a single 1 M HNO_3 , 0.01 M PO_4^{3-} , 0.01 M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$ scrub solution at a relative flow rate of 1.3 is satisfactory.

4.2 Acid Interim 23 Process

An Acid Interim 23 process was developed³⁷ to extract U^{233} and leave the thorium with the fission products (Fig. 19). Protactinium-233, present at short cooling times, also remains with the fission products. After the Pa^{233} has decayed to U^{233} , the wastes can be re-extracted by the same process to recover the U^{233} (and thorium, if desired, using the Acid Thorex process). The flowsheet shows the use of 5% TBP to illustrate a high processing rate. This is close to the maximum rate, since third-phase formation occurred with 10% TBP. In equipment in which criticality is not controlled by geometry, 2.5% TBP is used to limit the U^{233} concentration in the organic phase. Uranium loss was less than 0.01%, and the gross decontamination factor was approximately 10^5 . Advantages of the Interim 23 process include (1) rapid recovery of U^{233} and resultant low inventory charge and (2) high processing rate. Principal disadvantages are the necessity of processing the fission product and organic-degradation-product-bearing waste solution a second time to recover Pa^{233} and the relatively large waste volume.

4.3 Kilorod Program

A solvent extraction flowsheet was developed⁴² for purifying recovered U^{233} to be used in the fabrication of fuel elements by the Sol-Gel process⁴³ (Fig. 20). In laboratory countercurrent batch extraction experiments, the uranium was decontaminated from Th^{228} by a factor of greater than 10^4 . Di-sec-butyl phenyl phosphonate (DSBPP) is used rather than TBP because the separation factors for U/Th are

Fig. 19. Acid Interim-23 process.

Fig. 20. Kilorod Interim-23 process.

higher by a factor of 4 in the DSBPP system at thorium concentrations less than 100 g/liter.^{44,45,46} The increase in separation occurs principally in the scrub section of the column. The acid deficient aluminum nitrate scrub produces a low acidity product, with a nitrate-to-uranium ratio of 2.18 as required by the Sol-Gel fuel preparation process which follows in the Kilorod Program. Decontamination from Th^{228} and its' daughters is approximately 10^4 . Since DSBPP is not soluble in dodecane, an aromatic diluent, diethylbenzene (DEB) is used. The DSBPP in DEB is not as stable to chemical degradation as TBP in n-dodecane. When DSBPP in DEB was stirred 16 hr with nonradioactive feed and then used in a laboratory experiment, the distribution coefficient of uranium in the scrub section decreased by a factor of about 2. Decontamination from Th^{228} , however, was unaffected.

This separation of uranium from the daughters of U^{232} provides a product which can be handled in the semiremote, Sol-Gel vibratory-compaction equipment for at least ten days without overexposure to workers. The growth of activity in the product (Fig. 21) duplicates that predicted for the growth of the daughters of U^{232} in the natural activity of the U^{233} .⁴⁷

4.4 Protactinium Recovery Systems

The presence of relatively long half-life (27 days) Pa^{233} in short-decayed thorium reactor fuel, constitutes a major difficulty in the reprocessing of such fuel. Immediately after discharge from the reactor the protactinium is responsible for 90 to 99% of the beta-gamma activity and as much as 10% of the potential U^{233} in the fuel. With either the Interim 23 or the Acid Thorex flowsheet, the protactinium is hydrolyzed or precipitated in the acid feed solution and is not extracted with the solvent. Two processes being studied in the laboratory for possible recovery of the protactinium from short-decayed thorium fuel solutions are: (1) adsorption of protactinium from highly acidic dissolver solution on silica gel or on unfired powdered Vycor glass or (2) the coextraction of the protactinium with the thorium and uranium, using a Thorex-type solvent extraction flowsheet.

Solubility studies on Pa^{231} showed that protactinium remained homogeneously dispersed in solutions equivalent to those to be obtained in dissolution and feed of

Fig. 21. Growth of activity in U-233 following solvent extraction purification.

Consolidated Edison fuel irradiated to 20,000 Mwd/ton. The solutions contained 116 g/liter Th, approximately 0.07 g/liter Pa, 11 $\underline{\text{M}}$ HNO_3 , 0.1 $\underline{\text{M}}$ Al, less than 0.1 $\underline{\text{M}}$ F, and 40 g/liter Th, 0.09 g/liter Pa, 5 $\underline{\text{M}}$ HNO_3 , 1 $\underline{\text{M}}$ Al, approximately 0.1 $\underline{\text{M}}$ F. Such solutions showed no decrease in protactinium concentration after standing in a plastic container for a month at room temperature. These solutions also showed no change in concentration after contacting either welded or unwelded type 347 stainless steel coupons for one week at room temperature.⁴⁸ The solubilities are in agreement with the observations of Hardy et al.⁴⁹ that protactinium stock solutions containing 10^{-3} $\underline{\text{M}}$ Pa in 6 $\underline{\text{N}}$ HNO_3 were stable for many months.

Laboratory experiments demonstrated that at least 95% of the protactinium in the synthetic dissolver solution could be adsorbed on columns containing either unfired Vycor glass or laboratory-prepared silica gel.⁴⁸ When the experiments were terminated, the columns contained 5.0 and 3.2 mg of protactinium per gram of adsorbent, respectively. The amount of protactinium not adsorbed remained constant throughout the experiment. The protactinium was eluted at six times the feed concentration with 0.5 $\underline{\text{M}}$ oxalic acid. These laboratory experiments indicate that the protactinium in short-decayed thorium fuel may be adsorbed on radiation-stable inorganic materials directly from the dissolver solution. The decrease in activity of the thorium-uranium solution due to 95% removal of protactinium is equivalent to about a four-month decay of the fuel.

A low-decontamination "Acid Co-Extraction Process" is also being developed⁵⁰ for the recovery of protactinium in which protactinium, uranium, and thorium are simultaneously extracted from highly acid feed solutions with 30% TBP. In experiments with tracer protactinium, about 90% of it was extracted from 5 $\underline{\text{M}}$ HNO_3 --1 $\underline{\text{M}}$ $\text{Al}(\text{NO}_3)_3$, resulting in a decontamination factor of 70 from ruthenium and about 10^5 from rare earths. About half of the zirconium-niobium extracts with the product. A partitioning strip or a second solvent extraction cycle could be used to separate protactinium from uranium and thorium and to increase decontamination from fission products. Much of the zirconium-niobium will accompany the protactinium in this system, but additional decontamination is obtained by the decay of 65-day half-life Zr^{95} during the decay of the 27-day half-life Pa^{233} .

Either of these short decay processes results in the separation of protactinium, which will decay to U^{233} almost free of U^{232} . Such U^{233} is valuable for special uses.

5. CHOICE OF REPROCESSING METHOD

5.1 Thorium Fuel Processes

The choice of a processing method for the recovery of irradiated thorium fuels depends on which of the following objectives must be met: (1) short cooling times with immediate co-recovery of U^{233} , thorium, and protactinium vs long cooling for complete decay of Pa^{233} to U^{233} before recovery of U^{233} and thorium; or (2) short cooling time and recovery of U^{233} alone in a first cycle followed at a later time by recovery of additional U^{233} (and thorium, if desired) after complete decay of Pa^{233} . These considerations do not particularly affect the choice of fuel decladding or dissolution methods but seriously affect the choice of solvent extraction method. Items to be considered are: (1) solubility of protactinium in nitrate systems, (2) separation chemistry of protactinium in systems containing macro amounts of protactinium, (3) relative processing rates, and (4) volume of radioactive wastes. A summary of the extraction system variables taken from Figures 18 and 19 is given in Table 7.

The objective of recent solvent extraction development work has been to define these variables and thus obtain the data necessary for the choice of a processing method based on economics rather than chemical engineering limitations. For example, at present, short-cooled processes for direct extraction of Pa^{233} from nitrate systems could not be operated with guaranteed success since most development work on Pa^{233} recovery from nitrate solution has been done on a tracer scale. Experiments with macro amounts of Pa^{231} are in progress to confirm promising tracer-scale results. The solubility of protactinium appears to be sufficiently high in nitric acid Thorex dissolver solutions to warrant consideration of direct processing. At least 90% of the protactinium can be adsorbed directly from this solution on unfired Vycor or on silica gel. Thus the Acid Thorex process could be used for direct recovery of U^{233} and thorium in short-cooled processing after protactinium adsorption or after complete decay of Pa^{233}

Table 7. Choice of Acid Extraction Process

Process	Cooling (days)	No. Cycles	Rate* (tonnes Th/day)	Waste Vol. (gal/tonne Th)
Interim 23	< 90	2, U	0.5	530
	> 120	1, U	1	530
Thorex	> 120	1, U and Th	0.5	53
Co-Ext. Thorex	< 90	1, U Pa and Th	0.2	~ 60

* For AEC conceptual plant; not applicable to plant optimized for thorium and uranium recycle processing.

but is not suitable for co-extraction of uranium, protactinium, and thorium since the protactinium is hydrolyzed in the acid-deficient feed. However, the low-decontamination Acid Co-Extraction process can probably be used to recover uranium, thorium, and protactinium simultaneously. The low decontamination factors for zirconium and niobium obtained in this process may not be significant since zirconium and niobium have low cross sections, and remote fuel fabrication is required in any event. The high-cross-section fission products are removed by factors of about 10^4 (see Sec 4.4).

The Interim 23 process, where only U^{233} is recovered, has a significant advantage over the Acid Thorex process in terms of maximum processing rate in a given set of critically safe equipment. With 5% TBP solvent, the thorium processing rate is 2 to 3 times that of the Acid Thorex process. But if the solvent concentration is limited to 2.5%, as is customary for criticality control, the processing rates are about the same.

The Acid Thorex process, where both uranium and thorium are recovered, has a distinct advantage over the Interim 23 process in terms of volume of high-level waste. Since the thorium remains in the aqueous raffinate with the fission products in the Interim 23 system, the evaporated waste volume is 10 times greater than for the Acid Thorex process.

Obviously, a final choice between the Interim 23 and Acid Thorex processes will depend on many variables. So long as thorium reactors are fueled with U^{235} and fresh

(unirradiated) thorium or U^{235} containing small amounts of recycled U^{233} and U^{232} and fresh thorium, direct fuel fabrication with minimal shielding is possible. In this case, the Interim 23 process will probably be preferable because of its potential quick recovery of U^{233} for short cooling times, and hence, low fuel amortization costs. However, when reactors are fueled with U^{233} , complete remote fuel fabrication will be required with either fresh or recycled thorium, and the Acid Thorex or Acid Co-Extraction processes may be preferable. Calculations by E. D. Arnold show that the specific activity of infinitely recycled thorium and infinitely recycled uranium will be approximately equal and hence that the shielding required for fabrication of U^{233} -thorium fuels will be increased by only 20% if recycled thorium is used. A complete re-evaluation of fuel cycle economics will be required when U^{233} fuels are to be fabricated and the additional results are available from the new technology now under development.

5.2 Processing Costs

A brief survey of the costs of recovery processes for irradiated thorium-uranium fuel was made with the assistance of A. D. Ryon, E. L. Nicholson, J. O. Blomeke and J. J. Perona (Table 8). For comparison purposes Acid Interim-23 (Fig. 18) and Acid Thorex (Fig. 19) flowsheets were drawn which use the same feed solution and represent nearly maximum throughput. The total volumetric capacities of the extraction columns were estimated by A. D. Ryon as 900 and 600 g/hr·ft² for the Acid Thorex and Acid Interim-23 flowsheets, respectively. This indicates Acid Interim 23 thorium capacity for thorium extraction 2.03 times greater than Thorex for a given column size. An evaluation of thorium processing in the conceptual AEC multipurpose fuel processing plant by E. L. Nicholson indicated that the plant capacity would be governed by the solvent system and that the Interim 23 process would have a capacity twice that for Thorex and that the difference in the cost of the fuel processing is not significant (Table 8). However, in this case the system is optimized for uranium recovery with the Purex process. A comparison of two plants with equal thorium processing capacity and optimized for the Acid Thorex or Acid Interim 23 processes showed an insignificant increase in capital and operating costs for the Acid Thorex process. The increase results

Table 8. Comparative Overall Cost of Acid Interim 23 and Thorex Processes in the AEC Conceptual Plant⁵¹

Either process will recover U²³³, which, based on 5% fuel, will be valued at \$750,000 (50 kg U²³³ at \$15 per gram in each tonne of thorium)

	Dollars per Metric Tonne Thorium	
	Acid Interim 23	Acid Thorex
Fuel Processing ^a	16,500	33,000
Waste Management ^b	9,500	1,900
	<hr/>	<hr/>
	26,000	34,900
Credit for Thorium ^c	---	11,000
	<hr/>	<hr/>
	26,000	23,900

^aBased on capacity for 1 tonne of thorium per day by the Interim 23 process, or 1/2 tonne per day by Thorex. Since it is optimized for uranium recovery by the Purex process it is not optimum for Thorex processing. Includes storage, head-end processing, solvent extraction, operation, utilities, amortization, etc., but not waste management.

^bSee Table 10.

^cBased on U. S. price of \$5 per lb thorium.

from amortization of larger solvent equipment required for the Acid Thorex process. Previous estimates⁵¹ have shown that the total cost of extraction equipment is only about 12% of the cost of the complete plant. Under these conditions the Thorex plant results in a much lower fuel processing cost (Table 9).

Estimates by J. O. Blomeke and J. J. Perona for management of the high-level wastes from Interim 23 and acidic Thorex processing were based on previous cost studies made for Purex and Thorex wastes⁵² (Table 10), Interim 23 processing is assumed in the first case with thorium remaining in the waste through final disposal. In the second case, recovery of thorium from Acid Interim 23 raffinate after 12 years of storage is assumed. Cost of the reprocessing of the solution for thorium recovery is not included.

The value of the thorium is assumed to pay for its recovery cost. The third case is for Acid Thorex. The raffinate volumes and compositions given in Figs. 18 and 19 were used as a basis for comparison. In all cases, the wastes were assumed to be evaporated, stored 12 years as liquids, converted to solids by pot calcination, stored for 18 years as solids in water-filled canals, shipped 1000 miles to a salt mine, and finally, disposed of permanently by burial in salt mines.

Both acid flowsheets being compared are at about the same level of development; they have resulted in excellent operation in laboratory equipment using tracer solutions but have not been evaluated at full-activity levels or in engineering equipment. Neither is sufficiently different from previously demonstrated processes (other than the chemistry of protactinium) that major operational difficulties would be expected.

Table 9. Comparative Overall Cost of Acid Interim 23 and Thorex Processes in Equipment Designed for Optimized Flowsheets^a

	Dollars per Metric Tonne Thorium	
	Acid Interim 23	Acid Thorex
Fuel Processing	16,500	18,500 ^b
Waste Management	9,500	1,900
	<u>26,000</u>	<u>20,400</u>
Credit for Thorium	---	11,000
	<u>26,000</u>	<u>9,400</u>

^aSame basis as for Table 8.

^b Allowances for solvent extraction equipment (12% of total charges) have been doubled to give a generous allowance for plant modifications.

Table 10. Waste Management Costs for Interim 23 and Acid Thorex Processes

	Cost (Dollars per tonne Thorium)		
	Acid Interim 23	Acid Interim 23 and Th Recovery	Acid Thorex
1. Raffinate evap	80	80	360
2. 12-yr interim liq storage	1940	1940	330
3. Raffinate evap	---	360	---
4. Reduction to solids	3210	520	520
5. 18-yr interim solids storage	3030	175	175
6. 1000-mile shipment	720	65	65
7. Disposal in salt mine	565	450	450
Totals	\$9500	\$3600	\$1900

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Session III
Paper 18

SEPARATION OF IMPURITIES FROM THORIUM BY EXTRACTION WITH MAGNESIUM
AND BY OXIDATION-REDUCTION REACTIONS IN A ZINC-SALT SYSTEM

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Separation of Impurities from Thorium by Extraction
with Magnesium and by Oxidation-Reduction Reactions
in a Zinc/Salt System*

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A method for the pyrometallurgical reprocessing of thorium-uranium fuel or blanket material and some pertinent basic data have been presented in previous publications¹⁻⁶. A flow diagram showing the steps involved is reproduced in Figure 1. Thorium forms a low-melting eutectic with magnesium which contains about 40 wt % thorium and melts at 585°C. The solubility of uranium in the eutectic is very small and at 650°C, $98 \pm 0.5\%$ of the uranium in a Th-1.0% U alloy is precipitated^{4,5}. Impurities such as yttrium, rare earth, alkali and alkaline earth metals concentrate in the magnesium while protactinium, chromium, iron, niobium, molybdenum and similar metals follow the uranium. The impurities which follow the magnesium may be extracted with KCl-LiCl eutectic, 44.4 wt % LiCl, containing 15 wt % MgCl₂. One purpose of this paper is to summarize data pertinent to this step of the process.

The physical separation of uranium from the Mg-Th solution and the recovery of the thorium by precipitation with hydrogen have been investigated by Murbach and coworkers⁷. The volume of uranium precipitate from a Th-1.0% U alloy is only about 0.6 ml

Fig. 1. Flow diagram for reprocessing Th-U fuel.

per liter of eutectic solution and some method of agglomerating the precipitate would be desirable. It has been shown that the addition of chromium results in the formation of an immiscible U-5% Cr-0.5% Th liquid phase at temperatures above 860°C ⁴. Metallic chromium may be added to the uranium concentrate as indicated in Figure 1, or the chromium may be introduced by contacting the concentrate with salt containing CrCl_2 . The latter method may result in the formation of finely dispersed chromium which should facilitate alloying of the uranium particles. The separated uranium or U-Cr alloy can be further purified by oxidation-reduction reactions in a KCl-LiCl/zinc system^{1,2}. If a high degree of separation of uranium from thorium is not desired a thorium-uranium fuel could be similarly processed and the magnesium extraction step eliminated. A disadvantage of this procedure is that all the thorium must be oxidized by ZnCl_2 or chlorine and transferred along with the uranium and any protactinium present to the salt phase. Impurities such as chromium, iron, molybdenum, niobium and in general metals more noble than zinc concentrate in the zinc phase. The zinc phase can be separated from the salt and discarded or the zinc distilled and reused and the impurities isolated in concentrated form. The uranium, thorium and protactinium can be recovered by contacting the salt with Zn-Mg alloy. By controlling the

amount of magnesium added some degree of separation of uranium from thorium can be achieved. The second purpose of this paper is to examine the phase relations involved in this separation and to present some new data on the equilibrium distribution of thorium and uranium between the zinc and salt phases.

Extraction of components from Mg-40% Th solutions with KCl-LiCl-15% MgCl₂ salt

As indicated in Figure 1 the decontamination of the Mg-Th solution might be achieved by means of a KCl-LiCl-MgCl₂ salt which is recycled between the Mg-Th solution and a Zn-Mg alloy. Alternatively the salt may be in mutual contact with both alloys. Components will transfer from one alloy to the other until the activities of the components in the two alloys attain equal values. Due to the very low solubilities and activities of components such as cerium and yttrium in zinc, transfer to the Zn-3% Mg phase is expected to occur until the concentration in the Mg-Th solution has reached a very low level. A higher degree of decontamination of the Mg-Th solution can thus be achieved with a given amount of salt. The more active components such as divalent rare earths, alkali and alkaline earth metals are expected to concentrate in the salt. It is to be expected that magnesium as well as some thorium will transfer to the Zn-Mg

solution. In the transport of a component from the Mg-Th to the Zn-Mg, the reaction at the Mg-Th/salt interface is

where M may be yttrium, cerium, neodymium or some other component and the reverse reaction occurs at the salt/Zn-Mg interface.

It has been shown in previous work that the chlorides of cerium, uranium, thorium and yttrium can be effectively reduced from KCl-LiCl salt in contact with zinc by the addition of magnesium¹. Some of these data are presented in Table I. On the assumption that the activity coefficient ratio for reaction 1 is constant, distribution coefficients K_d^{**} for a concentration of 15% MgCl_2 in the salt and 3% magnesium in the zinc were calculated for cerium, uranium and thorium. At temperatures below 700°C the solubilities of these elements in zinc are very small and in the case of cerium and yttrium the precipitate phases for the binary system are CeZn_{11} and YZn_{11} respectively. The effect of magnesium on the solubility of these compounds in zinc is not known, but is probably not too pronounced in a Zn-3% Mg solution. Therefore, for a saturated Zn-3% Mg solution the reaction, with yttrium may be written as

The additional transfer of yttrium to the saturated Zn-rich

Table I. Reduction of cerium, uranium and thorium from KCl-LiCl eutectic with Zn-Mg alloy

Temp. °C	Concentrations in salt		Concentrations in zinc		K_N^*	$\frac{\% M(s)/\% M(m)}{K_d}$	K_d^{**}
	% Mg	% M	% Mg	% M		K_d	
700	0.32	0.07 Ce	0.03	0.47 Ce	2.2×10^2	1.5×10^{-1}	6.2×10^{-3}
700	2.34	0.024 Ce	0.43	0.82 Ce	4.0×10^2	2.9×10^{-2}	3.4×10^{-3}
700	0.38	0.01 U	0.011	1.0 U	2.0×10^3	1.0×10^{-2}	6.9×10^{-4}
700	2.02	0.0028 U	0.27	1.0 U	6.9×10^3	2.8×10^{-3}	2.0×10^{-4}
500	2.02	0.0051 U	0.096	0.033 U	5.8×10^3	1.5×10^{-1}	2.4×10^{-4}
700	0.18	0.0037 Th	0.0145	0.28 Th	3.1×10^3	1.3×10^{-2}	4.4×10^{-4}

$$*K_N = \frac{N_M(m)}{N_M(s)} \left(\frac{N_{MgCl_2}(s)}{N_{Mg}(m)} \right)^{3/2} \approx \frac{\% M(m)}{\% M(s)} \left(\frac{\% Mg(s)}{\% Mg(m)} \right)^{3/2} \frac{1}{1.08}, \text{ where M represents cerium,}$$

uranium or thorium, m refers to the zinc-rich liquid phase and s to the salt phase.

Estimated distribution coefficient for salt containing 15 wt% $MgCl_2$ and zinc alloy containing 3.0 wt% Mg, $K_d^{} \approx 1.375/K_N$.

Table II. Distribution of components between KCl-LiCl-15% MgCl₂ and Mg-Th alloy*.

Temp. °C	Component M and number of equilibrations	% M in salt	% M in Mg-Th alloy	% M(s)/% M(m) K _d
700	Nd-1	0.12	0.011	11
600	Nd-1	0.066	0.028	2.4
700	Sm-1	0.12	<0.0002	>500
600	Sm-1	0.16	<0.0002	>500
700	Th-4	0.08	40	(2.0±0.3)×10 ⁻³
600	Th-2	0.07	40	(1.8±0.5)×10 ⁻³
700	Ce-2	**	—	2.5±0.1
800	Ce-5	—	—	1.9±0.1
600	Y-3	—	—	7.5±0.8
700	Pa-1	—	—	2.0×10 ⁻³
650	Pa-1	—	—	0.8×10 ⁻³

* The concentration of thorium in the alloy was 40 ± 2 wt%, and the salt consisted of 85 wt% KCl-LiCl eutectic (44.4 wt% LiCl) and 15 wt% MgCl₂.

** Radioactive tracers used in this and the following experiments tabulated, see reference 1.

Table III. Distribution of components between KCl-LiCl-
15% MgCl₂ and Zn-3% Mg alloy

Temp. °C	Component M	% M in salt	% M* in zinc	% M(s)/% M(m) K _d
700	Y	0.19	0.63	3.0×10^{-1}
600	Y	0.035	0.30	1.9×10^{-1}
700	Ce	0.046	0.87	5.3×10^{-2}
600	Ce	0.0045	0.50	3.5×10^{-2}
700	Nd	0.015	0.72	2.1×10^{-2}
600	Nd	0.0049	0.54	3.8×10^{-2}
700	Sm	0.75	0.032	23.5
600	Sm	0.68	0.042	16.0

* The 600°C solubility limit for yttrium, cerium, and neodymium were assumed to be 0.18, 0.13, and 0.13 respectively in calculating K_d.

solution will not change the activity of yttrium. Consequently relatively large amounts of yttrium may be transferred to the zinc alloy without affecting the ability of the alloy to reduce the concentration of yttrium in the salt. This is essential if the proposed scheme for decontaminating the Mg-Th solution is to be practical. The optimum concentration of magnesium in the Zn-Mg alloy is not known but on the basis of the mass action law and available thermodynamic data the effect of magnesium concentration on the residual yttrium or cerium in the salt will probably follow the trend shown in Figure II.

Experimentally determined distribution coefficients for various components in a $\text{KCl-LiCl-15\% MgCl}_2/\text{Mg-40\% Th}$ system are presented in Table II and some distribution coefficients for the same salt in contact with Zn-3% Mg are presented in Table III. Some of the data presented in Table II were determined in a previous investigation¹. The data for neodymium, samarium and thorium were obtained by a similar procedure except that radioactive tracers were not used. Because of analytical difficulties in analysing for samarium and neodymium in the presence of large amounts of thorium their concentrations in the Mg-Th phase were determined by a material balance. All equilibrations were carried out in tantalum

Fig. 2. Estimated residual MCl_3 remaining in $KCl-LiCl-15\% MgCl_2$ salt as a function of magnesium concentration in zinc alloy.

containers under an inert atmosphere. The data show that samarium is effectively extracted by the salt and is not reduced by the Zn-3% Mg alloy. Reduction of the components from the salt by the Zn-3% Mg alloy is appreciably more effective at 600°C than at 700°C. These data show that the minimum concentrations of yttrium, cerium, neodymium and samarium in the Mg-40% Th alloy which can be achieved by recycling the KCl-LiCl-15% MgCl₂ salt between this alloy and Zn-3% Mg at 600°C are approximately 50, 25, 20 and 8 parts per million respectively. These final concentrations assume that the Zn-3% Mg alloy is saturated with yttrium, cerium and neodymium. To further reduce the amount remaining in the Mg-Th alloy it must be equilibrated with clean salt.

Experiments involving a total charge of 1000 to 1500 grams with the two alloys in mutual contact with the salt are in progress. The results thus far obtained agree fairly well with the above data.

Separation of uranium from thorium by oxidation in a KCl-LiCl/zinc system.

Previous work on the oxidation of thorium and uranium in a KCl-LiCl/zinc system was confined to experiments in which the initial U/Th ratio in the zinc phase was approximately one. The transfer of these components to the salt phase was measured as step-wise additions of ZnCl_2 were made to the system. The results of these experiments showed that for the competing reaction

the value of K_N , the mole fraction ratio of U/Th in the salt divided by the mole fraction ratio of U/Th in the liquid zinc phase, remained nearly constant. The value of K_N for a number of equilibrations at 500°C was found to be within the range 1.0 to 4.5. Equilibrations carried out at 700°C gave a K_N value of 9.6 ± 2 .

At 500°C the solubilities of uranium and thorium in zinc are 0.033 and 0.022 wt % respectively. Solubilities for ternary zinc-rich U-Th-Zn alloys have not been determined. If these ternary alloys consist of two solid phases and a zinc-rich liquid phase, then at constant temperature and pressure the compositions of the phases remain constant as either uranium or thorium are added or removed (transferred to or from the

salt phase). If only two phases are present, one solid and one liquid, the composition of each phase can vary.

The two compounds $\text{Th}_2\text{Zn}_{17}$ and U_2Zn_{17} have similar crystal structures and extensive solid solubility may be possible. A U-Th-Zn alloy, 5.9 mole % U, 5.9 mole % Th, was prepared, examined under the microscope and found to be primarily one phase with only a very small amount of a second phase present. Consequently under equilibrium conditions it may be expected that in zinc-rich alloys the liquid will be in equilibrium with a single solid solution phase.

A number of equilibrations were carried out in sealed tantalum containers. The charge consisted of about 18 grams of KCl-LiCl eutectic, 0.2 to 4.0 grams of ZnCl_2 , 150 grams of zinc and 10 to 18 grams of thorium plus uranium. The U/Th ratio was varied from 0.02 to 0.82. Each charge was equilibrated in a rocking furnace for a minimum of 24 hours at 500°C , permitted to settle for four hours and quenched. The salt phase was analyzed for uranium and thorium. For five of the equilibrations the top portion of the zinc billet, which was free of suspended compound crystallites, was also analyzed for uranium and thorium. The ratio of U/Th in the ternary solid solution existing in equilibrium with the zinc-rich

liquid was determined from a material balance. The data obtained and the results of calculations based on these data are summarized in Table IV.

At the temperature of equilibration the zinc alloy in each case consisted of a zinc-rich liquid and a solid alloy phase. Consequently the equilibrium constant for the reaction,

can be described in terms of the activities of UCl_3 and ThCl_3 in the salt phase and either the activities of uranium and thorium in the solid alloy phase or in the zinc-rich liquid phase. Similarly there are two possible choices for determining the mole fraction ratio K_N . The ratio K_N^{I} was determined on the basis of the U/Th ratio in the solid alloy phase and K_N^{II} on the basis of the U/Th ratio in the zinc-rich liquid phase. The amount of uranium and thorium in the liquid phase is negligible compared to that in the solid alloy phase. Consequently K_N^{I} is equal to the wt % U/wt % Th in the salt divided by wt % U/wt % Th in the zinc. The values of K_N^{II} are in good agreement with previously reported values². However, the data obtained in this investigation show that the U/Th ratio in the zinc-rich liquid varies as this ratio is varied in the zinc alloy. The K_N values vary by a factor of about 3. This variation is probably

Table IV. Oxidation of uranium and thorium in a KCl-LiCl/zinc system at 500°C

Exp. no.	Salt analyses		Concentrations in zinc		I K _N	Zinc solution		II K _N	% of initial U found in salt
	% U	% Th	% U	% Th		% U	% Th		
3	0.25	3.77	0.22	9.9	3.0	0.0033	0.060	1.2	9
5	0.90	4.67	0.52	11.3	4.2	—	—	—	19
6	3.18	4.94	0.82	9.4	7.4	0.012	0.038	2.0	38
7	2.57	5.65	0.67	9.9	6.7	—	—	—	35
8	1.78	6.94	0.40	10.0	6.4	0.005	0.031	1.6	36
9	8.74	7.19	1.6	8.7	6.6	—	—	—	43
11	12.33	2.61	3.0	5.8	9.2	0.018	0.016	4.2	36
12	11.24	2.32	3.5	6.1	8.4	0.066	0.028	2.0	33

due to changes in the activity coefficients with concentration. It is apparent from these data that multiple equilibration or extraction techniques would be required to achieve a high degree of separation of uranium from thorium.

Acknowledgements

The equilibrations on the oxidation of uranium and thorium presented in Table IV were carried out by W. C. Robinson, Jr. W. C. Robinson, J. S. Klepfer and C. H. Dock assisted in performing the other experiments described. Chemical analyses were conducted by the analytical group under the direction of R. Z. Bachman and Dr. C. V. Banks.

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BOOK II

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Division of Technical Information

PROCEEDINGS OF THE
THORIUM FUEL CYCLE SYMPOSIUM

Gatlinburg, Tennessee
December 5-7, 1962

Sessions IV-VII

Book II

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Session IV
Paper 19

ENGINEERING PROPERTIES OF THORIUM-URANIUM COMPOUNDS
FOR USE IN THERMAL BREEDER REACTORS

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ENGINEERING PROPERTIES OF THORIUM-URANIUM COMPOUNDS FOR USE IN THERMAL BREEDER REACTORS

J. A. DeMastry, A. A. Bauer, and R. F. Dickerson

That thorium-232 is a fertile material which can, upon absorption of a neutron, transmute to uranium-233, a fissionable material, is well-known. There is little information, however, concerning the engineering properties of arc-cast thorium-uranium compounds for fuel application. Investigations in the field of uranium technology have shown the necessity of using compounds when elevated operating temperatures are desirable. It is also to be assumed that elevated temperature operations (above 1100 F) in thorium breeder reactors will necessitate the utilization of thorium-uranium compounds. The purpose of the paper is to describe briefly an investigation of the engineering properties of three cast thorium-uranium compounds $(\text{Th}_9\text{U})\text{C}$, $(\text{Th}_9\text{U})\text{C}_2$ and $(\text{Th}_9\text{U})\text{B}_4$.

These above mentioned compounds were chosen for study from a large number of potential fuel materials because of the following considerations: (1) high melting point, (2) low thermal-neutron-capture cross section (assuming the use of boron 11), (3) high thorium and uranium density, and (4) ease of preparation by casting.

Material and Specimen Preparation

The thorium-uranium compounds were prepared by arc melting. National Lead thorium was used as the base material. A spectrographic analysis of the thorium is given below.

	<u>Al</u>	<u>B</u>	<u>Be</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mn</u>	<u>Mo</u>	<u>Ni</u>	<u>Ti</u>	<u>Si</u>	<u>Zr</u>
NLCO Th.	20	3	350	30	2	40	4	2	10	8	20	50

All other metallics were below the limit of detection. Chemical analysis showed that the carbon content was 0.017 w/o and the nitrogen content 0.007 w/o. Biscuit uranium, high purity boron, and spectrographic carbon were used as alloying additions.

Buttons of ThC, ThC₂, and ThB₄ with 10 mole per cent uranium added were prepared by arc melting stoichiometric proportions of the elements. The buttons were then drop cast into graphite molds 3/8 in. in diameter and 3 in. long. These castings were generally satisfactory, although the borides tended to show cracks due to rapid cooling rates. This tendency to crack was reduced by the use of a heated mold during casting.

Metallography and Hardness Measurements

Pieces were cut from cylinders for metallographic examination and hardness measurements. Metallographic examination of the carbides was difficult because of their extreme reactivity with water and their tendency to stain etch in air. Typical microstructures of (Th₉U)C₂ and (Th₉U)B₄ compounds are shown in Figure 1. The (Th₉U)C₂ as shown is single phase while the (Th₉U)B₄ compound shows traces of ThB₆. Metallographic examination was used to determine the suitability of a particular casting for study. Only material showing clean single phase or nearly single phase structures were used.

100X

RM-17043

Structure is single phase.

100X

RM-18331

This compound is essentially one phase with traces of ThB_6 .

FIGURE 1. TYPICAL MICROSTRUCTURE OF $(Th_9U)X$ COMPOUNDS

Hardness measurements were taken on the metallographically prepared specimens with a Knoop hardness tester using a 100-g load. The results of these measurements are shown in Table 1. The boride compound is extremely hard with the monocarbide and dicarbide exhibiting much lower hardness values.

Oxidation Behavior

The oxidation behavior of all three compounds was studied at temperatures between 700 and 2300 F. All tests for the carbides were performed in dry air because of their sensitivity to moisture. The boride was not affected by the moisture content of the air.

The results of oxidation tests of the $(\text{Th}_9\text{U})\text{C}$ compound are shown in Figure 2. This compound underwent rapid oxidation at all temperatures investigated and in most cases was completely oxidized after less than 24 hours exposure. The $(\text{Th}_9\text{U})\text{C}_2$ compound (Figure 3) behaved in essentially the same manner.

The $(\text{Th}_9\text{U})\text{B}_4$ compound behaved quite differently. At temperatures below 1900 F a dark oxide appeared on the surface of the material. This oxide was adherent and formed on the compound surface with no evidence of intergranular corrosion being observed. During testing at 2000 F a greenish, glassy surface oxide formed. This oxide coating was strongly adherent and protective. The limited results shown in Figure 4 indicate that this oxide formed at sometime below 6 hours and that after formation only negligible weight gains occurred.

TABLE 1. ROOM TEMPERATURE HARDNESS OF
THORIUM-URANIUM COMPOUNDS

Compound	Knoop Hardness (100-g load)
$(\text{Th}_9\text{U})\text{C}$	519
$(\text{Th}_9\text{U})\text{C}_2$	456
$(\text{Th}_9\text{U})\text{B}_4$	2663

FIGURE 2. OXIDATION BEHAVIOR OF (Th₉U) C

N-94847

FIGURE 3. OXIDATION BEHAVIOR OF $(Th_9U)C_2$

N-94848

FIGURE 4. OXIDATION BEHAVIOR OF $(Th_9U)B_4$

N-94849

Fracture Strength

The fracture strength was determined for all three compounds at 76, 1200 and 1800 F in compression. The results are shown graphically in Figure 5. The boride exhibited a steady decrease in fracture strength with increasing temperature while both of the carbides showed increased strength at 1800 F as compared with the fracture strength at either 76 or 1200 F. This is typical of a brittle material which becomes slightly ductile with increasing temperature. Still higher testing temperature should produce higher fracture strengths. No measurable ductility was observed even in the monocarbide which exhibited the largest increase in fracture strength.

Thermal Expansivity and Conductivity

The linear thermal expansion behavior of $(\text{Th}_9\text{U})\text{C}$ and $(\text{Th}_9\text{U})\text{B}_4$ is essentially the same up to 800 F. Above this temperature the thermal expansion coefficient of the boride is greater than that of the monocarbide. The $(\text{Th}_9\text{U})\text{C}_2$ compound expands more rapidly with increasing temperature over the entire temperature range than either of the other compounds studied. Thermal expansion values are given graphically in Figure 6.

Thermal conductivities are shown in Figure 7. The results show that the conductivity of all three compounds increases with temperature up to 1000 C and is significantly greater than that for UO_2 . The conductivity of the boride approaches that of unalloyed thorium at 1000 C.

FIGURE 5. FRACTURE STRENGTH OF THORIUM-URANIUM
COMPOUND

N-94850

FIGURE 6. THERMAL EXPANSION OF THORIUM-URANIUM COMPOUNDS

N-94852

FIGURE 7. THERMAL CONDUCTIVITY OF THORIUM-URANIUM COMPOUNDS, THORIUM AND UO₂

N-94851

Discussion

The results summarized above indicate that the borides and carbides are promising materials for thermal breeder application. The boride is, of course, handicapped in use since only the B_{11} isotope can be utilized. All three materials have acceptable thermal conductivity, are relatively easy to prepare, and possess significant compressive strength. Further studies, including irradiation tests, are necessary for a complete evaluation of their potential.

Session IV
Paper 20

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DEVELOPMENT OF THORIUM-URANIUM AND THORIUM-URANIUM
BASE ALLOYS FOR BREEDER APPLICATIONS

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INTRODUCTION

The conservation and economic utilization of nuclear fuels leads to the consideration of breeder reactors for the generation of nuclear power. Breeding can be accomplished either through the uranium 238-plutonium 239 cycle or through the thorium 232-uranium 233 cycle. However, in a thermal reactor, the possibility of achieving breeding clearly lies with the thorium-uranium cycle. The theoretical breeding gain is 0.31 for this cycle and only 0.03 for the uranium-plutonium cycle. These values represent the number of excess neutrons available for the accumulation of the fuel species after allowing for the neutrons required to replace the fuel burned and for the neutrons required to maintain the fission reaction. Naturally, this represents a maximum value since neutrons will be absorbed by structural components of the reactor system.

Despite the distinct advantages offered by the thorium-uranium fuel cycle for breeding with thermal and epithermal neutrons, thorium-uranium-base fuels have received little consideration. This lack of interest stems to a considerable extent from inventory and handling problems in reconstituting the fuel which will have a high degree of radioactivity associated with it necessitating remote fabrication. It is felt that this problem may eventually be encountered with uranium-plutonium fuels as the less desirable plutonium isotope concentrations increase during recycling. Whether or not this happens, the day that active consideration is given to the thorium-uranium fuel cycle will undoubtedly be speeded if significant advantage in fuel performance can be demonstrated for thorium-uranium as compared with uranium-base fuels.

There are indications that thorium-uranium fuels are indeed superior to uranium and alpha-phase uranium alloys.⁽¹⁾ Thorium alloys containing 5 to 20 w/o uranium appear to resist swelling during irradiation to temperatures of at least 600 and possibly 680 C.^(2,3,4,5) This is on the order of 200 C higher than the swelling temperature for alpha-phase uranium alloys based on American experience.

One might expect considerable improvement in irradiation performance for thorium-uranium alloys. Thorium possesses a face-centered cubic structure which is less susceptible to radiation embrittlement than either the orthorhombic alpha-uranium structure or the body-centered cubic structure of gamma-phase stabilized uranium alloys. Thorium, being cubic in structure and exhibiting no phase changes at conceivable reactor operating temperatures, is also not expected to undergo either the anisotropic growth or bumping and warping exhibited by uranium during irradiation and thermal cycling.

Based on the potential advantages of fuel irradiation performance afforded by thorium-uranium fuels a study was undertaken to investigate variables which might affect and also be controlled to improve this performance. Two factors received principal consideration as means of improving fuel performance. Briefly these involved the following reasoning.

(1) Thorium-uranium alloys consist of uranium dispersed in a thorium matrix. Since thorium is potentially more resistant to irradiation damage than uranium optimum behavior should be achieved if the uranium particles are small enough that the fission fragments lodge

in the thorium rather than the uranium, and also are uniformly dispersed so that damage to the thorium is uniform. Furthermore, it is regarded as desirable to keep the uranium in particle form. The uranium tends to form at grain boundaries, and if the uranium becomes continuous the danger exists that the alloy will exhibit the irradiation behavior of uranium.

(2) Increased resistance to radiation swelling can be imparted to the fuel by alloying to increase strength. Increased strength can be imparted in several ways. One can alloy to increase the strength of the thorium matrix or the uranium particles can be alloyed to increase their strength and fission-gas retention capabilities. Strengthening can also be accomplished by additions which are essentially insoluble in either phase but which precipitate in a fine dispersion to produce hardening. Zirconium and yttrium are viewed as potential solid-solution strengtheners and carbon and possibly beryllium as interstitial strengtheners of alpha thorium. Molybdenum and niobium, which are gamma-uranium phase stabilizers, and which exhibit limited solubility in thorium, are regarded as elements which will both strengthen and improve the radiation behavior of the uranium phase. Aluminum forms aluminides with both thorium and uranium and, if finely dispersed, can provide dispersion hardening.

In the studies performed a thorium-10 w/o uranium composition was selected as the base composition for investigation. A 5 w/o uranium composition was regarded as the minimum addition that would be considered for a reactor fuel and, particularly if alloying additions are to be considered, it was felt that some higher uranium composition would be of wider interest and potential application. Consequently, while other uranium concentrations were investigated, major comparisons are based on thorium alloyed with 10 w/o uranium.

Casting Studies

Binary Alloys

Thorium-5, -10, -15, and -20 w/o uranium alloys were prepared both by arc and by induction melting and casting. Duplicate alloys were prepared from Ames and from iodide thorium with biscuit uranium.

Finger bars were produced by arc melting buttons eight times on a copper crucible with a tungsten-tip electrode under a helium atmosphere and then arc casting into 1/2 in. diameter, 3 in. long bars. Vacuum-induction melting was accomplished in zirconia crucibles. The heats were cast into graphite molds to form 1/2 in. diameter, 5 in. long rods.

Spectrographic analyses of the Ames and iodide thorium are given below.

Analysis, ppm

	<u>Al</u>	<u>B</u>	<u>Be</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Mn</u>	<u>Ni</u>	<u>Si</u>	<u>Zu</u>
Ames	5	4	100	5	10	5	100	1	1	5	100	--
Iodide	10	0.5	---	5	--	2	5	4	--	2	13	3

All other metallics were below the limits of detection. The Ames material is seen to have a significantly higher metallic impurity content than the iodide material.

Wet-chemical and vacuum-fusion analyses of cast thorium-10 w/o uranium alloys are presented below:

	Analysis, ppm		
	Carbon	Nitrogen	Oxygen
Induction-melted iodide thorium	120	10	1660
Induction-melted Ames thorium	770	80	1560
Arc-melted iodide thorium	190	90	680
Arc-melted Ames thorium	710	90	1590

It can be seen that the carbon content of the Ames material is high compared with that of the iodide thorium. The oxygen content of the Ames material is also higher than that of the iodide materials, although this is not quite as obvious. It was found that the induction-melted iodide alloy apparently picked up oxygen from the zirconia crucible during melting. This was deduced from the fact that both induction melted alloys analyzed 100 ppm of zirconium spectrographically whereas before melting the zirconium content was negligible.

The type of thorium used in preparing alloys had no significant effect on the cast microstructure except for the greater number of thorium-oxide inclusions present in induction cast alloys and in alloys prepared from the Ames thorium.

The technique of casting had a much greater effect, particularly in alloys containing greater than 5 w/o uranium. At this lower level apparently much of the uranium is either retained in solid-solution, greater than 5 w/o uranium being soluble in alpha-thorium at elevated temperatures (see Figure 1) or else the uranium phase is so finely dispersed as not to be readily visible. However, at the higher levels differences are a product of differences in cooling rate during solidification, more rapid cooling rates being experienced by the arc-cast

FIGURE 1. THORIUM-URANIUM CONSTITUTIONAL DIAGRAM

TABLE 1. DENSITIES OF ARC-MELTED
THORIUM-URANIUM ALLOYS^(a)

Alloy Composition	Density, g/cm ³	
	Iodide Thorium Alloys	Ames Thorium Alloys
Thorium	11.71	11.60
Thorium-5 w/o Uranium	11.88	11.79
Thorium-10 w/o Uranium	12.10	12.01
Thorium-15 w/o Uranium	12.33	12.30
Thorium-20 w/o Uranium	12.58	12.59

(a) Cold Reduced 80 per cent by swaging prior to measurement.

alloys. Arc-cast alloy structures are shown in Figures 2a through c. The amount of uranium phase increases with uranium content but the uranium remains in a dispersed form. However, in the induction cast alloys the uranium precipitates at the grain boundaries and tends to become continuous. Figure 2d shows an induction cast 20 w/o uranium alloy microstructure, at which composition this tendency is most obvious. It was found that the continuity of the uranium grain boundary phase could be destroyed in the thorium-10 w/o uranium alloy by heating to 1000 C for 1 hr and water quenching. This heat treatment apparently led to spheroidization of the uranium phase, although the uranium particles still retained their grain-boundary outline form.

While the type of thorium used in preparing the alloys had no significant effect on microstructure, there were measurable effects both on density and hardness.

Density measurements appear in Table 1. The density of the iodide thorium is close to the theoretical X-ray density of 11.72 gm/cm³. The lower density of the Ames material is accounted for by the presence of ThO₂ inclusions resulting from the higher oxygen content of the Ames thorium. At higher uranium contents this effect becomes negligible being overshadowed by the density increment due to the denser uranium addition. A plot of density versus atomic per cent composition was linear over the range studied with minor deviations being associated with variations in nominal composition.

Hardness was also sensitive to the grade of thorium employed in alloy preparation. The higher impurity content of the Ames thorium,

particularly carbon, is regarded as responsible for this dependence. This aspect of alloy behavior will be discussed in more detail in a later section of this paper.

Ternary and Quaternary Alloys

Alloys containing various alloy additions were prepared by the same techniques used for the binary alloys. The basic additions to the thorium-10 w/o uranium alloy composition which received the most study were 1.5 w/o molybdenum, 2 w/o niobium, 10 w/o zirconium, 10 w/o zirconium plus 2 w/o niobium, and 0.1 w/o beryllium. Variations of these compositions were also studied along with material containing additions of carbon, aluminum, and yttrium.

The addition of 1.5 w/o molybdenum to the thorium-10 w/o uranium alloy had no significant effect on the as cast microstructure of the alloy. The effect of a 2 w/o niobium addition was slightly more pronounced. An increase in the amount of second phase was observed, indicating, at least in part a decrease of uranium solubility in the alpha and beta thorium phases. The microstructure of the arc-cast thorium-10 w/o uranium-2 w/o niobium is shown in Figure 2e. The as-cast structure of the thorium-10 w/o uranium-10 w/o zirconium alloy is shown in Figure 2f. It shows that small amounts of a uranium-rich phase exist in the grain boundaries as well as within the grains. The structure of this alloy can be varied considerably; heat treatment at 1000 C for 1 day yields a two phase structure containing a much greater amount of the uranium-rich phase as illustrated in Figure 2g. The thorium-10 w/o uranium-10 w/o zirconium-2 w/o niobium alloy exhibited a microstructure similar to that of the thorium-10 w/o uranium-10 w/o zirconium alloy.

500X

RM11498

(a) Thorium-5 w/o Uranium as Arc Cast,
Iodide Thorium

250X

RM11502

(b) Thorium-10 w/o Uranium As Arc Cast,
Iodide Thorium

250X

RM11523

(c) Thorium-10 w/o Uranium As Induction
Cast, Ames Thorium

500X

RM11530

(d) Thorium-20 w/o Uranium as Induction
Cast, Iodide Thorium

750X

RM12145

(e) Thorium-10 w/o Uranium-2 w/o Niobium as Arc
Cast, Iodide Thorium

250X

RM12149

(f) Thorium-10 w/o Uranium-10 w/o Zirconium
as Arc Cast, Iodide Thorium

FIGURE 2. MICROSTRUCTURES OF THORIUM-URANIUM ALLOYS

250X

RM14791

(g) Thorium-10 w/o Uranium-10 w/o Zirconium as Induction Cast, Heated at 1000 C for 1 Day and Water Quenched, Iodide Thorium

750X

RM15496

(h) Thorium-10 w/o Uranium-0.1 w/o Beryllium as Arc Cast, Ames Thorium

750X

RM16528

(i) Thorium-10 w/o Uranium-0.05 w/o Aluminum as Arc Cast, Ames Thorium

750X

RM12373

(j) Thorium-10 w/o Uranium Arc Cast, Cold Reduced 80% Longitudinal Section, Iodide Thorium

750X

RM12376

(k) Thorium-20 w/o Uranium Arc Cast, Cold Reduced 80% Longitudinal Section, Iodide Thorium

750X

RM12914

(l) Thorium-10 w/o Uranium Arc Cast, Cold Reduced 90%, and Annealed 1 Week at 800 C

FIGURE 2. (CONTINUED)

The structure produced by alloying thorium-10 w/o uranium with 0.1 w/o beryllium and 0.5 w/o aluminum are shown in Figures 2h and 2i, respectively. Beryllide and aluminide phase particles apparently form in conjunction with the uranium phase at the grain boundaries.

Working and Annealing Behavior

All of the alloys were satisfactorily hot rolled from 1/2 in. round bars to 0.2 in. sheet at 815 C (1500 F). This sheet was also cold reduced 90 per cent although all ternary and quaternary alloy material exhibited edge cracks which formed between 20 and 60 per cent cold reduction.

Cold- and hot-worked structures of the alloys were found to be essentially determined by the cast structure. If the cast structure contained a random dispersion of uranium particles, working did not appreciably alter this, although large reductions did cause elongation of the particles. If the cast structure contained uranium at the grain boundaries, working emphasized the already elongated particles, and a uranium stringered structure resulted. Thus stringering was more pronounced in the induction-cast and high-uranium alloys. Microstructures illustrating this general behavior are shown in Figures 2j and 2k, respectively.

Table 2 shows the effect of cold work and annealing on the hardness of hot rolled thorium-uranium alloys. With the exception of the alloys containing zirconium, alloys prepared from Ames thorium were harder and work hardened more rapidly than alloys prepared from iodide material.

TABLE 2. THE EFFECT OF COLD WORK AND ANNEALING
ON THE HARDNESS OF HOT-ROLLED THORIUM-
URANIUM ALLOYS, VHN (10 kg LOAD)

Alloy Content, a/o, Balance Thorium	Type of Thorium	Melting Method	Percentage Cold Reduction				Annealed 15 min at 700 c ^(a)	725 c ^(b)
			0	60	80	90		
5 U	Iodide	Arc	107	123	123	134	95	---
10 U	Iodide	Arc	103	130	135	143	114	84
10 U	Ames	Arc	122	151	159	177	---	---
15 U	Iodide	Arc	98	138	138	157	116	---
20 U	Iodide	Arc	105	141	150	157	116	---
10 U	Ames	Induction	123	153	159	175	125	92
10 U	Iodide	Induction	94	121	128	138	113	89
10 U-1.5 Mo	Ames	Induction	137	157	171	187	147	148
10 U-2 Nb	Ames	Induction	129	139	145	157	128	122
10 U-2 Nb	Iodide	Induction	110	130	144	148	---	---
10 U-10 Zr	Ames	Induction	144	171	192	198	144	142
10 U-10 Zr	Iodide	Induction	153	187	199	218	---	---
10 U-10 Zr-2 Nb	Ames	Induction	149	169	182	203	143	146

(a) After 80 per cent cold reduction.

(b) After 90 per cent cold reduction.

FIGURE 3. HOT HARDNESS OF THORIUM-URANIUM BASE ALLOYS.

This higher hardness is apparently due to the comparatively high carbon concentration in the Ames thorium. In the case of alloys containing zirconium those prepared using Ames thorium were softer. It is believed that the formation of ZrC decreased the solid-solution hardening effect of both carbon and zirconium, thus yielding an alloy softer than the iodide base thorium-uranium-zirconium.

The effect of annealing on the hardness of cold-worked thorium-uranium alloy can be seen in Table 2. With increased annealing times hardness values dropped to minimum values which were maintained upon further annealing. Microstructural examination of these alloys in conjunction with the hardness measurements indicated that recovery but not complete recrystallization had occurred. Annealing at higher temperatures was found to be required for recrystallization. A thorium-10 w/o uranium specimen recrystallized by annealing for 1 week at 800 C is shown in Figure 21; it exhibits a duplex grain size.

Hot Hardness

Hot hardness measurements were used for preliminary evaluation of the high temperature strength of various thorium-uranium-base alloys.

As-cast, polished specimens were subjected to a load of 730 g at various temperatures up to 900 C. A Vickers indenter was used and the indentations were measured after the specimens had cooled.

The results of the hot hardness tests are given in Table 3 and Figure 4. Carbon is one of the more potent strengtheners of thorium.

TABLE 3. HOT HARDNESS OF AS-CAST THORIUM-BASE ALLOYS

Composition (Balance Th), w/o	Melting Method	Thorium	Vickers Hardness Number, kg/mm ²						
			25 C	200 C	400 C	500 C	600 C	800 C	900 C
5 U*	Arc	Ames	139	102	81.6	62.8	45.4	24.0	14.1
	Arc	Iodide	100	76.5	58.6	51.2	41	--	--
	Induction	Ames	134	100	73.9	65.4	45.1	9.0	--
10 U*	Arc	Ames	137	96.6	76.4	65.5	45.4	22.1	11.2
	Arc	Iodide	111	--	71.5	59.5	44.0	17.1	10.6
	Induction	Ames	141	102	76.2	62.2	47.3	24.6	--
	Induction	Iodide	104	80.5	66.3	55.4	38.8	18.8	11.8
15 U*	Arc	Ames	145	--	82.3	65.8	39.2	10.6	4.2
	Arc	Iodide	115	90.1	67.9	56.2	34.4	13.6	--
20 U*	Arc	Ames	148	120	90.0	68.6	46.2	14.0	--
	Arc	Iodide	119	92.2	73.2	57.0	43.3	--	--
	Induction	Ames	148	101	78.5	66.0	41.8	15.3	10.2
	Induction	Iodide	118	102	82.5	59.3	37.5	12.5	9.2
10 U-1.5 Mo	Arc	Iodide	72.9	59.4	54.4	48.4	41.1	22.4	--
	Induction	Ames	121	99.6	82.0	77.3	73.3	43.3	30.4
10 U-2 Nb	Arc	Iodide	89.4	71.3	60.7	57.2	42.7	20.3	--
	Induction	Ames	112	88.0	78.0	74.3	58.7	30.1	23.4
	Induction	Iodide	84.7	65.2	59.4	57.6	54.1	33.1	20.4
10 U-10 Zr	Arc	Iodide	161	152	128	116	54.5	22.2	--
	Induction	Ames	173	152	141	120	68.7	23.2	14.5
	Induction	Iodide	172	142	133	125	69.7	23.9	13.4
10 U-10 Zr-2 Nb	Arc	Iodide	138	119	110	96.4	73.2	17.2	8.5
	Induction	Ames	149	125	117	106	78.6	27.9	18.0
10 U-20 Zr	Arc	Iodide	153	--	140	109	42.4	10.7	7.1
	Induction	Ames	159	157	146	126	46.6	19.0	9.7
10 U-25 Zr	Arc	Ames	153	191	191	129	38.0	6.9	3.4
	Arc	Iodide	160	--	165	113	39.2	11.8	7.5
	Induction	Ames	161	171	186	130	40.7	14.7	8.1
	Induction	Iodide	171	157	131	129	46.7	17.3	9.0

TABLE 3. (Continued)

Composition (Balance Th), w/o	Melting Method	Thorium	Vickers Hardness Number, kg/mm ²						
			25 C	200 C	400 C	500 C	600 C	800 C	900 C
10 U-0.1 Be	Arc	Ames	110	91.0	76.0	73.8	69.1	27.3	17.6
10 U-0.2 Be	Arc	Ames	110	--	91.2	71.8	62.3	29.6	17.0
10 U-0.2 C	Arc	Ames	24.7	137	114	101	67.3	22.5	14.0
10 U-0.5 Al	Arc	Ames	128	125	106	94.1	75.7	26.9	18.3
10 U-2 Mo	Arc	Ames	91.2	74.2	58.3	55.7	49.3	17.0	11.4
10 U-4 Nb	Arc	Ames	96.3	82.1	68.7	62.9	56.6	21.3	14.6
10 U-2 Nb-0.2 C	Arc	Ames	149	--	88.4	74.0	58.0	19.8	17.3
10 U-1.5 Mo-0.2 C	Arc	Ames	239	139	103	89.9	64.7	24.3	14.5
10 U-10 Y	Arc	Ames	90	91.2	78.4	69.6	66.1	22.4	13.8

* Tested in the hot rolled condition.

For this reason the alloys prepared from Ames thorium, which contains more carbon than iodide thorium, were generally harder. Comparison of the hot hardness values obtained on thorium-10 w/o uranium and thorium-10 w/o uranium-0.2 w/o carbon alloys (arc-melted using Ames thorium) shows that at 500 C, the alloy containing the carbon addition has nearly twice the hardness of the thorium-10 w/o uranium alloy. Above 600 C this hardness difference decreases. Apparently the lattice strain introduced by the interstitial carbon atoms at low temperatures is relieved by expansion of the thorium lattice as the temperature increases.

Increasing uranium content did not produce any high temperature hardening effect. In fact, at 800 C and 900 C, some decreases in hardness appeared to occur as the uranium content increased. Uranium is much softer than thorium at these temperatures, and would be expected to decrease the bulk hardness as the volume of uranium is increased.

The thorium-10 w/o uranium alloys containing 1.5 w/o molybdenum and 2 w/o niobium were softer than the corresponding binary alloys at temperatures up to 600 C. At higher temperatures these additions produce strengthening, especially in the induction melted Ames material. Most of the niobium or molybdenum concentrates in the uranium phase, producing stronger uranium particles which at high temperatures may act as dispersion hardeners. Slight increases in the molybdenum or niobium content of these alloys did not significantly improve the hot hardness above 600 C. Similarly the addition of 0.2 w/o carbon to the thorium-uranium-molybdenum and thorium-uranium-niobium alloys did not significantly improve hardness above 600 C.

Additions of zirconium to thorium-10 w/o uranium were very effective in increasing hot strength at temperatures of 600 C and below. However, at higher temperatures this effect was lost. The strengthening effect of zirconium is believed to arise primarily from solid-solution hardening of the thorium matrix, although there may be minor dispersion hardening effects.

Minor additions of aluminum and beryllium were very effective in improving the hot strength of the thorium-10 w/o uranium alloy; however these alloys soften near 600 C. The decrease in strength with temperature is gradual and at the high temperatures these alloys have greater strength than the zirconium containing alloys. The beryllium and aluminum form compounds with both the uranium and thorium and thus may harden by a dispersion mechanism, but solid-solution hardening may also contribute significantly to the increased hardness particularly in the case of beryllium.

The addition of 10 w/o yttrium to thorium-10 w/o uranium proved beneficial. The hardness drop with increasing temperature was gradual; however above 600 C the hardness was not significantly higher than that of the comparable thorium-10 w/o uranium alloy. Strengthening at the lower temperatures is believed to be due to solid solution hardening.

Tensile Tests

Tensile specimens were prepared from induction-melted, 1/2 in. diameter rod which was hot rolled to 50 mil thick flats. The rolled material was stress relieved by heating in vacuum for 24 hours at 1000 C

followed by a furnace cool. The sheet was machined into tensile specimens 30 mils thick with a 1-in. test section 1/2 in. wide.

The tensile tests were performed at room temperature, 600 and 700 C, and a strain rate of 0.003 in/in/min. High temperature tests were performed in a furnace under a vacuum of less than 0.5 microns.

The results of the tensile tests are reported in Table 4. Thorium is included as a standard for comparison. The thorium-uranium alloys were investigated to provide data on the variation of tensile strength with uranium content while other alloys were studied generally because of their superior hot-hardness characteristics.

At room temperature it is noticed that the addition of uranium to thorium reduces the yield strength although there is some improvement in tensile strength. The addition of 1.5 w/o molybdenum or 2 w/o niobium to thorium-10 w/o uranium has little effect on the tensile properties of the base alloy. However the addition of 10 w/o zirconium or 10 w/o zirconium-2 w/o niobium increases the yield strength of the thorium-10 w/o uranium alloy by 30 and 45 per cent respectively, while the tensile strengths are increased by about 40 and 60 per cent respectively.

At 600 and 700 C it is noticed that in general the addition of uranium to thorium increases the tensile strength; however, when as much as 20 w/o uranium is added, the tensile strength drops to about the same value as pure thorium. The thorium-10 w/o uranium-1.5 w/o molybdenum and -2 w/o niobium alloys did not show behavior that was significantly different from the thorium-10 w/o uranium alloy despite the fact that the

TABLE 4. TENSILE PROPERTIES OF THORIUM-BASE ALLOYS

Composition (Balance Th), w/o	Test Temp.	0.2 % Offset Yield, psi	Tensile Strength, psi	Elongation %, in/in
Ames Thorium	Room	34,900	37,700	13
5 U	Room	27,900	39,300	23
10 U	Room	26,900	37,700	13.5
20 U	Room	32,100	42,000	30
10 U-1.5 Mo	Room	26,400	41,000	15
10 U-2 Nb	Room	22,900	35,400	22
10 U-10 Zr	Room	35,200	53,200	12
10 U-10 Zr-2 Nb	Room	39,200	60,400	14
Ames Thorium	600 C	13,800	15,700	26
5 U	600 C	11,600	15,950	44
10 U	600 C	13,800	17,970	41
20 U	600 C	11,200	15,160	50
10 U-1.5 Mo	600 C	11,220	17,700	43
10 U-2 Nb	600 C	12,550	18,000	37
10 U-10 Zr	600 C	19,600	28,400	44
10 U-10 Zr-2 Nb	600 C	19,200	25,640	48
Ames Thorium	700 C	4,280	8,090	58
5 U	700 C	6,590	11,700	51
10 U	700 C	8,800	10,300	44
20 U	700 C	6,700	8,170	58
10 U-2 Nb	700 C	8,400	10,800	66
10 U-10 Zr	700 C	15,400	20,000	39
10 U-10 Zr-2 Nb	700 C	12,100	13,910	77
10 U-0.1 Be	700 C	8,610	11,200	47

hot hardness of these alloys is considerably higher than the base alloy at 600 and 800 C. The addition of 10 w/o zirconium to thorium-10 w/o uranium led to the greatest increases in strength, in fact the 700°C tensile strength was nearly doubled by this addition. The thorium-10 w/o uranium-10 w/o zirconium-2 w/o niobium alloy also showed significant increases in strength over that of the thorium-10 w/o uranium alloy.

Creep Tests

Creep tests were performed using tensile-type specimens. Strain was recorded periodically by use of a ruled platinum-strip strain gage which was attached to the test section of the tensile specimen. A vacuum of less than 0.5 microns was maintained within the creep furnace during the test period. Examination of the test specimens showed that no appreciable oxidation of the specimen surface occurred during test.

The results of the creep tests are shown in Figures 4, 5, 6 and 7 in which the secondary creep rate is plotted as a function of stress at 600 and 700 C. Each point plotted represents the result of one test.

Of the binary thorium-uranium alloys tested (Figure 4 and 5) the 5 w/o uranium alloy exhibited the lowest strain rate. The creep resistance of thorium-uranium alloys diminishes as the uranium content is increased from 5 to 20 w/o. This effect is most probably due to the uranium which, in the induction melted alloys, resides mainly in the grain boundaries. At these high temperatures the uranium is much softer than the matrix material. Thus intergranular flow is enhanced by increasing the uranium content, and creep resistance diminishes.

The strongest ternary alloys in creep (Figures 6 and 7) contained additions of 0.1 w/o beryllium, 1.5 w/o molybdenum or 2 w/o niobium. The beryllium containing alloy showed the lowest creep rate at both 600 and 700 C, in agreement with hot hardness data; however tensile data at 700 C did not indicate high strength in comparison with other alloys. This comparatively excellent creep performance is probably due to dispersion hardening effected by the formation of small amounts of thorium and uranium beryllides. The unimpressive hot tensile strength of this alloy indicates that this hardening mechanism is more effective at low strain rates.

The thorium-10 w/o uranium alloys containing 1.5 w/o molybdenum and 2 w/o niobium also exhibited superior creep resistance, their creep resistance being significantly greater than that of the thorium-10 w/o uranium alloy. Apparently the presence of higher strength uranium phase particles in the grain boundaries is more effective than unalloyed uranium in the reducing creep of the thorium. The superior creep performance of the 1.5 w/o molybdenum and 2 w/o niobium alloys is generally indicated by their hot hardness behavior but not by their hot tensile properties indicating that these alloys, like the beryllium containing alloy, exhibit increased strength at low strain rates.

The thorium-10 w/o uranium alloys containing -10 w/o zirconium and -10 w/o zirconium-2 w/o niobium showed disappointing creep properties despite the fact that they possess the highest yield and ultimate strengths of the alloys tested at 600 and 700 C. The failure of these zirconium-containing alloys to exhibit good creep properties may possibly be related to the fact that a phase transformation occurs below 600 C. This transformation may have a

FIGURE 4. CREEP STRENGTH OF THORIUM-URANIUM ALLOYS AT 600 C.

N-94783

FIGURE 5. CREEP STRENGTH OF THORIUM-URANIUM ALLOYS AT 700 C.

N-94782

FIGURE 6. CREEP STRENGTH AT 600 C OF THORIUM-10 W/O URANIUM ALLOYS CONTAINING INDICATED ADDITIONS.

FIGURE 7. CREEP STRENGTH AT 700 C OF THORIUM-10 W/O URANIUM ALLOYS CONTAINING INDICATED ADDITIONS.

deleterious effect on creep resistance. Also, the microstructure of these alloys with zirconium contains greater amounts of uranium-rich phase than the other alloys. It is probable that the creep rate is strongly influenced by this uranium-zirconium phase as well as phase instability.

It is to be noted that the addition of 0.1 w/o beryllium, 2 w/o niobium or 1.5 w/o molybdenum to thorium-10 w/o uranium is sufficient to increase its 600 C creep strength (at a strain rate of 0.01 %/hr) by about 50 to 75 per cent. At 700 C the thorium-10 w/o uranium-0.1 w/o beryllium alloy has a creep strength (at a strain rate of 0.01 %/hr) which is almost 75 per cent higher than that of the thorium-10 w/o uranium alloy.

DISCUSSION

Though the irradiation resistance of thorium-uranium alloys is excellent compared to that of uranium-base alloys, improvement in their properties to extend their use to higher temperatures is desirable. This problem was attacked by two methods: structural control and improvement in hot strength.

Structural control of the thorium-uranium alloys is possible by choice of casting technique. The desired product is a uniform dispersion of small, uranium particles in a thorium matrix. This type structure should allow a large portion of the fission fragments produced to lodge in the thorium rather than in the uranium which is less resistant to radiation damage. Arc-casting was found to produce the desired structure more closely than induction-casting techniques. However, when the uranium content becomes greater than 10 w/o the tendency for the uranium to concentrate in the grain boundaries becomes excessive and even arc-cast material does not have the desired structure.

Further structural control is possible by alloying to stabilize gamma-uranium. The addition of 1.5 w/o molybdenum or 2 w/o niobium, both of which exhibit low solubility in thorium, to thorium-10 w/o uranium yields an alloy which consists of gamma-uranium particles dispersed in a thorium matrix. This structure is thought to be superior to that of thorium-10 w/o uranium. The addition of 10 w/o zirconium to thorium-10 w/o uranium results in partitioning of the zirconium to both the thorium and the uranium, the extent of which varies greatly with temperature. Since the amount of uranium phase, and thus the size and gamma stability of the uranium particles will vary with temperature, prediction of irradiation stability is difficult on the basis of structure.

The second approach to improved irradiation resistance at high temperatures involved increased strength. Because swelling is basically a creep phenomena, it is felt that creep data are the most indicative hot strength data which can be used.

The creep data at 600 and 700 C indicate that in the binary thorium-uranium alloys creep resistance decreases with increasing uranium content. The thorium-5 w/o uranium alloy was the most creep resistant of the binaries. With regard to the ternaries, the thorium-10 w/o uranium alloys containing 0.5 w/o beryllium, 1.5 w/o molybdenum and 2 w/o niobium exhibited the lowest creep rates.

The best combination of high-temperature creep resistance and structure was exhibited by thorium-5 w/o uranium and thorium-10 w/o uranium with additions of 0.5 w/o beryllium, 1.5 w/o molybdenum or 2 w/o niobium. The thesis that these latter alloys should perform better than thorium-10 w/o uranium under high temperature irradiation conditions remains to be proven.

Acknowledgement

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Session IV
Paper 21

THORIUM-URANIUM CARBIDE FUEL DEVELOPMENT

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THORIUM-URANIUM MONOCARBIDE FUEL DEVELOPMENT

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Introduction

Research and development for an Advanced Epithermal Thorium Reactor is being conducted at Atomics International under the sponsorship of the Southwest Atomic Energy Associates, a group of 15 investor-owned utilities in the Middle-South area. This reactor concept specifies a compact, high specific power core and requires a fuel system that is designed to take advantage of the heat transfer potential inherent in sodium coolant systems: Information developed in the uranium carbide fuel program under AEC sponsorship demonstrated that a carbide fuel has a number of physical characteristics that would make carbide fuel a strong contender for use in an AETR.

Chief among the favorable physical characteristics of carbides are high uranium density, relatively high thermal conductivity, and a high melting point. High uranium density permits design of a compact core, and high thermal conductivity allows the reactor designer to take full advantage of the excellent heat transfer characteristics of liquid metal coolants. High thermal conductivity of the fuel allows fabrication of fuel rods of relatively large diameter compared to other ceramic fuel systems, with a consequent lowering of element fabrication cost and possibly more favorable hydraulic and mechanical characteristics for the core. The high melting point of carbide fuel permits fuel element operation over an extremely wide temperature range, giving the reactor designer

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some latitude in practical fuel operating temperatures in conjunction with basic design variations such as coolant velocity and method and type of bonding and cladding. While current technology has been concerned primarily with liquid metal-bonded carbides cast into rod type elements, a contact bonded carbide fuel would seem to offer the advantage of a higher heat flux core for advanced reactor concepts.

With specific reference to thorium-uranium monocarbides, fabrication technology is still in its early stages. While a limited number of thorium carbide and thorium-uranium compound properties have been reported in the literature by a number of laboratories, data on mechanical properties, physical properties, compatibility, corrosion, and irradiation behavior of thorium-uranium carbides in the composition range of interest to AETR were not available from the literature. For this reason, we are currently establishing some of the basic design characteristics of AETR-oriented thorium-uranium monocarbides. This work is under the sponsorship of the Southwest Atomic Energy Associates as part of the AETR Phase II program.

Fabrication Development

It was known from the work of others and confirmed early in the course of our investigations that thorium-uranium monocarbides having a high thorium content are extremely reactive to moisture and decrepitate readily under atmospheric storage and handling conditions. (Figure 1) Fuel storage conditions that had been found to be satisfactory for uranium monocarbide, such as storage under ACW-803 cutting oil, did not prevent fairly rapid and complete disintegration of cast mixed-carbide fuel pins to a powder. It became obvious, then, that we either had to conduct all thorium-uranium carbide fabrication and evaluation under controlled atmosphere glove box conditions or attempt to develop an alloy fuel composition of greater corrosion resistance. Primarily from the viewpoint of ultimate fuel fabrication economics, it was decided to concentrate our effort on alloyed mixed carbide compositions.

Battelle had previously reported in BMI-1504 that incorporation of 5 m/o silicon carbide to ThC-10 w/o UC improved the oxidation resistance

Fig. 1. Thorium-Uranium Carbide Specimens in Various Stages of Decrepitation.

of the mixed carbide by a factor of two. Our initial attempts at casting mixed carbides containing silicon met with casting and composition control difficulties, but carbides containing zirconium, molybdenum, or niobium were easily cast.

Castings of fuel pins were made by reacting elemental thorium, uranium, carbon, and the reactivity-stabilizing metallic additive in a vacuum arc furnace. The charge was arc melted using a non-consumable (graphite) electrode. Two methods of casting were investigated, drop casting and tilt-pour. Drop casting generally produced castings of inferior quality, which exhibited random porosity, internal piping, and surface cold shuts. Castings by the tilt-pour method yielded satisfactory fuel slugs because of better flow control of the melt (Figure 2). Sound slugs of good to excellent physical properties were cast, with very little surface cold-shutting and minor internal porosity.

Tilt-pour is basically a skull casting process. In our adaptation of this process, a graphite "tilt block" assembly was made (Figures 3 and 4). This consists of a graphite block having a melting hearth adjacent to a mold receptacle. During the melting cycle, the plane of the mold receptacle is inclined roughly 30 degrees from horizontal and held in this position by spring loading. To cast the molten charge into the mold receptacle, the furnace operator moves a lever against the spring and allows the mold receptacle to assume a vertical position while the melting hearth is simultaneously tilted into pouring position. Use of the tilt-pour method resulted in improved composition control, i.e. primarily better control over carbon pickup, and improved casting quality. Silicon-containing mixed carbides were successfully cast by the tilt-pour method, in contrast to our earlier difficulties with drop casting. The melt cycle for a 1,000 gram charge varied from two to four minutes at 2000 to 3000 amps and 32 to 28 volts under a static argon atmosphere at a pressure of 500 mmHg.

Mixed Carbide Stability

The relative stability of alloyed thorium uranium monocarbides was determined on the basis of weight gain of test specimens stored under

AS-CAST U₂C-ThC
SLUGS
VARIABLE COMPOSITIONS

Fig. 2. As-Cast Alloyed Thorium-Uranium Monocarbide.

Fig. 3. Graphite Tilt-Block Casting Assembly.

Fig. 4. Graphite Tilt-Block Casting Assembly Components.

normal atmospheric conditions. The thorium-to-uranium ratio of test specimens in this particular series was 7:1. Alloying element content was in the 0.6 to 0.9 w/o range. Uranium monocarbide served as a reference standard in all the tests. Figure 5a is a plot of cumulative weight gain in milligrams per hour per gram of initial sample weight versus time of atmospheric exposure in hours. For purposes of comparison, data from the same test are plotted in Figure 5b as cumulative weight gain in milligrams per hour per square centimeter of initial sample surface area versus time of atmospheric exposure in hours. On either a unit mass or unit area basis, the least reactive material was the reference uranium monocarbide, while unalloyed thorium-uranium monocarbide was the most reactive. Of the various additives, zirconium appeared to be the most effective; molybdenum and niobium interchanged in effectiveness, depending upon whether they were compared on a unit mass or initial unit area basis.

Weight gain per unit of initial mass may be the more applicable measure of fuel stability, and weight gain per unit of initial surface area is probably a misleading parameter because of a continuous change in test specimen surface area as the specimen decrepitates, develops cracks, and crumbles. Test results involving silicon-alloyed mixed carbides are not plotted in Figures 5a and 5b because of erratic data stemming from inadequate composition control in our initial drop casting series. In general, it was found that thorium uranium carbides alloyed with silicon are difficult to cast.

Both zirconium-alloyed and silicon-alloyed thorium uranium monocarbides were successfully machined in the absence of a protective inert atmosphere (Figure 6). While the weight gain screening tests indicated that zirconium-alloyed thorium-uranium carbide approached the stability and handling characteristics of uranium carbide, a number of small-diameter zirconium alloy test specimens failed in machining tests because of propagation of radial microcracks. However, consistent success was achieved with silicon alloy compositions.

WEIGHT GAIN OF THORIUM-URANIUM CARBIDES

a. ON BASIS OF INITIAL MASS

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b. ON BASIS OF INITIAL SURFACE AREA

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Fig. 5. Effect of Additives on Cumulative Weight Gain of ThC-UC as Function of Time of Exposure to Atmospheric Conditions.

MACHINE - GROUND

UC-ThC

Fig. 6. Machined Arc-Cast Alloyed Thorium-Uranium Monocarbide.

Mechanical Properties

A number of mechanical properties were determined, including Young's Modulus and fracture stress in tension. As shown in Table I, for the limited number of tests there does not appear to be any correlation between grain size and fracture stress or between carbon content and fracture stress.

Table 1. Mechanical Properties of Alloyed Thorium Uranium Monocarbide (Th:U=7:1)

Sample Number	ASTM Grain Size, Des. E-91	Stabilizing Addition, < 1 w/o	Carbon w/o	Fracture Stress σ_f , 10^3 psi	Young's Modulus E , 10^6 psi
LA-2B-4	10	Si	5.28	12.18	15.9
LA-2B-5	10	Si	5.18	12.13	16.6
LA-2B-8	8	Si	5.52	12.63	14.1
LA-2B-9	9	Si	5.58	16.03	15.5
LA-2B-10	10	Si	5.76	13.17	15.2
AETR-21-E	4	Zr	5.60	13.83	14.5
AETR-21-F	4	Zr	5.95	16.67	13.5
AETR-21-9	5	Zr	5.67	15.05	14.5

It should be noted that silicon-alloyed mixed carbides exhibited consistently finer grain size than did zirconium-alloyed carbides. As a point of reference for fracture stress values, the corresponding values for UC and UO₂ in tension are ~ 13,000 psi and ~ 12,000 psi, respectively.

Physical Properties

Physical properties to be measured include thermal expansion and thermal conductivity of alloyed thorium uranium carbide.

Thermal conductivity tests on silicon-alloyed and zirconium-alloyed mixed carbides are now in progress. To determine the effect of varying thorium-to-uranium ratio, test specimens of 4:1 and 7:1 thorium-to-uranium ratio have been prepared.

Thermal expansion tests were carried out in a dilatometer incorporating a differential optical system which measures the unrestrained fuel movement directly. The tests were conducted from room temperature to 2400°F under a dynamic vacuum of $\sim 1 \times 10^{-5}$ mmHg. Arc cast alloyed carbide specimens were machined to 1/2 inch diameter $\times$ 5 inch length, and ranged in carbon content from 3.8 to 5.92 w/o. Thorium-to-uranium ratio was 7:1 except for the 3.8 w/o C specimen which had a 4:1 Th:U ratio. As shown in Figure 7, linear thermal expansion ranges from 1.3 to 1.4% at 2400°F. The values plotted in Figure 7 were derived from six test specimens and indicate no significant differences in thermal expansion characteristics for the composition range under investigation.

Compatibility Tests

Fuel-cladding compatibility tests are of interest to AETR for both sodium-bonded and contact-bonded fuel rod design concepts. A number of compatibility tests have been completed, while others are still in progress at this time. Fuel composition in all tests was thorium-uranium monocarbide of 7:1 Th:U ratio, alloyed with 0.5 to 1.0 w/o zirconium or silicon.

The test capsules for sodium bonded compatibility tests were 1/2 inch diameter $\times$ 0.010 inch wall type 304 stainless steel tubing. Arc-cast fuel slugs were surface ground to 0.440 inch diameter $\times$ 3/4 inch length, and sodium loading was done in a stainless-steel vacuum dry box under a purified argon atmosphere. Test temperatures were 1200°F and 1600°F, and test duration ranged up to 750 hours.

Contact-bonded diffusion couples were made by sandwiching fuel slugs between two polished wafers of either type 304 stainless steel, niobium-1 Zr alloy, or 3Z1 (zirconium base containing ~ 1 w/o Mo, Al, and Sn) alloy. The couple assemblies were encapsulated in an evacuated heavy-wall

LINEAR THERMAL EXPANSION OF ALLOYED ThU CARBIDE

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Fig. 7. Thermal Expansion of Arc-Cast Alloyed Thorium-Uranium Monocarbide.

stainless-steel container to eliminate interaction with the atmosphere during the diffusion test, which consisted of maintaining the couples under compression for 240 hours at 1200°F.

In thorium, carbon exhibits a solubility range extending from 3.9 to 4.9 w/o. When uranium and thorium are combined in a ratio of 1:7 and carburized, one would expect a carbon solubility approaching that of thorium carbide. The addition of ~ 1 w/o of alloying agent such as silicon or zirconium makes prediction of the phase relationships somewhat more complex. The photomicrograph in Figure 8 shows that a thorium-uranium carbide containing 0.87 w/o Zr and analyzing 4.85 w/o C does indeed exhibit a single phase structure. By contrast, Figure 9 shows a photomicrograph of thorium-uranium carbide alloyed with 0.86 w/o Zr and analyzing 5.29 w/o C, exhibiting the typical dicarbide precipitation in a hyperstoichiometric carbide.

The sodium-bonded compatibility tests showed that carburizing tendencies of thorium-uranium carbides in a sodium environment are relatively nil until the fuel carbon content is significantly greater than 4.9 w/o. This is demonstrated graphically in Figure 10 showing a photomicrograph of type 304 stainless steel cladding after 750 hours at 1200°F and sodium bonded to 0.87 w/o Zr-alloyed thorium-uranium carbide analyzing 4.85 w/o C. Above the 4.9 w/o carbon range, carburization of the type 304 stainless steel cladding ranged from one or two mils to complete 10 mil penetration along the grain boundaries. This is illustrated in Figure 11, a photomicrograph of type 304 stainless steel cladding after 580 hours at 1200°F and sodium bonded to Zr-alloyed thorium-uranium carbide analyzing 5.01 w/o C.

Based on free energy considerations, it had been hoped that carbon in excess of monocarbide stoichiometry might be tied up as ThC_2 and thus not be available for stainless-steel cladding carburization. The observed carburizing tendencies of hyperstoichiometric thorium-uranium carbide in a sodium environment can probably be explained by a mechanism postulated by P. E. Elkins at Atomics International in connection with uranium carbide fuel work. He postulates that sodium reduces the dicarbide to monocarbide plus carbon, permitting carbon to be taken into solution in

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Fig. 8. Thorium-Uranium Carbide (4.85 w/o C) Alloyed with 0.87 w/o Zr (250X).

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Fig. 9. Thorium-Uranium Carbide (5.29 w/o C) Alloyed with 0.86 w/o Zr (250X).

Fig. 10. Type 304 Stainless Steel After 750 hours at 1200°F, Sodium-Bonded to 0.87 w/o Zr-Alloyed Thorium-Uranium Carbide Containing 4.85 w/o C (250X).

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Fig. 11. Type 304 Stainless Steel After 580 hours at 1200°F, Sodium-Bonded to Zr-Alloyed Thorium-Uranium Carbide Containing 5.01 w/o C (250X).

the sodium. Microcracks forming in the fuel as a result of this reaction allow further penetration of the fuel by sodium, thus shortening the excess-carbon diffusion path.

It should be noted here that some scatter occurred in test data on depth of carburization, probably due largely to the well-known reactivity of the carbide fuel surface and to a lesser extent due to possible minor carbon composition gradients in the fuel specimen.

In contact-bonded compatibility tests, no perceptible reactions were observed at 250X magnification between type 304 stainless steel, 3Z1, or Nb-1Zr alloy and Zr- or Si-alloyed thorium-uranium carbide after 240 hours at 1200°F. The carbon contents of the fuel specimens in the diffusion couples ranged from 4.89 to 5.29 w/o, or well past the point of stoichiometry. Contact compatibility in UC systems has also been observed by others at Atomics International for much longer times at the same temperature. It is a result of the limiting mechanism for carburization being that of carbon diffusion through the fuel material, diffusion being very slow at 1200°F. Significantly greater rates of diffusion would be expected to occur in a contact bonded fuel rod which would exhibit a steep temperature gradient from the center line fuel temperature to a nominal 1200°F fuel-cladding interface temperature.

Conclusions

- (1) The decrepitation tendencies of thorium-uranium monocarbide can be minimized by alloying with ~ 1 w/o of a stabilizing additive such as silicon or zirconium. However, even alloyed mixed carbides developed to date do not equal uranium monocarbide in resistance to atmospheric corrosion.
- (2) Mechanical and physical property tests of alloyed thorium-uranium monocarbides have so far confirmed the suitability of this fuel for reactor application. Thermal conductivity tests still remain to be completed.

(3) Sodium-bonded fuel-cladding compatibility tests have shown that carburizing tendencies of alloyed thorium-uranium monocarbide in a sodium environment are relatively nil until the fuel carbon content is greater than stoichiometric.

(4) Preliminary contact-bonded fuel-cladding compatibility tests under isothermal 1200°F conditions indicate that contact bonding may be preferred to sodium bonding of hyperstoichiometric mixed carbide fuels.

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Session IV
Paper 22

THE SOL GEL PROCESS FOR PREPARATION OF THORIA BASE FUELS

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INTRODUCTION

The early development of the sol-gel process was described at two previous symposia at Rome and at Windsor, Connecticut.¹ The purpose of this paper is to report recent progress on engineering scale-up studies and improvements in the basic procedure. The process starts with the products of the Thorex process (see Fig. 1) and produces high-density thoria-base fuel suitable for loading into fuel tubes by vibratory compaction. Vibratory compaction was chosen as a method for filling fuel tubes because its simplicity makes it particularly adaptable to remote operation, and its development will be discussed in a later paper.² Remote processing and fabrication is necessary for thorium fuels because of the presence of U^{232} and its decay products as was discussed in an earlier paper.^{3,4}

The development emphasis has been placed on the preparation of 3 at. % uranium oxide-thorium oxide suitable for the Kilorod Project, discussed in detail in an earlier paper.⁵ The process was successfully demonstrated on a 10-kg scale, more than 20 batches of this size having been prepared for vibratory compaction studies. Engineering equipment was developed and tested for each of the steps and is now being installed in the Kilorod Facility which will also serve as a small pilot plant for the process.

The work summarized in this status report was performed by many people. The authors owe much to the help of Analytical Chemistry Division personnel, to S. D. Clinton, D. E. Ferguson, K. H. McCorkle, and C. E. Schilling of the Chemical Technology Division, and to W. O. Harms, J. D. Sease, R. L. Hamner, and W. S. Ernst, Jr., of the Metals and Ceramics Division in preparing this paper.

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Fig. 1. Sol-Gel process in the thorium fuel cycle.

DESCRIPTION OF THE PROCESS

The sol-gel process consists of four simple steps (Fig. 2).⁶ Thorium nitrate, a product of the Thorex process,^{7,8} is denitrated in a current of superheated steam to a readily dispersible oxide product that contains a closely-controllable 2 to 3 mole % residual nitrate. This denitrator product is dispersed to a stable oxide sol by agitating it in dilute nitric acid or uranyl nitrate at 80°C. After dispersion and adjustment of the pH to 3.8, the sol is evaporated at 85 to 90°C to produce a gel that has about 5 wt % of residual water and a density of about 5 g/cc. In air calcination the temperature is raised 300°C/hr to 1150°C and held for 1 hr. Argon containing 4% hydrogen (a noncombustible mixture) is then passed over the charge at 1150°C for 4 hr to reduce the uranium to UO₂. The product is a completely homogeneous solid solution practically free from pores and occluded gas in which the U/Th ratio is uniform in all size fractions, an important advantage over other methods of preparing oxides for vibratory compaction fabrication.

A flowsheet similar to the one shown in Fig. 2 was used to prepare 4% plutonium-thorium oxide of greater than 98% of theoretical density. Irradiation test capsules were prepared by vibratory compaction and are now being irradiated.

PROCESS DEVELOPMENT

Steam Denitration

Heating hydrated thorium nitrate crystals in a stream of air at 185°C gives a molten dihydrate and decomposes only a negligible fraction of the nitrate.¹ The highly hydrated nitrate contains only the coordinated nitrate group, and as thermal

Fig. 2. The Sol-Gel process.

dehydration proceeds, the nitrate group is converted completely to the ionic nitrate form.⁹ Subjecting the partly dehydrated nitrate to superheated steam, with temperature slowly increasing from 185 to 475°C, removes greater than 99% of the nitrate as completely condensable HNO₃ solution, and leaves ThO₂ denitrator product which is readily dispersed in dilute nitric acid or uranyl nitrate solution.

The denitration step was effectively carried out batchwise in a 14-in.-diam by 48-in.-long rotary calciner (shown in Fig. 3 tilted to the discharge position). It is loaded at the same end (when tilted upward) with thorium nitrate crystals or thorium nitrate solution that contains the equivalent of 15 to 22 kg of ThO₂. The horizontal calciner is heated by means of clamshell electric heaters between which it rotates as air is passed through its interior. When the drum reaches a temperature of 180 to 200°C, the air is discontinued, the temperature of the electric heaters is raised to 500°C, and 350 to 400°C-superheated steam is passed through the charge. The hydrolysis produces HNO₃ in the absence of air, which is swept out of the calciner and condensed with the exhaust steam, along with about 0.5% of the solid product, in the total condenser (not shown). The temperature of the charge rises as fast as permitted by the endothermic hydrolysis to a final 475°C, where it is held 1 to 2 hr.

The evolution of nitrate was slow by the time the temperature had reached 350°C. The residual nitrate in the product, expressed by the NO₃⁻/ThO₂ mole ratio depended on the time held at 475°C, as shown in Fig. 4. For a given set of operating conditions the nitrogen content of the products was remarkably constant (see Table 1). Thorium nitrate that contained 3% uranyl nitrate was also successfully codenitrated to a dispersible oxide.

Fig. 3. Kilorod facility rotary steam denitrator.

Fig. 4. Nitrogen to thorium mole ratio vs run time for 30 kg charges of $\text{Th}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$

Table I. Hydrothermal Denitration of Thorium Nitrate Crystals

Rotary calciner 14 in. diam x 48 in. long; walls preheated to 185°C; steam, 350°C, 1 atm, 20 lb/hr; calciner temperature increasing, 185–475°C

No. of Runs	Steam		Air Calcination	Product	
	Total Time (hr)	Time at 475°C (hr)	Time at 475°C (hr)	Wt (kg)	NO ₃ /ThO ₂ Mole Ratio
5	6	2	0	15	0.027 $\pm$.009
5	4	0.1	1	15	0.059 $\pm$.005
3 ^a	6.5	2.5	0	22.5	0.050 $\pm$.006

^aInitial steam, 30 lb/hr for 2 hr at 405°C.

Sol Preparation

The apparatus for dispersing the thorium oxide denitrator product in uranyl nitrate solution is shown in Fig. 5. The thoria is flushed with a stream of water into dilute uranyl nitrate solution circulated by a centrifugal pump through a heated pipe loop external to the critically safe mixing tank. The uranyl nitrate is adjusted to the correct uranium and nitrate content, heated to 90°C, and circulated from the bottom to the top of the tank before and during the addition of thoria. Complete dispersion of the thoria is obtained by recirculation and digestion for 1 hr; then the pH of the sol is adjusted to 3.8 to 4 by the addition of ammonia solution at the intake of the pump, and circulation is continued for an additional hour. In the development of the sol preparation step for the Kilorod Project, the atomic ratio, U/U + Th, was fixed by specification at 0.03 $\pm$ 0.0003. In practice, the ThO₂ concentration of the sol is 2 M, although preparations of 5 M ThO₂ sols were demonstrated in the system without difficulty or sacrifice of

Fig. 5. Sol preparation tank.

product quality. With the above conditions fixed, the variables of sol preparation are the nitrate/thoria mole ratio and the pH. Both are important to uniform distribution of the U/Th atomic ratio and to the compactability of the product.

By the measurement of optical densities, the pH, and the electrical conductivity of thoria sols, it was found that maximum dispersion of the thoria occurs at a $\text{NO}_3^-/\text{ThO}_2$ mole ratio corresponding to occupancy of one-half the thoria surface sites for chemisorption estimated by M. E. Wadsworth and co-workers.¹⁰ The system is colloidal, in which the thoria crystallites have an average size of 70 Å. The particle-size distribution in the sol is not as yet accurately known, but it is believed that in an optimum sol, where the maximum dispersion is obtained, the ThO_2 is mostly dispersed to single crystallites. Dispersion of ThO_2 and adsorption of uranium oxide are surface phenomena and depend on nitrate and hydrogen ion concentration in the electrolyte surrounding the particles.

The conductimetric titration of a ThO_2 -water slurry provides a convenient method for determining the nitrate required for a thoria powder. Figure 6 shows a plot for the electrical conductivity of a sol of steam-denitrated thoria with added increments of HNO_3 . The conductivity of the sol is changed but little by additions of nitric acid up to the critical point, corresponding to one-half occupancy of chemically active sites by nitrate. Beyond this point, added nitrate causes larger uniform increases in conductivity, the slope being that expected for the increasing conductivity of dilute HNO_3 assuming no thoria to be present. In another plot, the nitrogen surface area of a gel obtained by evaporating a sol having a specified $\text{NO}_3^-/\text{ThO}_2$ mole ratio was divided by the surface area calculated by assuming independent crystallites to obtain each point. The maximum dispersion occurred at the "break point" of the conductivity-

Fig. 6. Effect of added HNO₃ on conductivity and surface area of thoria.

nitrate curve.

When 3 at. % uranium is present in the sol, the "break" occurs at about a 10% lower $\text{NO}_3^-/\text{ThO}_2$ mole ratio, and the changing slope at higher values suggests a complex relationship between a succession of soluble uranium species of variable equivalent conductance and free nitric acid. Maximum dispersion in this kind of sol usually occurs at a $\text{NO}_3^-/\text{ThO}_2$ mole ratio about 10% in excess of that for thorium powder alone. Based on this information, the $\text{NO}_3^-/\text{ThO}_2$ mole ratio employed in the uranium-thorium oxide sol preparation is 10% above the nitric acid demand of the thorium. The sol is then neutralized with NH_3 to an $\text{NO}_3^-/\text{ThO}_2$ mole value corresponding to the break point (usually 0.06). The apparent pH of the sol at this value is about 3.8 to 4.0, and this condition is believed to be necessary to convert uranium to an anionic species which will remain adsorbed onto the thorium surface.

Table II shows the effect of $\text{NO}_3^-/\text{ThO}_2$ mole ratio and ammonia neutralization

Table II. Sol Preparation Conditions and Uranium Distribution in Sol-Gel Oxides

Typical batches of ~7 kg oxide, 3 at. % U

Run	Sol Conditions			Uranium Distribution in Product, % Deviation from Mean U/Th		
	Moles Nitrate Added per Mole ThO_2	Moles NH_3 Added ^a per Mole ThO_2	Adjusted pH	% Deviation from Mean U/Th		
				Coarse Fraction ^b	Medium Fraction ^c	Fine Fraction ^d
28	0.077	0.017	3.92	+0.03	+1.18	-0.03
31	0.080	0.020	3.80	-0.40	+1.09	+1.56
9-AB	0.096	0	2.82	-4.37	+6.58	+6.58
20-5M	0.067	0	3.31	-1.62	+3.76	+1.75
14-H	0.086	0.014	4.18	-0.70	+1.92	+0.46

^a Added after dispersion of ThO_2 .

^b 6/16 mesh, 60 wt %

^c 50/140 mesh, 15 wt %

^d -200 mesh, 25 wt %

on the uranium distribution in the various size fractions of the fired product. For these powders, the nitric acid demand was about 0.07 moles per mole of ThO_2 . A uniform product is obtained when about 10% excess nitrate is used to ensure complete dispersion, followed by neutralization to about 10% below HNO_3 demand (run 28). High nitrate, not neutralized by ammonia, results in a low sol pH and an enrichment of the fines in uranium, due to the concentration of the soluble uranium in the liquid phase as the sol evaporates. This liquid, which evaporates last, gives a brittle gel, which is the major source of the fines. When an attempt is made to use nitrate equivalent to the nitric acid demand with no neutralization the distribution is improved, but not ideal.

Table III shows the effect of the $\text{NO}_3^-/\text{ThO}_2$ mole ratio and ammonia

Table III. Effect of Sol Preparation Conditions on Density of Sol-Gel Oxides
7 kg batches; 3 at. % U- ThO_2

Batch No.	Sol Conditions			Density, % of theoretical	
	Moles Nitrate Added per Mole ThO_2	Moles NH_3 Added ^a per Mole ThO_2	pH ^b	Particle	Vibrated Bulk
1	0.067	0	3.31	99.3	90.6
2	0.086	0	2.90	99.9	89.6
3	0.093	0	2.90	96.5	86.0
4	0.170	0.041	2.72	97.9	83.4
5	0.170	0.093	3.45	97.5	87.8
6	0.080	0.020	3.80	98.6	87.8
7	0.077	0.015	3.48	99.5	89.4

^aAdded after dispersion of ThO_2 .

^bTaken just prior to evaporation of sol.

neutralization on particle and vibrated densities of the fired and sized oxides.

Batch 1 gives the optimum sol conditions for high-density particles of good compactability. The added nitrate, 0.067 mole per mole of ThO_2 , is equivalent to the nitric acid demand of the ThO_2 powder, and no ammonia is added. The use of higher nitrate, particularly 0.093 and greater, as in batches 3, 4, and 5, decreases the particle density. The use of ammonia to neutralize high nitrate partly corrects a special negative effect of high nitrate on packing as in batch 5, but imparts toughness to the particle which interferes with self-grinding during packing as is also evident in batch 6. Keeping the NH_3/ThO_2 mole ratio to less than 0.015 minimizes the negative effect of ammonia on packed density (batch 7). Batch-7 conditions represent the optimum compromise in sol conditions for obtaining maximum density and at the same time, uniform distribution of uranium.

Evaporation

The digested, pH-adjusted sol is batch-evaporated in trays under a stream of heated air at 85 to 90°C. The kilorod trays are arranged in cascade so that sol from the top tray overflows to the one immediately under it. Twenty liters of sol, containing 10 kg of oxide, are pumped into the top tray. A drying time of 48 hr is used to prevent the formation of bubbles in the gel product, and to remove all except 4 to 6% of the volatile matter. The particle size range is from $>1/2$ in. to about 35 mesh, about 90% of which is larger than 16 mesh. The density of the gel is about 5 g/cm^3 , giving a concentration factor during drying of about 10. The particle size is affected by the drying rate, which in turn is dependent on air temperature, rate, and humidity. These factors are being studied for control of particle size.

Firing

The gel from the trays is dumped into a funnel, which directs the charge to two 6-kg capacity crucibles. The volatile material is removed and the oxide densified in air by increasing the furnace temperature 300°C/hr to 1150°C and holding 1 hr. After flushing the furnace for 10 min with argon, the charge is reduced in an atmosphere of argon containing 4% hydrogen at 1150°C for 4 hr. At this composition, the blanket gas is noncombustible. After cooling to below 100°C in argon, the product is dumped to a hopper that feeds the sizing equipment.

In a laboratory study (Table IV), using 55-g samples of 3% uranium oxide-

Table IV. Effects of Calcination Atmosphere on Particle Density and Residual Gas Content

Samples: 55 g 3% U-ThO₂

Firing: 300°C/hr to 1150°C; at 1150°C, 20 min in air; then in the indicated gases for the indicated times

Calcination Atmosphere	Calcination Time (hr)	Cooling Atmosphere	Particle Density (g/cc)	Gas Release, cc/g at 1200°C vacuum
Air	0.5	Argon	9.91	0.14
Air	0.5	Nitrogen	-	0.037
Argon	0.5	Argon	9.92	0.024
Argon	1.5	Argon	9.94	0.014
Nitrogen	3.5	Nitrogen	9.95	0.001
Argon-4% H ₂	3.5	Argon	9.95	0.001

thorium oxide, it was found that densification, reduction, and degassing of the oxide were nearly complete with 1/2 hr of heating at 1150°C in air. Densification and degassing were complete with an additional 3-1/2 hr of heating in nitrogen or argon-4% hydrogen. The highest possible temperature of withdrawal of the cooled charge without serious reoxidation was 200°C. Although the data from small-scale firings show that a blanket of nitrogen is as effective as argon-4% hydrogen for eliminating sorbed gases from the products, Table V shows that firing larger batches in a blanket

Table V. Residual Gas Content and O/U Ratio of Calcined Product

Batch size: 5-7 kg

Firing: 300°C/hr to 1150°C; at 1150°C, 1 hr, in air; then in indicated gases for 4 hr

Calcination and Cooling Atmosphere	O/U Ratio		Total Gas Released at 1200°C, Vacuum, st. cc/g			
	+16 mesh ^a	-35 mesh ^b	Before Grinding		After Grinding	
			+16 mesh ^c	-35 mesh ^d	-6+16 mesh ^c	-200 mesh ^d
A-4% H ₂ ; A ^e	2.026	2.019	0.004	0.067	0.012	0.170
N ₂ ; N ₂	2.099	2.157	0.018	0.120	0.017	0.320
A; A	-	-	0.015	0.130	0.021	0.210

^aComposes 90 wt % of product.

^bComposes 3 wt % of product.

^cComposes 60 wt % of product.

^dComposes 25 wt % of product.

^eCooled in argon.

of argon or nitrogen in a larger furnace gave products of higher residual gas content than when an argon-4% hydrogen blanket was used. The fines had more residual gas than the coarse particles, suggesting some readsorption during cooldown. The analyses of the gases liberated from the coarser oxides showed those from the nitrogen- and

argon-blanketed firings to contain about 80% oxygen and 20% CO₂, while gases from argon-hydrogen reduced oxides contained about 30% water plus hydrogen, 20% CO, and 50% CO₂. The finer oxides gave off less oxygen and more CO₂. All oxides ground in contact with air readsorbed large quantities of gas, mainly CO₂.

It was concluded that exposure of the product to oxygen and carbon dioxide should be minimized during powder preparation and tube filling. While some reoxidation occurred on cooling and exposure to air, as shown by the O/U ratios of the argon-hydrogen blanketed products, it was obvious that for this furnace and these charges, reductions in nitrogen and argon were incomplete and that reducing gas should be used unless the furnace can be well sealed.

In Fig. 7a the O/total metal is given as a function of O/U ratio for oxides containing 3 at. % uranium. From this it can be seen that O/U ratios of 2.3 would be within the specifications (indicated by the dashed line) for uranium oxide fuels. Figure 7b shows the volume per gram that the excess oxygen would occupy at standard conditions if it were totally released. The squared points below curve B give total gas released at 1200°C, vacuum for argon-hydrogen- and nitrogen-reduced samples while the shaded circles give the gas release for the same samples after grinding. It is obvious that not all the oxygen shown to be present by O/U analysis was released at 1200°C, under vacuum, and that the ground samples contained gases in addition to free oxygen.

Product Quality

For products containing 3 at. % uranium prepared under flowsheet conditions and reduced in argon-4% hydrogen for 4 hr, the uranium distribution is uniform in all

Fig. 7. O/U ratio in 3 at. % U-ThO₂: effect on O/metal ratio; excess oxygen volume: gases released at 1200°C, vacuum.

size fractions to $\pm 1\%$ of the mean; the particle density is $>99\%$ of theoretical; the sized oxide consistently vibratorily compacts to 90% of theoretical density; the gas released at 1200°C in vacuum is 0.01 cc/g or less; the O/U ratio is 2.03 or less. One of the large batches, prepared for irradiation specimens was exhaustively analyzed and found to have a total impurity content of 1050 ppm, of which 640 ppm were Al, Fe, and Na. The macroscopic neutron cross section of the total impurities was equivalent to that of 5 ppm of boron. All evidences from x-ray diffraction, metallography, petrography, and electron micrography show the sol-gel product to be a single-phase solid solution. At up to 500X magnification, etched sections show no grain structure. At 69,000X magnification a fractured surface shows grains of 5000-7500A, with the grains fitted so as to suggest some degree of gel particle ordering during firing. A comprehensive irradiation testing program is being conducted at Oak Ridge National Laboratory on fuel rod specimens containing vibratory-packed sol-gel uranium-thorium oxide. The program and its results will be described in a later paper.¹¹

Sol-Gel Spheres¹²

Figure 8 shows samples of kilogram batches of rounded sol-gel pellets. By milling the dried gel in high-fired ThO_2 powder the rounded shapes were obtained. Pellets up to 1/4 in. diam could be fired to 1150°C with only negligible breakage, and even larger ones survived if supported in ThO_2 powder while being fired. As with the fragment preparation, electrolytic conditions in the sol preparation step strongly affected the density and porosity of the fired oxide. Conditions contributing to high

3 % U

9.93 g/cc

0.005 % /hr

I

9.87 g/cc

0.04 % /hr

Fig. 8. Sol-gel spheres.

density also gave higher structural strength and resistance to attrition, which was determined by a spouted bed test developed by catalyst bead manufacturers. In Fig. 8, the ThO_2 preparation was the result of optimum adjustment of $\text{NO}_3^-/\text{ThO}_2$ mole ratio and pH in sol preparation. The presence of uranium enhanced both density and attrition resistance.

Figure 9 shows 150 to 200-micron sol-gel particles containing 3 at. % uranium oxide-thorium oxide which were spheroidized by R. L. Hamner of the Metals and Ceramics Division. The diametral shrinkage which can be varied from 25% to 0% by increasing the firing temperature from 90 to 1100°C makes this material attractive for use in large-particle dispersion fuels since residual shrinkage can be matched to that of many matrix materials. These particular spheres were successfully incorporated into a high-density BeO matrix.

Fig. 9. Sol-gel uranium oxide-thorium oxide microspheres.

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Session IV
Paper 23

METALLURGICAL STUDIES OF THORIUM-URANIUM-PLUTONIUM ALLOYS

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Ceramic nuclear fuels, particularly oxides and carbides, offer the great advantage of allowing very high burnups and high-temperature operation. They are, nevertheless, less attractive from the standpoint of heat transfer, fuel processing and fabrication. No method comparable to the simplicity of pyrometallurgical processing and injection casting has yet been devised for oxides and carbides. Thus, the reactor engineer still desires to have a metallic fuel which has a high density, good thermal conductivity and simple processing characteristics, a fuel which may be used at a high temperature and is less susceptible to swelling than the presently available uranium-plutonium alloys.

In that respect thorium, a face-centered cubic metal with the high melting point of 1790°C stands out as an attractive potential matrix. The binary thorium-plutonium and thorium-uranium alloys have been shown to have good irradiation stability.¹⁻⁸ Experiments at ANL, AI and BMI show that these alloys may be useful at much higher temperatures than for instance the uranium-plutonium-fissium alloys presently earmarked for a loading of EBR-II.⁹ Although the three elements thorium, uranium and plutonium are at the base of the atomic energy field, the literature contains no information on the ternary thorium-uranium-plutonium alloys. Therefore, an investigation was initiated at ANL to study the constitution, properties and irradiation resistance of these alloys and to evaluate them as a potential fuel for power reactors from a metallurgical fabrication, processing, nuclear and reactor engineering point of view.

As a first step the solid solubility of uranium and plutonium in thorium is being determined. The alloys are prepared by arc melting from high purity materials, encapsulated, annealed at various temperatures and water quenched. Metallography and density determinations are presently the method of investigation. Aside from the binary boundary systems the initial alloy series contain 10, 20, 30, 40, 50 and 60 wt % plutonium and 2, 4, 6, 8 and 10 wt % uranium.

The preliminary results indicate that the solid solubility of plutonium in thorium in the temperature range of 700 to 900°C follows more nearly the diagram by Poole, Williamson and Marples¹⁰ according to which the solid solubility at 700 and 900°C are 35 at. % and 45.5 at. % respectively, than the

Russian phase diagram¹¹ in which the respective concentrations are 25.0 at. % and 32 at. %. It may be expected that the useful ternary alloys will be two-phase alloys consisting of alpha thorium and alpha uranium with the plutonium in solid solution in both the thorium and the uranium phases.

The binary thorium-uranium alloys with 30% uranium and more are badly segregated due to the liquid miscibility gap in the system. It may be expected that the miscibility gap will extend into the ternary system. A ternary alloy with 20% uranium and 20% plutonium balance thorium lies outside the ternary miscibility gap.

Density measurements proved to be a useful tool in studying these alloys since the densities of the boundary phases (thorium: 11.68, uranium: 19.01, and $\text{Pu}_{13}\text{Th}_6$: 13.96 g/cm³) differ considerably. Alloys of variable composition and heat treatment have sufficiently large density differences to give significant information on alloy structure. In the binary boundary systems plots of specific volume vs composition, in keeping with the laws of mixing, show a straight line relationship with a break at the solid solubility limit (Figs. 1 and 2). This carries over into the ternary system at least in part as shown in Fig. 3.

Three ternary thorium-uranium-plutonium alloys have been selected for the initial series of property determinations and irradiation tests with a view toward their potential as a fast reactor fuel. Their compositions in weight percent are:

1. 60 Th-20 Pu-20 U
2. 75 Th-20 Pu-5 U
3. 80 Th-10 Pu-10 U

Alloy 1 was chosen as a potential fuel for EBR-II. Alloy 2 is a fuel composition which is potentially suitable for intermediate size power reactors. Alloy 3 may satisfy the fuel requirements of a very large power reactor.

The alloys were prepared from commercial thorium, 93% enriched uranium and reactor plutonium. Alloy 1, 60-20-20, which has a liquidus temperature of around 1250°C was then injection cast into Vycor molds in our experimental

Fig. 1. Specific Volume of Thorium-Uranium Alloys

Fig. 2. Specific Volume of Arc Melted High Purity Thorium-Plutonium Alloys

Fig. 3. Specific Volume in cm^3/g vs Composition in Wt % of Thorium-Uranium-Plutonium Alloys

injection casting unit. Good pins were obtained of 12 in. in length, nominally 0.144 in. in diameter and of uniform density as observed by cobalt-60 radio-graphs.

The 60-20-20 alloy is ready to be placed in the reactor for irradiation testing. The alloy will be tested as cast and as heat treated for 1 hr at 720°C. This heat-treatment was chosen to β heat-treat the alpha uranium phase of the ternary alloy. Ingot casting and rolling are other fabrication methods presently under investigation.

The density data obtained for the binary boundary systems and for the binary alloys are shown in Tables 1 and 2 and in Fig. 4.

The density measurements were made with an accuracy of $\pm 0.005 \text{ g/cm}^3$ an order of magnitude better than earlier density measurements on plutonium alloys. The measurements were made by the hydrostatic weighing method using monobromobenzene as a liquid taking into account not only the customary buoyancy correction, but also temperature differences between the glovebox atmosphere and the liquid. A detailed report on the method is in preparation.

Other properties are under investigation and it is intended to cover the entire range of properties of reactor engineering interest.

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Table 1.
Density of Commercial Thorium
and Arc Melted Thorium-Uranium Alloys

Number	Alloy Nominal Th	w/o U	Density at 25°C in g/cm ³	Mean Value at 25°C in g/cm ³
B751	100	0	11.679 11.676	11.678
B752	90	10	12.113 12.112	12.113
B753	80	20	12.604 12.608	12.606
B754	70	30	13.155 13.163	13.159
B755	60	40	13.762 13.764	13.763
B756	50	50	14.439 14.437	14.438
B760	0	100	19.009 19.016	19.013

Table 2.
Density of Crystal Bar Thorium and
High Purity Thorium-Plutonium Alloys

Number	Alloy Nominal Th	w/o Pu	Density at 25°C in g/cm ³	Mean Density at 25°C in g/cm ³
B772	100	0	11.713 11.717	11.715
B766	90	10	11.913 11.916	11.914
B767	80	20	12.134 12.127	12.131
B768	70	30	12.367 12.374	12.371
B769	60	40	12.741 12.746	12.744
B770	50	50	13.139 13.139	13.139
B773	40	60	13.660 13.670	13.665

Fig. 4. Densities in g/cm^3 Vs Composition in Wt % of Thorium-Uranium-Plutonium Alloys

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Session V
Paper 24

EXTRUSION FABRICATION OF RECYCLED THORIA-URANIA
IN THE PCUT PLANT

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1. INTRODUCTION

The previous paper¹ in this symposium, relating to the PCUT project, described the rationale of the integrated plant, the mode of operation for the ERR-PCUT program, and the facility and chemical processes employed. This paper describes the warm-cell design philosophy and process selection, summarizes the extrusion development work, describes the ERR fuel assembly designed for remote refabrication, and describes the refabrication process and equipment.

2. WARM-CELL PROCESS AND EQUIPMENT

Figure 1, a schematic of the complete PCUT plant process, illustrates the warm-cell operations in the plant. Steps 5 through 17 are performed in the warm cell. However, this paper is concerned with the fabrication of the calcined mixed-oxide powder; therefore, only steps 8 through 17 will be described in detail.

Figure 2 shows the general arrangement of the hot cell and the warm cell and illustrates the means of operating the warm-cell process equipment, e.g., the through-the-wall manipulators, the overhead General Mills bridge-mounted manipulator, the overhead crane, and the various shielded windows, which permit direct operator observation of the fabrication process steps. At the extreme right of the cell complex, the decontamination cell can be seen.

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Fig. 1. Reprocessing Sequence

Fig. 2. Hot Cell and Warm Cell

2.1 WARM-CELL EQUIPMENT DESIGN BASES

The most important factor in the warm-cell equipment design is the achievement of reliability through simplicity. Wherever possible, standard or proven equipment should be modified, and simplified, to perform the required functions, rather than designing special equipment. In any event, the modifications should all be aimed at remote operation (by the through-the-wall and bridge-mounted manipulators), as opposed to automated operation.

The second major factor in warm-cell equipment design is the use of throwaway maintenance. That is, individual items or subassemblies of process equipment can be removed from the warm cell and taken to the decontamination cell for examination, simple maintenance, or, as is most likely, preparation for burial. The design of the more complicated mechanical devices emphasized unitized or modular construction for ease of replacement.

2.2 SELECTION OF EXTRUSION PROCESS

Although the choice of a ceramic fabrication process for the warm cell involved a rather complicated procedure, three main factors led to the specification of extrusion rather than the more common cold pressing and sintering.

- (1) The extruder is mechanically simpler than the automatic pellet press.
- (2) Extrusions are longer than pellets; therefore, the handling steps in fuel-element fabrication are either simplified or reduced in number or frequency.
- (3) Results from other extrusion programs suggested the elimination of grinding.

Examples of the kind of surface finish and dimensional tolerance control that can be achieved in the more common ceramic extrusion processes can be found in the carbide fabrication industry. Results from UO_2 extrusion development also indicated that long, straight bodies of highly reproducible diameter and surface finish could be produced by a simple process of extruding, drying, and sintering.

3. EXTRUSION DEVELOPMENT

3.1 CONTINUOUS EXTRUSION PROCESS

An initial extrusion development program was begun as a logical extension of the UO_2 extrusion work carried out under AEC and EURATOM sponsorship. The objective of this program was to develop and demonstrate a process that would use a continuous auger extruder. The mixed-oxide powder produced by the PCUT reference ammonia-oxalate precipitation process was considerably different from that produced by the standard processes used in this country for ceramic-grade UO_2 , and the auger-mill program was not successful. Rather than enter into a long-range auger-mill extrusion development program, it was decided to use the piston extruder for the PCUT process.

3.2 PISTON EXTRUSION SCOUTING TESTS

Using the initial auger-mill extrusion program clay-composition results, a series of scouting tests was undertaken to establish proper values for the process variables. On the basis of these tests, a mixture of Methocel and polyacrylamide was chosen for the binder-plasticizer and a small amount of bentonite clay was added as an extrusion aid and sintering promoter. After drying for 16 hr at 90 C, the green bodies were sintered for 4 hr at 1700 C in a hydrogen furnace.

3.3 PROCESS REPRODUCIBILITY STUDY

The conditions for clay preparation, extrusion, drying, and sintering having been established, the major portion of the extrusion development program was initiated, namely, the determination of process reproducibility. The specific objectives of this program were to establish the within-lot and between-lot variance in green density, sintered density, sintered diameter, and sintered straightness. Nine 10-kg batches of mixed-oxide powder were prepared from mixed-nitrate solution by the ammonia-oxalate precipitation process under closely controlled conditions. The procedure used in processing each batch in the reproducibility test is shown in Fig. 3.

Although preliminary calcining, pressing, and sintering studies carried out by the CNEN Materials Division had indicated that calcining the coprecipitate (thorium oxalate and ammonium diuranate) in air for approximately 90 min at 900 C gave a very sinterable product, it was determined in this investigation that the mixed-oxide powder so prepared had a skeleton-like structure that retarded sintering to high density. In an attempt to eliminate the density-limiting characteristic, the recalcination step indicated in the test procedure was introduced. Recalcining the powder at a temperature higher than that at which it was initially calcined tended to densify, or coalesce, the skeleton-like material into aggregates of a density much nearer the theoretical. This reduced the surface area of the powder too much for good sinterability; accordingly, the product of the recalcining step was wet ball-milled in alcohol for 16 hr. The alcohol was evaporated and Methocel (1/4 weight per cent) and bentonite (1/2 weight per cent) were added to the dry mixed-oxide batch. This mixture was then dry blended for 30 min in the muller mixer. The

REPRODUCIBILITY TEST PROCEDURE

Fig. 3. Reproducibility Test Procedure

extrusion clay was then prepared by adding a water solution of polyacrylamide of such a concentration that approximately 11 weight per cent water and 1/4 weight per cent polyacrylamide were introduced to the batch. Mulling was then continued for 25 min to ensure a thoroughly wet, homogeneous extrusion clay. The batch was then extruded vertically downward and taken up by hand. Green extrusions approximately 10 in. long were taken from the die and placed on drying trays. The green product was dried 16 hr at 90 C and cut into 4-in. lengths with squared ends and the specimen weight, diameter, straightness, and length were recorded.

Samples were then loaded into molybdenum sintering boats and passed through a continuous sintering furnace with a hydrogen atmosphere at such a rate that the material was soaked for 4 hr at the maximum temperature 1700 C. After cooling and discharge from the furnace, the sintered pieces were measured and evaluated as the green pieces had been. The initial portion of the reproducibility test centered on the determination of within-lot variation and accordingly used two of the nine mixed-oxide batches. Eleven dried green specimens were selected at random from each of the approximately 25 green bodies produced from each extrusion batch, for use in determining reproducibility.

Within-lot variations in the green and sintered density, sintered diameter, and camber are shown in Table I. Camber is a measure of curvature of the sintered piece determined by dividing its maximum deflection by its length (maximum deflection was measured by placing the piece on a surface plate and alternately traversing its length with a dial indicator and then rotating it). The camber was similarly determined in the green state for all the specimens. The average value of the camber is approximately 2 mils and, because the sintered

TABLE I
REPRODUCIBILITY STUDY WITHIN-LOT VARIATION

Sample		Powder Characteristics		Extrusion Process Characteristics		Product Characteristics			
Batch	Specimen	Fisher Particle size, μ	B.E.T. Surface Area, m^2/g	Moisture Content, w/o	Extrusion Force, tons	Density, g/cc		Sintered Diameter, in.	Camber, mills/in.
						Green	Sintered		
E1	10	1.30	1.19	10 to 11	7-1/2	5.16	8.54	0.4250	3.2
	11					5.17	8.53	0.4250	2.0
	12					5.16	8.51	0.4258	1.2
	13					5.17	8.49	0.4258	1.0
	15					5.18	8.50	0.4260	3.5
	16					5.21	8.51	0.4248	1.6
	18					5.19	8.51	0.4265	1.2
	19					5.20	8.53	0.4265	2.3
	20					5.18	8.52	0.4255	1.2
	21					5.17	8.51	0.4262	2.0
	22					5.20	8.52	0.4252	2.4
Batch mean						5.181	8.514	0.4257	1.96
Batch standard deviation						0.02	0.02	0.001	0.8
F1	7	1.23	1.475	11	5 - 7	5.07	8.41	0.4253	1.6
	8					5.08	8.42	0.4250	3.2
	9					5.08	8.43	0.4255	1.2
	10					5.08	8.39	0.4260	1.2
	11					5.08	8.39	0.4258	0.4
	12					5.11	8.40	0.4250	3.2
	13					5.09	8.42	0.4250	3.1
	14					5.07	8.40	0.4255	2.0
	15					5.07	8.42	0.4257	1.6
	16					5.07	8.43	0.4258	2.0
	17					5.08	8.43	0.4250	0.6
Batch mean						5.08	8.413	0.4254	1.83
Batch standard deviation						0.01	0.02	0.001	1.0

TABLE II
REPRODUCIBILITY STUDY LOT-TO-LOT VARIATION

Sample		Powder Characteristics		Extrusion Process Characteristics		Product Characteristics			
Batch	Specimen	Fisher Particle size, μ	B.E.T. Surface Area, m^2/g	Moisture Content, w/o	Extrusion Force, tons	Density, g/cc		Sintered Diameter, in.	Camber, mills/in.
						Green	Sintered		
A2	16	1.40	1.75	10	5-1/2 - 7	5.243	8.280	0.4327	1.5
	17					5.249	8.313	0.4322	1.5
	18					5.271	8.364	0.4307	1.9
Mean values for batch →						5.254	8.319	0.4319	1.63
B2	16	1.25	2.11	11	5 - 6	5.102	8.440	0.4250	1.0
	17					5.111	8.432	0.4253	1.9
	18					5.117	8.450	0.4248	1.9
						5.110	8.441	0.4250	1.60
C1	16	1.22	1.72	10	5 - 6	5.340	8.473	0.4290	1.2
	17					5.264	8.499	0.4288	1.9
	18					5.261	8.423	0.4302	0.6
						5.288	8.465	0.4293	1.23
D1	16	1.43	1.74	10	5 - 6	5.246	8.383	0.4305	2.3
	17					5.241	8.435	0.4293	1.2
	18					5.241	8.394	0.4303	1.5
						5.243	8.404	0.4300	1.67
G1	16	1.40	1.53	10	5-1/2	5.221	8.397	0.4291	1.5
	17					5.201	8.383	0.4298	1.5
	18					5.224	8.373	0.4298	1.9
						5.215	8.384	0.4296	1.63
H1	13	1.88	1.34	10-1/2	10 - 11	5.399	8.205	0.4385	1.2
	14					5.406	8.194	0.4387	1.2
	15					5.405	8.273	0.4367	0.8
						5.403	8.224	0.4380	1.07
I1	16	1.46	1.43	9	10 - 11	5.449	8.388	0.4363	1.9
	17					5.455	8.365	0.4368	3.1
	18					5.460	8.354	0.4367	3.5
						5.455	8.369	0.4366	2.83
Over-all mean						5.281	8.372	0.4315	1.67
Standard deviation						0.12	0.08	0.005	0.6

length is approximately 3 in., the total deflection is about 6 mils for each piece. The powder characteristics, extrusion-clay moisture, and extrusion force are also noted for the two extrusion batches.

Table II shows similar experimental data for between-lot variation in the green and sintered density, sintered diameter, and camber. Note that the over-all standard deviation of the sintered diameter is only 5 mils and that the over-all standard deviation of the camber is only 6/10 mil. The sintered densities also suggest that either the skeleton-like nature of the mixed oxide was not eliminated by the recalcination step, or the recalcined aggregates were too hard to be sufficiently reduced by the specific wet-ball-milling treatment used.

Figure 4 is a photomicrograph of a typical sintered ammonia-oxalate precipitated mixed-oxide specimen. The green and sintered densities of this specimen were 5.19 and 8.51 g/cc, respectively.

The conclusions of the test program were that the green density, sintered density, and sintered diameter are sufficiently reproducible to ensure a low recycle ratio, and the sintered straightness is both sufficiently reproducible and good enough to permit surface grinding to meet fuel-pellet diametral tolerances. The sintered density of the ammonia-oxalate precipitated mixed-oxide was lower than the desired 93 per cent of theoretical.

3.4 CNEN MIXED-OXIDE EXTRUSION DEMONSTRATION TEST

At this point, the results of an alternate mixed-oxide preparation method, developed by the CNEN Materials Division, became available: the uranium⁺⁴ reduction and oxalate

Fig. 4. Photomicrograph of Sintered Ammonia-Oxalate Precipitated Mixed Oxide Specimen

coprecipitation process described in the PCUT plant paper given previously. Preliminary studies showed that the uranium⁺⁴-thorium oxalate mixed-oxide was more sinterable than that prepared by the ammonia-oxalate process and, accordingly, a very limited extrusion demonstration was conducted; the results are presented in Fig. 5. Only a very small amount of the CNEN uranium⁺⁴-thorium oxalate mixed-oxide powder was available for these tests, so it was decided to demonstrate the reproducibility of this process only if the required sintered density could be achieved.

As can be seen in the curves summarizing the experimental results, densities up to 9.4 g/cc were obtained, owing in part to the higher green density of the extruded bodies, which were obtained with a relatively low extrusion-clay moisture content. The very dry clay, of course, required considerably higher extrusion force. Typically, an extrusion force of 20 tons produced a green density of approximately 5.5 g/cc from extrusion clay containing 9 to 10 weight per cent water. Figure 6 is a photomicrograph of a typical sintered CNEN mixed-oxide specimen. The green and sintered densities of this specimen were 5.10 and 9.31 g/cc, respectively.

Because densities over 93 per cent of theoretical were achieved, this extrusion process was retained as the PCUT plant reference fuel-fabrication process. The previous reproducibility test indicated that a reproducible fabrication process can be achieved with mixed-oxide powder of reproducible characteristics. A demonstration of the reproducibility of the uranium⁺⁴-thorium oxalate mixed-oxide extrusion process will be obtained as part of the development program currently in progress. The objective of this program is the preparation of an extruded thorium-fully enriched uranium, boiling-water-reactor fuel assembly for irradiation proof testing (Sec. 6).

Fig. 5. Density and Extrusion Force vs. Moisture Content for CNEN Mixed Oxide

Fig. 6. Photomicrograph of Sintered CNEN Mixed Oxide Specimen

Some of the laboratory equipment used in these initial extrusion development studies is shown in Figs. 7 through 9. Figure 7 displays the laboratory extrusion device that was operated by the laboratory hydraulic press. Figure 8 shows the muller-mixer used for powder blending and clay mixing. Figure 9 shows some of the dry, green extrusions positioned in the molybdenum sintering boat.

4. FUEL-ASSEMBLY DESIGN MODIFICATION

Figure 10 is an outline drawing of the Elk River Reactor (ERR) fuel assembly modified for remote fabrication. The two principal design modifications are (1) the use of snap rings to attach the individual fuel elements to the top and bottom grid pieces, and (2) the use of a mechanically prefabricated fuel-assembly spacer grid. The first ERR fuel assemblies were prepared by assembling the spacer grids in place, and welding to complete the assembly of the spacer as well as to ensure firm clamping to the individual fuel-element tubes. The operations involved in producing the modified assembly in the PCUT plant are described below.

5. WARM-CELL EQUIPMENT ARRANGEMENT AND MATERIAL FLOW

Figure 11 shows the location of the warm-cell equipment and the flow of material through the warm-cell process as indicated by the arrows. To improve the clarity of the drawing, the drying of green extrusions has not been shown. The green extrusions are dried in an oven before being cut to size for sintering. A few of the warm-cell service equipment items are indicated but not identified specifically. The most important of these is an ultrasonic cleaner, which is used primarily for cleaning the extruder. The cleaner could also be used

Fig. 7. Laboratory Extruder

Fig. 8. Muller Mixer

Fig. 9. Dry, Green Extrusions in Sintering Boat

Fig. 10. Modified ERR Fuel Assembly

Fig. 11. Warm-Cell Equipment Arrangement and Material Flow Diagram

for removing excessive surface contamination from the completed fuel assemblies if the normal protective envelopes and contamination barriers fail during assembly fabrication or handling operations.

5.1 EXTRUSION SYSTEM

One of the unique pieces of equipment developed for the PCUT plant is the remote extrusion system, which is shown schematically in Fig. 12. The basic units of the extrusion system are (1) the hydraulic cylinder, which provides the force to extrude the clay through the die; (2) the extrusion chamber, die, and die holder; (3) the hauloff device, which is synchronized with the extrusion rate by a servomechanism; and (4) the cutoff device, which ensures that green extrusions of the maximum allowable length are produced.

Figure 13 is a line drawing of the extrusion equipment, and provides a better indication of the size of the equipment. Note that the complete unit is mounted on a single bed to ensure proper alignment of the extrusion chamber with the hauloff device.

5.2 SINTERING FURNACE

The other major warm-cell design task was that undertaken to achieve a reliable sintering furnace. Various kinds of furnace failure were identified in discussions with vendors and ceramic-development personnel, and the design concept shown in Fig. 14 was evolved. Because most failures are likely to occur in the high-temperature section, the warm-cell furnace is arranged with the preheat and cooling sections mounted on moving dollies and the center (high-temperature) section a tank that can be simply plugged into or unplugged from the furnace bed. Figure 14 shows the location of the pusher, which moves the

Fig. 12. Extrusion System Schematic Diagram

Fig. 13. Extrusion Equipment

Fig. 14. Sintering Furnace Schematic Diagram

sintering boats through the furnace, the side port through which the boats enter the furnace, and the side port through which the boats emerge from the furnace. The high-temperature portion of the furnace is designed to be as inexpensive as possible. Thus, disposal, rather than repair, of failed units will permit a considerable savings in maintenance time without imposing excessive maintenance costs.

5.3 OTHER WARM-CELL EQUIPMENT

The other major items of warm-cell fuel-assembly fabrication equipment are shown in Figs. 15 through 17. These have already been described but are included here to indicate the size of the equipment and the type of design that has been found to lend itself to operation with through-the-wall manipulators as opposed to almost completely automatic operation by control systems external to the cell itself.

5.3.1 Pellet Loader

The pellet loader, shown in Fig. 15, takes the cladding tube already leak-tested and with one end plug welded in place. The tube is fabricated entirely outside the warm cell, including corrosion testing, if it is made of Zircaloy. These prefabricated subassemblies are loaded with inspected fuel pellets, and the second end plug is inserted. The fuel element is then ready for transfer to the end-plug welder.

In the end-plug welder (which is not illustrated), the pellet-filled tube is evacuated and back-filled with helium to approximately atmospheric pressure. This is accomplished through an end plug with a partial keyway milled in it. Once the helium atmosphere is established in the fuel-element tube, the end plug is inserted fully, covering the keyway and containing the helium. The second end closure weld is then made.

Fig. 15. Pellet Loading Machine

Fig. 16. Helium Leak and Weld Tester

Fig. 17. Fuel-Element Assembly Machine

5.3.2 End-Weld Leak Tester

Figure 16 shows the end-weld leak tester, which tests groups of 25 welded elements at high temperature with a helium mass-spectrometer. If a faulty closure is detected, the 25-element batch is then inspected individually to identify the particular leaking element. A gross leak could, of course, be detected by a simpler immersion test. Leaks of intermediate size would necessitate repurging the assembly and re-establishing the helium atmosphere before the mass spectrometer could be used to inspect or reinspect an individual element.

5.3.3 Assembly Machine

The assembly machine (Fig. 17) takes 25 completely inspected and accepted fuel elements and fabricates them into a finished fuel assembly by installing the two intermediate spacer grids and securing the 25-element bundle in the top and bottom end fittings. As previously described (Sec. 4), the fuel-element end plugs lock into snap rings when the bundle of elements is pushed into the upper and lower grid pieces. Some inspection capability is built into the assembly machine and completed fuel assemblies can be inspected both in place on the machine and after they are removed.

6. IRRADIATION PROOF TEST

One item of the PCUT development program is still in progress: the manufacture and irradiation of a test fuel assembly for a boiling-water reactor. The fuel bodies are being fabricated according to the reference PCUT plant process. This includes both fuel preparation and

extrusion fabrication. The results of this test will be useful in providing adequate assurance that operation of the ERR with the recycle of fuel to the reactor is not significantly different from operation with the first core loading. The satisfactory completion of the irradiation proof test will assure the AEC that the ERR operating schedule will not be jeopardized in any way by recycling of the PCUT fuel. That is, the reliability or integrity of the PCUT refabricated fuel will have been demonstrated in a reactor before the PCUT-refabricated ERR assemblies have to be accepted for loading in the ERR itself.

7. SUMMARY

The principal results obtained to date in the PCUT program, particularly in that portion of the program related to the warm-cell fuel reconstitution and refabrication, are:

- (1) The oxide-fuel extrusion fabrication process has been demonstrated to be reproducible.
- (2) The various items of equipment required to carry out this process remotely in the warm cell have been designed and are now being procured.

Completion of construction, startup, and initial operation of the PCUT facility with the first ERR core as feed material will clearly demonstrate the feasibility of recycling fuel on an engineering scale. The data collected on this scale of operation will permit the evaluation of the economic potential of the integrated reprocessing plant in the 300- to 600-Mwe reactor central station.

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Session V
Paper 25

RECENT VIBRATORY-COMPACTION STUDIES ON THORIA-URANIA

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INTRODUCTION

The major radiation hazard associated with the recycling of Th-U²³³ oxide fuel is that due to energetic gamma rays from the decay products of U²³². For decay times of interest in fuel fabrication, the gamma activities of primary concern are those from Tl²⁰⁸ (2.6 Mev) and Bi²¹² (2.2 Mev). Radiation intensities calculated for a realistic situation in a thorium fuel cycle for power reactors¹ indicate that remote fabrication behind 8 cm of lead will be required for safe handling. A simple fabrication process which requires a minimum of hand manipulation, inexpensive and simple equipment, and a short residence time for the fuel is therefore desirable.

One of the chief objectives of the Fuel Cycle Program at Oak Ridge National Laboratory (ORNL) is the development of a simple process that can be readily adapted to remote fabrication of irradiated Th-U oxide fuels. The most promising of several possible ceramic fabrication processes for this application is vibratory compaction. In this process vibratory energy is used to arrange size-graded granular matter into a dense configuration in a metallic tube. In order to achieve high bulk densities it is important, of course, that the fuel particles charged to the process be of very high density. Particles derived from a fusion process or from the sol-gel process^{2,3} are regarded as acceptable from this standpoint.

Six criteria have been established for evaluating the vibratory-compaction process. These criteria, which must be met simultaneously, are listed below.

1. The process must be simple in equipment and operation.
2. A bulk fuel density greater than 90% of theoretical should be obtainable in rod-type fuel elements.
3. At least 95 wt % of the starting material must appear in acceptable fuel rods.
4. The axial variation of fuel density within a rod should be no greater than $\pm 2\%$ of the bulk density in the rod.
5. The variation in bulk density from rod-to-rod should be no greater than $\pm 1/2\%$ of the average for all rods.
6. The fuel element must perform acceptably during irradiation.

The first five criteria are concerned with the vibratory-compaction process itself and are given major consideration in this paper.

DESCRIPTION OF THE PROCESS

Vibratory compaction is a straightforward fabrication process that consists of five basic steps: comminution, sizing, blending, loading, and vibrating. Figure 1 shows a simplified flow diagram of this process. Simplicity is derived primarily from the equipment required. Equipment suitable for this application is inexpensive and readily adaptable for remote operation.

Fig. 1. Simplified Flow Diagram for Vibratory Compaction Process.

Material Preparation

The comminution process requires a crude crusher and a fine reduction mill. For the development studies at ORNL, high-density oxide materials are comminuted by a jaw crusher and a ball mill which produce irregularly shaped particles. The only practical method for carrying out the sizing operation is through the use of sieves. Blending, which is a two-step operation, consists of proportioning the proper size fractions by weight and homogeneously mixing these fractions together. Tumbling the material in a container much larger in volume than the volume of the material provides satisfactory mixing.

The Compaction Process

The blended material is poured from the mixing container onto a vibrating trough that feeds the particles into the metallic tube. The feeder is operated while the fuel tube is vibrating and the filling operation normally requires several minutes. The tube containing all of the fuel is then vibrated for an additional six or eight minutes to complete the compaction process.

The vibratory energy required for compaction may be generated by either electric or pneumatic systems. In these two classes there are three types of vibratory exciters which have been used extensively for this application and which are being evaluated at ORNL. These exciters are the electrodynamic vibrator, a pneumatic, reciprocating piston vibrator, and a pneumatic impact vibrator.

Electrodynamic Equipment. An electrodynamic vibrator has been adapted for remote fabrication at Hanford Laboratories Operation.⁴ A similar vibrator and its power supply, procured from the MB Manufacturing

Company, are shown in Figs. 2 and 3 as installed in the Vibratory Compaction Laboratory at ORNL. The principal use for this equipment at ORNL is for relatively basic process parameter studies. The system is physically too large for the remote fabrication facility that is under construction at ORNL;⁵ in addition, it is much more expensive and complex in operation than the pneumatic systems described below. Thus, if the simplicity criterion is regarded as an important one, the suitability of electrodynamic equipment of this type for a practical remote operation may be questionable.

Reciprocating Piston Vibrator. The National Air Vibrator Company (NAVCO) manufactures a pneumatic, reciprocating piston vibrator designed primarily for attachment to very large storage hoppers which are vibrated to aid material flow. For compacting oxides fuels into tubes, the NAVCO Bin Hopper (BH) Vibrator is simply bolted to a rigid steel plate as shown in Fig. 4, and the fuel tube is attached to the plate with a pipe-to-tube coupling. This assembly is suspended on springs or other elastic configurations and produces a rather complex vibratory energy spectrum. The air pressure controls the frequency and acceleration level of this system. At air pressures of 70-80 psi, for example, the frequency range is 40-70 cps and the acceleration level is approximately 100 g.

This vibrator assembly, shown schematically in Fig. 5, is obviously simple and relatively inexpensive; it is not, however, entirely suitable for remote fabrication in its present stage of development. Because the vibrator and plate assembly oscillate about 40 to 70 cycles per second, the guide pins and high-pressure-air connector are subjected

Fig. 2. Electrodynamic Vibrator Installed in the Vibratory Compaction Laboratory at ORNL.

Fig. 3. Power Supply and Control Console for the Electrodynamic Vibrator Shown in Fig. 2.

Fig. 4. NAVCO BH Pneumatic Vibrator Mounted for Fuel Compaction.

Fig. 5. Schematic Drawing of NAVCO BH Pneumatic Vibrator Mounted for Fuel Compaction.

to fatigue-promoting alternating stresses and fail unpredictably. For remote operation frequent and unpredictable failures of this type cannot be tolerated.

Variable Impact Vibrator. A pneumatic system that has demonstrated satisfactory performance for remote fabrication is shown in Fig. 6. In this system, a variable impact vibrator made by the Branford Company generates a mechanical shock wave in an external steel anvil coupled only to a fuel tube. A schematic drawing of the variable impact vibrator, including the external anvil and the support system, is presented in Fig. 7. The vibratory energy is generated by a piston that periodically imparts an impact load on an internal anvil that in turn produces a mechanical shock wave in the external anvil. (At air pressures as low as 25 psi there are approximately six impulses per second and each impulse lasts about 15 μ sec.) Because the energy is transmitted by the external anvil through the support plate, very little of it is dissipated in the vibrator housing or plate. The use of a mechanical wave guide makes it practicable to design and incorporate an alpha seal between the fuel rod and the vibrator.

This system, in which all external parts are rigidly fixed, is relatively free of the fatigue problems encountered in the reciprocating piston assembly and requires only a small fraction of the air volume needed for operation of the reciprocating piston. The shock system generates pulses whose acceleration levels are from two to three orders of magnitude greater than those developed by the reciprocating piston.

Fig. 6. Branford Variable Impact Vibrator Mounted for Fuel Compaction.

Fig. 7. Schematic Drawing of Branford Variable Impact Vibrator Mounted for Fuel Compaction.

RELATION OF EQUIPMENT- AND PROCESS PARAMETERS TO CRITERIA

General Considerations

Although the equipment selected can be operated remotely after necessary initial adjustments are made, the mere fact that it has been installed does not necessarily mean that the first criterion - simplicity - can be met. For the process to be considered simple, operating procedures involving direct hand adjustments must be eliminated or kept to a minimum. This added requirement can be met provided the particle size distribution loaded into the fuel tube is properly chosen; if it is not, the jaw crusher, for example, may require adjustments that only direct handling can accomplish.

The particle size distribution selected also determines in large measure whether the other equally important criteria can be met. The choice is difficult because independent optimization with respect to each of the first four criteria does not, in general, make for an overall compatible situation. Moreover, it must be recognized that independent optimization with respect to the sixth criterion - acceptable performance during irradiation - may not be consistent with that established for the other criteria.

The fifth criterion - variation in bulk density from rod-to-rod - appears to be relatively independent of the particle size distribution. On the other hand, variations in comminution procedures, physical properties of the oxide fuel, and the vibrator-to-fuel-tube coupling strongly affect the reproducibility of the vibratory-compaction process. Data obtained from many specimens fabricated for irradiation testing

have indicated that it is not difficult to meet this criterion. In fact, if proper care is exercised, the reproducibility of the density among all rods for a given reactor fuel loading should be better than $\pm 1/2\%$ of the average value.

In view of these considerations, a major portion of the ORNL program has been concerned with studies to find particle size distributions that serve to optimize conditions relative to the first four criteria. As indicated previously, the use of pneumatic vibrating devices has been favored in the interest of simplicity. The comments which follow, however, apply generally to any type of vibratory compaction system.

Particle Size Distribution

Simple size distributions are of great interest because of practical limitations in the sizing operations, particularly during remote fabrication; therefore, most of the work at ORNL has been directed toward the attainment of high bulk densities within simple classes of size distributions. In many studies the initial approach has been to find a distribution that will meet the second criterion - bulk densities greater than 90% of theoretical - and to modify the distribution as required to satisfy the other criteria.

Two classes of starting size distributions that have shown considerable promise are the ternary, or 3-size-fraction, class, and the binary, or 2-size-fraction, class. The separate size fractions that constitute the ternary class are generally referred to as coarse, medium, and fine. The binary class is obtained by eliminating the medium size fraction of the ternary class. This is desirable because the medium size fraction is difficult to generate remotely. Within a class

the various distributions are systematized according to the sieve sizes of the fractions.

Table I lists seven particle size systems which have been studied extensively and which are of interest for Th-U oxides in fuel rods with inside diameters of approximately 5/16 to 5/8 in.

Table I. Particle Size Systems Studied for Vibratory Compaction of Th-U Oxides in Fuel Rods with Inside Diameters of 5/16 to 5/8 In.

	System	Size Fraction (U.S.S. Sieve Size)		
		Coarse	Medium	Fine
Ternary Class	I	-10/+16	-70/+100	-200
	II	-6/+10	-35/+65	-200
	III	-6/+16	-50/+140	-200
	IV	-4/+16	-50/+140	-200
Binary Class	V	-10/+16	None	-200
	VI	-6/+16	None	-200
	VII	-4/+16	None	-200

Optimization with Respect to Simplicity, Density, and Yield.

Optimization of the particle size distribution must be performed experimentally because existing theories of particle packing do not accurately relate particle size and distribution with bulk density of a mixture of irregularly shaped particles. Effective semiempirical procedures, guided, however, by existing theory, have served to define the areas of interest for more detailed study and have significantly decreased the number of experiments required to determine an optimum distribution.⁶

In general, for ThO_2 -3 wt % UO_2 made by the sol-gel process, Systems I, II, III, and IV (Table I) have yielded bulk densities from 88 to 91% of theoretical. In these systems an approximate composition of 60 wt % coarse, 15 wt % medium, and 25 wt % fine appears to be nearly optimum.

The process yield is clearly controlled by the coarse-fraction yields from the comminution step; therefore, the particle size distribution selected strongly affects the materials preparation procedures. For example, in the remote fabrication facility designed by ORNL⁵ in which a jaw crusher is used, Systems I and II cannot be seriously considered. To obtain sufficient yields of the coarse- and medium-size fractions in these systems requires either a large number of recycles through the crusher with changes in jaw opening, or a semicontinuous ball-milling procedure. Both of these procedures are laborious and time consuming. (In spite of this disadvantage, however, System I may find application in the fabrication of fuel rods of approximately 0.3-in. ID because this system is the only one of the four ternary systems listed for which the coarse particles will fit into the space available in rods of this size.)

Yields of the coarse fraction greater than 60% by weight of the total starting material can be obtained with one crusher setting and a minimum of recycling simply by increasing the range of the coarse-size fraction. Thus, as many as 50 recycles of the +6 material and three different crusher settings were required in order to obtain sufficient yield of a -6/+10 fraction. On the other hand, for a single crusher setting sufficient yield for a -4/+16 fraction was obtained with only

one pass through the crusher, and only a few recycles were required for a -6/+16 fraction. The labor required for the semicontinuous milling procedure is decreased by increasing the range of the medium fraction.

System III is preferred to System IV for remote fabrication of fuel rods sheathed with 1/2-in. OD x 0.035-in. wall tubing. For System IV, blockage of the tube by a single large particle tends to occur in about 6-10% of the rods. System IV, however, is obviously a strong candidate for fuel rods with diameters greater than 1/2 in.

As cited previously, the binary distributions are attractive because elimination of the medium-size fraction greatly reduces the labor required for operating a remote facility. However, the binary distributions require a greater amount of the coarse fraction (65 to 75% by weight) than do the ternary distributions to achieve acceptable bulk densities. The basis for the selection of a particular binary system is similar to that described for the ternary systems.

Optimization with Respect to Density Uniformity. It has been shown that all seven of the systems listed in Table I can simultaneously meet the criteria associated with bulk density and rod-to-rod density uniformity. However, only four of these (Systems III, IV, VI, and VII) have simultaneously met the criteria concerned with simplicity, bulk density, yield, and rod-to-rod density uniformity.

It is not known at present whether any of these systems can meet the axial density uniformity criterion. Whether they can, in fact, meet this criterion depends upon the specification of the incremental length over which the axial density must be measured and, therefore, upon the method used for measuring this property. If the length

increment involved in the measurement is very large compared with the size of a coarse particle - as is the case, for example, when fuel rods 4 ft long are cut into four or five sections - then the density variations from section to section are very small and the criterion can be met easily. However, if this increment is only several times greater than the size of a coarse particle, then density variations become large. This latter situation arises when the density is measured by the attenuation of a gamma-ray beam of small cross section. Of the seven systems listed it is believed that only System I can meet a density uniformity specification based on the gamma-ray technique. The other systems are at best borderline for a gamma-ray beam having a cross section approximately the same as that of a coarse particle.

Optimization with Respect to Irradiation Performance. There are as yet no established rules for selecting a particle size distribution to meet the irradiation performance criterion. Most of the irradiated specimens prepared at ORNL have arbitrarily been made with System I. There has been only one experiment in which System III was used and in this experiment the cladding failed for unknown reasons. Rods incorporating System IV have been irradiated, but the material was sintered-and-ground UO_2 and the coarse particles may have degraded substantially during fabrication. It is recognized that particle size, and, therefore, the distribution selected, will greatly influence the retention of fission gases and the thermal performance of the material. Of particular concern is the possible burnout of the metal cladding by a very large particle in direct contact with the inside surface of the cladding.

SUMMARY

Vibratory compaction is being developed for remote fabrication of recycled Th-U oxide fuels because of its inherent simplicity. Six criteria have been established for evaluating the process. The interaction of these criteria requires that careful consideration be given to the selection of the particle size distribution for the fuel. Because several simple size distributions yield bulk densities of approximately 90% of theoretical, the final selection for a given application can be made with respect to operational simplicity, yield, and density uniformity.

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Session V
Paper 26

PRELIMINARY FABRICATION INVESTIGATION OF
ORNL SOL-GEL THORIA-URANIA

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PRELIMINARY FABRICATION INVESTIGATION OF
ORNL SOL-GEL THORIA-URANIA

By

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INTRODUCTION

Since 1956, Babcock & Wilcox has applied the thorium fuel cycle to power reactors. In considering the fabrication of recycled U^{233} , mechanical compaction as a fabrication process shows the most promise. The most promising fuel to date has been the sol-gel process ThO_2-UO_2 , developed by Oak Ridge National Laboratory, as feed for mechanical compaction. To establish the commercial applicability of sol-gel material, a cooperative program was initiated between ORNL and B&W where it was agreed that ORNL would supply the sol-gel oxide and B&W would evaluate this material from a fabrication standpoint by using commercial techniques. The results from the sol-gel material were then to be compared to results previously obtained with fused UO_2 , utilizing identical techniques insofar as possible.

MATERIALS AND EQUIPMENT

The sol-gel oxide furnished by ORNL contained 3 wt % urania and 97 wt % thoria. The oxygen-uranium (O/U) ratios of the two batches blended together at ORNL and used in this evaluation program were 2.22 and 2.09. The gas volumes released at $1200^{\circ}C$ in a vacuum were 0.068 and 0.003 cc/g, respectively. The O/U ratio and gas volume determinations were performed at ORNL. The "as received" oxide had been pre-sized to approximately

60 wt % - 6 + 10 mesh
15 wt % - 35 + 65 mesh
25 wt % - 200 mesh,

which is a desirable particle size distribution for vibratory compaction. This mix will be referred to as mix A.

Two types of tubing were used, type-304 stainless steel and Zircaloy-2. Wall thicknesses were 0.010 and 0.020 in. for the 304 stainless steel and 0.025 in. for the Zircaloy-2. The OD of tubes vibratorily compacted was

0.436 in. The OD of the swaged tubes was originally 0.490 in. After a 20% reduction in the cross-sectional area of the rod, the OD was reduced to approximately 0.436 in. Type-304 stainless steel and Zircaloy-2 tubing were used since both materials are well-qualified for use in reactors. The 0.436-in. diam is the present design diameter for fuel rods in the Spectral Shift Control Reactor (SSCR).

The electronic vibrator was a 750-lb thrust unit made by the Savage Company. The Navco pneumatic vibrator used operated on air pressure at approximately 80 psi. The swager was a Fenn 4-F rotating die machine.

RESULTS

The following procedure was used to determine the bulk densities of vibratory compacted rods. The clad tubing was cut to length, an end cap was welded into one end, the empty tube volume was determined by filling with water, and the tube weight was determined. The weight of oxide that would fill all but 2 in. of the tube was then calculated assuming an arbitrary bulk density based on previous experience with fused UO_2 . The weight percents of the different particle sizes were calculated from the calculated batch weight. The powder was thoroughly mixed and loaded into the tube as the tube was being vibrated. After the powder had been fed into the tube, a rider weight and push rod, weighing 11.5 lb was placed on top of the oxide column and further vibration continued for approximately 5 to 10 min. The depth of the oxide was determined, and the oxide weight in the tube was redetermined. These values were then used to determine the bulk density of the oxide which was subsequently divided by 10.03 g/cc to obtain the percent of theoretical density.

Figure 1 shows the average rod bulk densities obtained with the mesh mixture supplied by ORNL (mix A) and the bulk densities obtained with other mixtures (mixes B and C, which were optimized for high densities by electronic vibration). These were based on the average from 103 rods fabricated. By electronic vibration of three-component mixtures, it was possible to exceed consistently 89% of theoretical density on 12 rods of 0.436 in. OD. By pneumatic vibration of three-component mixtures, it was possible to reach 86.8% of

Figure 1. Plot of Percent Theoretical Density of Rod Vs Particle Size Mixture of Sol-Gel Oxide

theoretical density. Again, these bulk densities were equivalent or slightly higher than those reached with fused UO_2 on the same equipment.

As indicated in Figure 1, increasing density gave a decreasing spread of data. Also, it is shown that mixes designed for high densities by electronic vibration do not necessarily yield high densities during pneumatic vibration. This is expected since the lower frequency pneumatic vibrator affects a smaller range of particle sizes in the powders than the more versatile electronic vibrator with its wide range of frequencies. In Figure 1, the 0.020-in. wall thickness stainless steel tubes generally gave slightly higher densities than the 0.010-in. wall thickness stainless steel and the 0.025-in. wall thickness Zircaloy-2 tubes. The reason for this is not clear.

Particle breakdown of the sol-gel oxide during vibration is less than 50% of that experienced with fused UO_2 . Post-vibratory compaction sieve analyses indicated less than a 2% change of the coarse and intermediate fractions with the sol-gel oxide. After swaging, sieve analyses indicated the sol-gel material had experienced only 70% of the particle breakdown experienced with fused UO_2 . This is an ample indication of the decreased friability of the sol-gel oxide as compared to fused UO_2 .

In the low reduction swaging process, two passes through the swager accomplished the necessary 20% reduction in area. Indentation of the cladding by the sol-gel oxide was observed to be similar to that experienced with fused UO_2 with a maximum depth of penetration of 2 to 2.5 mils. Table 1 shows the results from swaging sol-gel oxide. The densities obtained are comparable to those achieved with fused UO_2 . Density was measured by destructive techniques.

No visual changes were noted in the sol-gel oxide after vacuum annealing open sections of swaged rods at 1450°F for 2 hr. The fuel was still tightly held in the ends of the rods and no gross color changes had occurred.

Low magnification observation of the sol-gel oxide under transmitted light showed a marked difference between the batch used in this study and a small batch sent by ORNL for preliminary use. The color range of the material used in this study ranged from clear milky white to nearly opaque reddish brown.

TABLE 1

DATA FROM SWAGED RODS FILLED WITH SOL-GEL THORIA-URANIA

Rod	Filled Density, % of Theoretical	Nominal Pre-swage Wall Thickness of Zircaloy-2, in.	Post-swage Wall Thickness, in.	Post-swage OD, in.	% Length Change Over 20 in.	Average % of Theoretical Density (Post-swage)
109	79.7	0.025	0.027	0.435	12.2	92.2
110	79.1	.025	.027	.435	13.1	92.2
111	80.2	.025	.027	.436	12.8	92.2
112	79.1	.010	.012	.433	13.7	91.4
113	79.0	.010	.012	.432	13.4	91.8
114	79.4	0.010	0.012	0.433	14.4	91.6

The small batch was uniformly clear white to dark grey with no shades of red or brown noted. The reason for this is not clear since the only difference between these batches is the higher O/U ratio.

During the course of work, the sol-gel oxide mixtures picked up moisture rapidly and would not vibrate to satisfactory densities unless dried at 100°C for 30 min or longer in air. After receiving the particle size analysis of the -200 mesh fraction from ORNL, it was found that the powder had a logarithmic mean size of 15 microns with 38% less than 10 microns in diameter. This extremely fine powder tended to pick up moisture rapidly. This is not a serious problem, but steps must be taken to minimize exposure.

SUMMARY AND CONCLUSIONS

Sol-gel thoria-3 wt % urania, furnished by ORNL, was fabricated into rods approximately 2 ft long and 0.436 in. diam by both electronic and pneumatic vibratory compaction using B&W developed production techniques.

The data obtained from density determinations and post-fabrication sieve analyses of the sol-gel oxide were compared to data obtained from rods filled with Spencer Chemical Company fused UO_2 by the same procedures. Densities obtained on the sol-gel oxide were comparable to those obtained with fused UO_2 , and were consistently greater than 89% of theoretical density with electronic vibration and proper particle-size mixtures. During vibratory compaction, sol-gel oxide evidenced less than 50% the particle breakdown evidenced by fused UO_2 . No special efforts were made to obtain unusually high densities, and parameters, such as loading technique and time of vibration, were kept constant and similar to those used on larger rods. Bulk density values obtained are representative since they are based on a total of 103 rods fabricated from the sol-gel material by vibratory compaction.

The sol-gel oxide was also evaluated in B&W's swaging process and compared with fused UO_2 fabricated by identical methods. The sol-gel material achieved comparable densities to fused UO_2 ; that is, 92% of theoretical density. The sol-gel oxide experienced approximately 70% of the particle breakdown experi-

enced by fused UO_2 during swaging.

During fabrication, the sol-gel oxide exhibited fabrication characteristics as good or better in all respects as fused urania.

Session VI
Paper 27

THORIUM IRRADIATION IN D₂O-MODERATED REACTORS

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THORIUM IRRADIATION IN D₂O-MODERATED REACTORS

Introduction

In 1961 the U. S. Atomic Energy Commission authorized the production of 120 kilograms of U-233 for research and development for peaceful purposes. The over-all responsibility for production was assigned to the Savannah River Plant, with the U-233 to be delivered in nitrate form in late 1964 or early 1965. A total of 21 tons of thorium is to be irradiated, 13 tons of which will be used in the initial production irradiation.

Two different kinds of test assemblies, designated as Mark A and Mark B, were irradiated during the time the 21 tons of thorium was being procured and fabricated into shapes for reactor irradiation. This paper describes the test assemblies, their characteristics under irradiation, their growth characteristics, and the resultant isotopic production in the assemblies.

Discussion

U-232 Limit

The U-232 limit in the final product was unspecified at first, but was set later at 200 ppm maximum. Still later, after the first test design (Mark A) was irradiated, the U-232 limit was reduced to 170 ppm because of shielding limitations of U-233 fabricators. As a result of this lower limit, it was not economical to irradiate

the Mark A design to produce the planned amount of 120 kilograms of U-233, and so the Mark B design was developed and tested.

Assembly Design

Figure 1. The Mark A slug design is a hollow-core slug of thorium metal, clad with aluminum by the hot-press-bonding technique. For irradiation, the slugs were assembled in columns and placed inside a fuel tube containing enriched uranium, with the thorium separated from the nearest uranium by about 0.6 inch.

Cooling and neutron moderation during irradiation were provided by D₂O. It is well known that thorium slug power increases during irradiation, so the coolant flow needed at the end of the irradiation cycle had to be supplied continuously throughout the entire cycle. This unfortunate effect of wasting a certain amount of water and pumping power throughout most of the cycle cannot be avoided, unless means are provided to vary individual channel flow in a fuel assembly. Such means usually have severe safety drawbacks; thus flow regulation was not attempted in these assemblies.

Growth Properties

Table I. The irradiation of the Mark A test assemblies proceeded until an average exposure level of about 4500 g/T was reached in the slug columns (grams U-233 + Pa-233 per ton of thorium). As expected, the thorium behaved very well at this exposure level. There was no sign of corrosion or roughening on slug surfaces. The

FIGURE 1. MARK A THORIUM SLUG DESIGN
(From ST-MDX4-2879)

- Core: Metallic Thorium
- Cladding: 0.030" Aluminum
- Fabrication: Hot-Press-Bonded
- Nearest U-235: Surrounding Fuel Tube, ~0.6" Separation
- Weight: 5.86 Pounds
- Arrangement: Single Columns of Thorium Slugs

**TABLE I. MARK A DIMENSIONAL CHANGES DURING
TEST ASSEMBLY IRRADIATION**

(g/T Level: 4500 average)

Outside Diameter Change, mils

	g/T →	<u>Avg</u>	<u>Max</u>	<u>Min</u>
● ET-1				
Top of Slug		-1	-1	-1
Middle of Slug		0	-1	-1
Bottom of Slug		-1	-1	0
● ET-2				
Top of Slug		-2	+3	-2
Middle of Slug		0	-1	0
Bottom of Slug		-2	-1	-1

Average OD Change, mils

Diameter →	<u>0 - 180°</u>	<u>90° - 270°</u>
ET-1	-0.4	-1.1
ET-2	-1.1	-1.9

average change in the outside diameter of the slugs was a decrease of 1 to 2 mils. Because the change was so small, postirradiation measurements were not made on the length and inside diameter of the slugs.

Table II. The thorium metal irradiated in the two test assemblies of the Mark A design had quite different impurity contents, but the metal behaved similarly under irradiation, up to maximum exposure levels of 5800 g/T.

Isotopic Composition

Figure 2. The variation in neutron flux over the column of irradiated thorium slugs made it possible to select specific slugs for isotopic analysis from minimum, average, and maximum neutron flux positions. Figure 2 shows the effect of g/T levels on U-232 content, in parts per million U-233 + Pa-233, in the Mark A slug design.

Isotopic analyses on slugs of the Mark A design were made by the Analytical Chemistry Division of the Savannah River Laboratory. A small portion of a slug was dissolved, prepared to a 10 molar solution of hydrochloric acid, and passed through an anion exchange column. The thorium and most fission products passed through, while the protactinium and uranium were quantitatively retained. The protactinium was eluted with 9M hydrochloric - 0.5M hydrofluoric acid, and the uranium was finally eluted with 0.1M hydrochloric acid. Analyses for thorium were done colorimetrically¹, for

¹ Thomason, P. F., M. A. Perry, and W. M. Byerly. Anal Chem, 21, 1239. 1949.

TABLE II. MARK A DESIGN - IMPURITY CONTENT

<u>Impurity</u>	Test Assembly →	<u>ET-1</u>	<u>ET-2</u>
Thorium Oxide, %		3	1
Carbon, ppm		800	300
Fe + Cr + Ni, ppm		2000	200

**FIGURE 2. VARIATION OF U-232
WITH g/T LEVEL - MARK A**

protactinium by gamma pulse height analysis, and for uranium by alpha counting and alpha pulse height analysis.

The analyses showed a high U-232 content and indicated that the g/T value would have to be limited to around 4000 to limit the U-232 content to below 170 ppm. The Mark A design would thus require more thorium and more shutdowns to replace thorium because the more economical higher g/T values would be prohibited.

For the Mark A design, it was calculated that 70% of the fast neutrons contributing to the U-232 came from the surrounding fuel assembly, while 10% came from fissions in the U-233 product and 20% from adjacent fuel assemblies.

It was noted that the U-232 content in the bottom slug of the Mark A assembly was abnormally low. This is explained by the fact that the bottom slug extended some 5 inches beyond the bottom of the surrounding fuel tube, and thus the source of fast neutrons at the bottom slug was reduced.

Fuel-Less Design

The calculated U-232 variation for the fuel-less Mark B design is also shown in figure 2. In this design the fuel tube surrounding the thorium slugs is removed, and fast neutrons are produced only in the U-233 product and in adjacent driver fuel elements. Thus at a g/T level of 7000, the U-232 content in the Mark B is only half that in the Mark A.

Figure 3. The Mark B assembly was designed explicitly to reduce the U-232 content in the 120 kilograms of U-233 to be produced. To do this the U-235 fuel in the lattice was located as far as

FIGURE 3. FUEL-LESS DESIGN - MARK B
(From SSK3-3-329B)

- Core: Metallic Thorium
- Cladding: 0.025" Aluminum
- Fabrication: Hot-Press-Bonded
- Nearest U-235: Adjacent Driver Tubes, >5"
- Weight: 1.84 Pounds
- Arrangement: 4 Columns Grouped

practicable from the thorium targets. Figure 3 shows one slug of a Mark B assembly. These slugs are arranged in columns, and four columns are grouped and inserted in a housing tube that channels the flow around and through the columns of slugs and provides flow and temperature monitoring during irradiation.

In this design, the nearest U-235 fuel is about five inches away, as contrasted with a spacing of about 0.6-inch in the Mark A design. All of the fast neutrons, of course, cannot be eliminated in a practical design. For example, the reactions

can still contribute to the formation of U-232 in the Mark B design, in addition to the usual fast neutron reaction with thorium:

Mark B design test assemblies were irradiated in central positions in the reactor as well as in peripheral, or blanket positions. In the blanket positions, although the production rate of U-233 is less, the U-232 fraction is also less.

Table III. Mark B test assemblies in the central positions of the reactor were irradiated to average g/T levels of about 7100, or 1.6 times the level in the Mark A assemblies. The dimensional changes are shown in table III. Shown first are the average dimensional changes for 50 slugs: -4 mils in length, +1 mil in outside diameter, and no change in warp. Also shown are the dimensional changes of individual slugs irradiated to considerably different g/T levels. There is no correlation between dimensional changes and g/T level for thorium slugs.

**TABLE III. MARK B DIMENSIONAL CHANGES DURING
TEST ASSEMBLY IRRADIATION**

(g/T Level: 7,100 g/T avg, 11,000 g/T max)

Average of 50 Slugs

	<u>Dimensional Change, mils</u>	
	<u>Average</u>	<u>Range</u>
Length	-4	-11 to +1
Outside Diameter	+1	-5 to +5
Warp	0	-1 to +2

Individual Slugs

	g/T Level →	<u>Dimensional Change, mils</u>		
		<u>1000</u>	<u>7100</u>	<u>11,000</u>
Length		-11	-3	0
Outside Diameter		-5	-2	-1
Warp		0	+1	0

Figure 4. Photographs of three slugs irradiated to approximately 1000, 7100, and 11,000 g/T are shown in figure 4. Marks made in discharging the slugs by sliding them out of their housing tube and marks produced by handling tongs are evident. There was no swelling. The slightly rippled or folded effect on the surface of the slug irradiated to about 11,000 g/T is the result of using too much lubricant when the slug was hot-press bonded.

Figure 5. The U-232 content as a function of g/T level is shown in this figure.

Thorium Procurement

Two methods were used to obtain the necessary 21 tons of thorium in the form of ingots.

- ▶ 1) Converting thorium nitrate tetrahydrate to oxide,
- 2) reducing the oxide to thorium metal with calcium,
- 3) washing, drying, and compressing the reduction mass, and
- 4) induction melting and vacuum casting to thorium ingots.
- ▶ 1) Converting thorium scrap metal to refined thorium powder by a fused chloride salt electrolysis, and
- 2) compressing the metal powder and arc-melt casting it to thorium ingots.

The ingots were extruded to rod form on a 4000-ton extrusion press, the rods were cut and machined to slug cores, and the cores were hot-press bonded with aluminum. Most of the slugs for the production irradiation are on hand.

FIGURE 4. SURFACE CONDITION OF IRRADIATED THORIUM SLUGS - MARK B

**FIGURE 5. VARIATION OF U-232
WITH g/T LEVEL - MARK B**

Production Irradiation

Table IV. Production of the 120 kilograms of U-233 will be divided between central positions in the reactor and blanket or peripheral positions, as shown in table IV. After irradiation, the U-233 will be extracted in nitrate form at the Savannah River Plant and delivered to the Atomic Energy Commission.

**TABLE IV. ESTIMATED U-233 PRODUCTION
FOR FUEL-LESS MARK B**

<u>Position</u>	<u>Thorium, tons</u>	<u>U-233, kg</u>	<u>U-232, ppm</u>
Blanket	7.7	40	140
Central	13.3	88	190
Total →	21	128	~170

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Paper 28

IRRADIATION TESTING OF THORIA-URANIA FUEL
FOR THE INDIAN POINT REACTOR

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The Indian Point Reactor irradiation program consisted of a series of loop and capsule in-pile tests on mixed oxide ThO_2 with 6.5 wt % UO_2 or 9.1 wt % UO_2 as fuel under conditions that equalled or exceeded the predicted Core I operating condition. The purpose was to study the effects of irradiation on the design, fabrication techniques, and materials to be utilized. Specimens were irradiated at heat fluxes ranging from 100,000 to 586,000 Btu/hr-ft², to burnups of 20,000 MWD/tonne oxide, with little change exhibited on post-irradiation examination except for cracking. Shown in Figures 1 and 2 are photomicrographs of the fuel contained in a low-heat-flux-loop specimen and a high-heat-flux-capsule specimen.

Capsule specimen 303-3 is of particular interest in that it was exposed to a test reactor excursion that caused a short-term overpower of the intended experiment conditions. This overpowering resulted in void and fuel distribution changes at the pellet center. Compare the structure of the edge of the pellet with the center of the pellet as shown in Figures 3 and 4. No other specimen exhibited this change.

Specimen 303-3 was one of seven of the same design shown in Figure 5. Each specimen consisted of a 2.34-inch stack of ThO_2 (6.5 wt %) fully enriched UO_2 fuel pellets with an Al_2O_3 insulating pellet at each end. The clad was 0.020 inch of Type 304 stainless steel. The fuel rod OD was 0.3125 inch; the pellet diameter was 0.2675. These diameters were selected to provide the 0.005-inch diametrical clearance.

The fuel pellets were fabricated by calcining $\text{Th}(\text{OH})_4$ to ThO_2 at 1850 F, dry ball milling with the required amount of UO_2 , pressing into pellets under 20 thousand psi with camphor added as a binder, and sintering at 2800 F for 1 hour in a hydrogen atmosphere. The average bulk density was 91.5% theoretical.

The specimen fuel rod was placed in a NaK-filled stainless steel capsule, Figure 6, and irradiated to a burnup of approximately 1000 MWD/tonne oxide. Because this experiment was intended to simulate a high surface-heat-flux core condition, thermocouple instrumentation was included for operational follow. The irradiation was conducted in the Engineering Testing Reactor.

Fig. 1. Post-Irradiation Macrophotograph
of MTR Loop Specimen Operated at an Exposure
Average Surface Heat Flux of $100,000 \text{ Btu/hr-ft}^2$.
Magnification 6X HC-3618

Fig. 2. Post-Irradiation Macrophotograph
of ETR Capsule 303-3 Specimen Operated at an
Exposure Average Surface Heat Flux of $586,000 \text{ Btu/hr-ft}^2$.
Magnification 6X HC-4272

Fig. 3. Post-Irradiation Microstructure at
the Edge of Pellet, Sample 303-3.

Magnification 250X, as polished HC-4244

Fig. 4. Post-Irradiation Microstructure at
the Center of Pellet, Sample 303-3.

Magnification 250X, as polished HC-4246

Fig. 5. Capsule Irradiation Specimen Cross-Section.

Fig. 6. Irradiation Program Capsules.

The middle thermocouple in the experiment measured the extent of the reactor excursion. This thermocouple indicated a normal temperature of 620 F and reached a peak value of 850 F during the reactor excursion. By assuming that the 850 F excursion temperature indicated by the thermocouple reading approximates the cladding surface temperature by the same differential as exists during normal operation, the cladding surface temperature is 950 F. To achieve this temperature, a specimen surface heat flux of 700 thousand Btu/hr-ft² is required. See Table 1 for capsule 303-3 operating conditions.

TABLE 1
CAPSULE 303-3 OPERATING CONDITIONS

	Normal	Excursion
Thermocouple 4	620 F	850 F
Heat Rating, $\int_{T_s}^{T_o} k d\theta$	31.6 watts/cm	43.7 watts/cm
Clad Surface Temperature	720 F	950 F
Fuel Surface Temperature	1780 F	2400 F
Heat Flux - clad surface	506,000 Btu/hr-ft ²	700,000 Btu/hr-ft ²
- fuel surface	586,000 Btu/hr-ft ²	810,000 Btu/hr-ft ²

B and W's Alliance Research Center did work¹ on the thermal conductivity of thorium-uranium and uranium which corroborated the work of other investigators^{2,3} (see Figure 7). The thermal conductivity of thorium falls with increasing temperature which is expected for a lattice conduction. Also, the conductivity decreases with foreign atom concentration and density variation as shown. This decrease in thermal conductivity with increasing temperature is similar to that for uranium. The data can be approximated by

$$k_1 = \frac{44.3}{T - 160}$$

where T is Kelvin temperature.

Fig. 7. Thermal Conductivity of Thoria and Thoria-Urania vs. Temperature - Values Corrected to 100% Theoretical Density.

Using the heat rating method of analysis proposed by Robertson,⁴

$$\int_{T_s}^{T_o} k d\theta = \frac{1}{4\pi} Q \frac{a^2 - r^2}{a^2}$$

The integrated thermal conductivity with respect to temperature on the left side of the equation is expressed as a product of two terms. The term $\frac{1}{4\pi} Q$ is a measure of the heat rating of the specimen, and the second term is a geometric correction factor. $\int k d\theta$ versus temperature is plotted in Figure 8 utilizing the B and W derived thorium thermal conductivity data. Using the previously calculated excursion heat rating, 44 watts/cm, the fuel surface temperature, Curve A of Figure 8, points to a center temperature of 3300 C. But, the capsule 303-3 central pellet structure does not indicate melting, only the onset of structure alteration as observed for urania.

The apparent thermal conductivity of urania increases by radiant energy transfer at temperatures above 1400 C.⁵ Using the same argument for thorium calculations that Bates used for urania (because of the physical similarity of thorium and urania) the "effective" thermal conductivity of thorium versus temperature was derived (see Curve C, Figure 9). From this information, the $\int k d\theta$ versus temperature curves for thorium and thorium with 5 to 10% urania were constructed after correcting for the 91.5% theoretical density of the fuel pellets. The 100% thorium curve is included for comparison. Utilizing Figure 8 again, the ThO_2 -5 to 10% UO_2 indicates that during the excursion the central temperature was 2400 C. An absolute analysis cannot be determined owing to the non-stabilized thermal condition existing during the excursion.

The thorium-uranium thermal conductivity that is suggested here is a summation of lattice conductivity and radiant energy transfer. It is interesting to note the results of Niemark⁶ who assumed sublimation growth for thorium as observed in urania and, applying thorium vapor pressure data, calculated that this mechanism of fuel structure change would occur between 2150 and 2400 C for pure thorium and at a lower temperature for mixtures of thorium and urania between this temperature range and 1800 C observed for pure urania.⁷

Fig. 8. Heat Rating, $\int_{T_1}^{T_2} kd\theta$, vs. Temperature for Thoria and Thoria-Urania.

Fig. 9. Effective Thermal Conductivity of Thoria vs. Temperature.

It is interesting to compare the useability of thoria-urania and urania on the heat rating basis. Using the heat rating versus temperature for thoria and thoria-urania that is derived and that relationship for urania determined experimentally⁸ and plotted in Figure 10, it can easily be seen that to reach the higher temperatures required for melting and sublimation structure alteration for thoria-urania as compared to urania, even with coincident Curve B, the heat rating must be raised. That is, the heat rating for thoria-urania for melting and sublimation structure alteration would be approximately 150% of that required for a urania body.

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Fig. 10. Comparison of Thoria, Thoria-Urania, and Urania Heat Rating, $\int_{T_1}^{T_2} k d\theta$, vs. Temperature.

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Paper 29

THORIUM FUEL CYCLE IRRADIATION PROGRAM AT
THE OAK RIDGE NATIONAL LABORATORY

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INTRODUCTION

The Oak Ridge National Laboratory (ORNL) is currently engaged in a comprehensive Fuel Cycle Program to study the technology of recycling Th-U²³³ fuel materials for use in heterogeneous reactors. It is well known that fuel systems utilizing U²³³ are attractive because of their breeding potential. The disadvantage of Th-U²³³ fuels is the fact that both materials are sources of radioactivity and thus require shielding and remote handling for reprocessing and refabrication.

One of the aims of the ORNL program is to develop suitable techniques for reprocessing and remotely fabricating fuels containing U²³³ and to then appraise these materials as fuels for application in power reactors. As a part of this evaluation, investigations of vibratory-compacted thoria-base fuels are being conducted. This process appears to be particularly amenable to remote operation. An important feature of this program is an assessment of the irradiation behavior of these ceramic fuels.

This report summarizes the progress made to date on the irradiation program and related work, and describes plans for future experiments.

FUEL PREPARATION

The characteristics desired in the fuel material for vibratory compaction are that the particles be of near theoretical density, of controlled particle size, and resistant to fragmentation during subsequent fabrication. The materials currently under investigation include oxide powders made by either the arc-fusion or sol-gel routes.¹ The latter process, as outlined in Fig. 1, lends itself to remote operation because of its simplicity. It is a chemical process which produces homogeneous, coarse, dense fragments while limiting the maximum processing temperature to 1200°C. The method as evolved consists of (1) the steam denitration of a thorium nitrate solution, (2) dispersion of the resultant thoria in water, (3) blending with uranium nitrate hexahydrate at 80°C to produce a ThO₂-UO₃ sol, (4) evaporation at approximately 90°C to form a gel, (5) calcination at 1200°C, first in air and then in 4% H₂-A, and (6) cooling in an

Fig. 1. Sol-Gel Process for Preparation of Dense Thorium-Uranium Oxide.

inert atmosphere. Properties of the sol-gel and arc-fused oxides incorporated in the irradiation specimens are summarized in Table 1. Representative photomicrographs are depicted in Figs. 2 and 3. It is notable that the sol-gel oxide is virtually 99.9% dense and single phase. However, arc-fused oxide contains numerous cracks, pores, and a second-phase, metallic, white precipitate which is probably uranium. Other characteristics of the sol-gel material are a very fine natural porosity and a particle structure which consists of agglomerates of fine crystallites.

VIBRATORY COMPACTION

Vibratory compaction is a significant process simplification over either the cold-pressing and sintering or swaging techniques for producing bulk oxide ceramic fuels. Moreover, this fabrication route is readily adaptable to remote operation. After comminution of the oxide to a selected size distribution, the powder is compacted in the fuel tubes using simple and inexpensive pneumatic vibrators. With appropriate process control, the compacted bulk densities of the sol-gel oxide are comparable to those attainable using arc-fused material and generally range from 85 to 90% of theoretical density.

The bulk density of the compacted powder is primarily a function of particle size distribution. For optimum conditions, mixtures of coarse, medium, and fine size fractions are generally selected. The most widely used distribution for the irradiation capsules was 60 wt % -10 +16 mesh, 15 wt % -70 +100 mesh, 25 wt % -200 mesh. Typical densities achieved with vibratory compaction for several of the irradiation capsules are listed in Table 2.

BROOKHAVEN NATIONAL LABORATORY KILOROD PROGRAM

Also included in the current thorium utilization program is the production of fuel rods containing U^{233} and thorium oxides for Brookhaven National Laboratory (BNL). This job entails development of the required processes, design and construction of a pilot plant facility, and production of 1000 U^{233} -bearing rods.

Table 1. Summary of Properties of Uranium-Thorium Oxides Used
in Fabrication of Irradiation Specimens

	Sol-gel A	Sol-gel B	Sol-gel C ^a	Sol-gel D ^a	Sol-gel E ^a	Arc Fused	Sol-gel S	Sol-gel Batch 26
Total uranium, wt %	4.31	4.39	4.01	2.50	4.0	3.96	5.21	5.35
Uranium enrichment, %	93	93	93	93	93	93	93	93
Carbon, ppm	110	100	60	40	130	120	80	40
Nitrogen, ppm	22	21	55	29	31	1130	30	13
Iron, ppm	100	50	265	140	160	130	300	215
Silicon, ppm	600	500	<20	<10	<10	20	20	<25
BET surface area (N ₂), m ² /g	0.20	0.26	0.03	0.008	0.011	0.11	0.17	0.047
O/U ratio	2.0	2.0	2.03	2.02	2.02	2.01	2.01	2.02
Volatile matter released in vacuum at 1200°C, cc/g	0.125	0.151	0.055	0.012	0.027	0.24	0.284	0.244
Lattice parameter, Å	5.591	5.592	5.593	-	5.593	5.594	5.594	-
Crystalline size, Å	2400	1700	2200	-	-	-	1800	-
Particle density, g/cc ^b	9.94	9.92	9.76	9.97	9.92	10.11	10.0	-
Packed density, g/cc ^c	8.69	8.69	8.36	8.74	8.74	8.6	8.8	-

^aCooled in pure argon after calcination in hydrogen.

^bToluene intrusion, pycnometric method. Theoretical density: 10.04 g/cc.

^cNAVCO air vibrator, 1/25-in. piston; 5/16-in.-OD x 11-in. stainless steel tube.

Fig. 2 Spencer Arc-Fused ThO_2 -4.5 Wt % UO_2 Powder. The white second-phase precipitate, found in varying percentages in the particles, is probably uranium. The particles exhibit both transgranular and intergranular cracking. (a) As-polished. (b) No microstructural change was observed after etching for UO_2 (7 parts H_2O , 1 part HNO_3 , 2 parts 30% H_2O_2 for 2-1/2 min).

Fig. 3 ORNL Sol-Gel E (ThO_2 -4.5 Wt % UO_2 Powder). No impurities were found in this material. Small surface cracks may be seen in the particles. (a) 150X. As-polished; (b) 500X. Etchant: boiling HNO_3 -HF. At higher magnification very fine natural porosity and extremely fine crystallites (spheroidal white particles) may be observed. No large grain boundaries are evident.

Table 2. Typical Densities of Vibratory Compacted Sol-Gel
ThO₂-UO₂ in Irradiation Capsules

Oxide Lot	Uranium ^a (wt %)	Nominal Tube Dimensions (in.)			Bulk Density (g/cc)
		Length	Outside Diameter	Wall Thickness	
A	4.3	11	5/16	0.025	8.70
B	4.4	11	5/16	0.025	8.67
C	4.0	22	5/16	0.025	8.31
D	2.5	7	5/8	0.020	8.55
E	3.9	11	5/16	0.025	8.65
S	5.0	39	5/16	0.025	8.84

^aFully enriched in U²³⁵.

The proposed method of producing these fuel rods² consists of essentially three processes: (1) solvent extraction purification of the U²³³, (2) preparation of a mixed sol-gel ThO₂-UO₂ fuel suitable for vibratory compaction, and (3) oxide densification by vibratory compaction in Zircaloy-2 tubes. The process flow diagram is illustrated in Fig. 4.

It will be observed that there is a close correlation between this fabrication scheme and that previously discussed with the exception that U²³³ will be substituted for U²³⁵. It is hoped that this facility will provide a means for producing irradiation specimens using the full Th-U²³³ fuel cycle. Such an effort would be a satisfying demonstration for the fuel cycle program and would measurably aid in determining the merits of U²³³ as a reactor fuel.

IRRADIATION PROGRAM

General Description

In support of the thorium fuel cycle program, irradiation experiments to evaluate the in-pile behavior of fuel material prepared in the manner described above have been completed or are in progress in the NRX, MTR, and ORR. A summary of these tests is presented in Table 3. The more salient features of this program are as follows:

Fig. 4 Rod Fabrication Flow Diagram.

Table 3. Summary of Fuel Cycle Irradiations^a

Experimental Facility	No. of Capsules	Type of Oxide	Vibrated Density (% T.D.)	Clad Temp (°F)	Average External Pressure (psia)	Fuel Rod Dimensions (in.)			Linear Heat Rating (Btu/hr-ft)	Estimated Burnup (Mwd/MT Metal)	Status
						Length	Outside Diameter	Wall			
ORR Poolside	2	Sol-gel D	85-86	1000 1300	315	7	0.625	0.020	40,000	7,000	Out 9-23-62
NRX (Group I)	8	Sol-gel A, Sol-gel B	84-86	~200	130	11	0.312	0.025	24,000	20,000	Out 5-22-62
NRX (Group II)	4	Arc-fused, Sol-gel C	84-86	~200	130	22.5	0.312	0.025	20,000	3,500	Out 2-16-62
MTR (Group I)	7	Arc-fused, Sol-gel E	86-87	~200	40	11	0.312	0.025	41,800- 47,600	12,300- 100,000	5 in-pile, 2 out 4-2-62
NRX (Group III)	6	Sol-gel S	88-89	~200	130	39	0.312	0.025	28,000	23,000	In 5-24-62
NRX (Group III)	3	Sol-gel ThO ₂ -PuO ₂	74-76 ^b	~200	130	11	0.312	0.025	27,000	22,000	In 5-24-62
ORR Loop (L-1)	3-rod cluster	Sol-gel 26	84-85	~500	1750	21.5	0.460	0.015	43,000- 52,300	2,500- 3,000	Out 10-31-62

^aFuel = ThO₂-UO₂ except for three (NRX Group III) ThO₂-PuO₂-bearing capsules.

Clad = Type 304 stainless steel except for experiment L-1 (one clad with type 304 stainless steel and two with Zircaloy-2).

^bTamp packed.

1. A comparison is being made between oxides produced by the sol-gel and arc-fusion routes (MTR Group I and NRX Group II capsules).

2. Type 304 stainless steel fuel tubes, 0.312 in. OD x 0.025 in. wall, are specified as the cladding for many of the experiments. This approximates the 0.304 in. OD x 0.0205 in. wall geometry of the fuel pins for the Consolidated Edison Thorium Reactor (CETR) at Indian Point, New York.

3. The experimental peak linear heat ratings of 47,600 Btu/hr-ft (Ref. 3) for the sol-gel oxide may be compared with 37,000 Btu/hr-ft in the CETR.

4. Maximum burnups of 100,000 Mwd/MT metal (2.06×10^{21} fissions/cc) are anticipated in the ORNL program, as compared to 60,000 Mwd/MT metal expected in the CETR.

5. Two capsules were irradiated in the ORR poolside facility (06-5 and 03-5) to investigate the suitability of sol-gel oxide for advanced gas-cooled reactors with high surface temperatures. Each capsule (Table 3) had an axial molybdenum thermowell containing a tungsten-rhenium thermocouple to continuously measure the center-line temperature. Nominal clad temperatures were 1000°F (540°C) and 1300°F (700°C). The external pressure was 300 psi. This experimental arrangement furnished some indication of the effective in-pile thermal conductivity of the sol-gel fuel material.

6. The $\text{ThO}_2\text{-PuO}_2$ fuel-bearing capsules were placed in pile in May 1962. For expediency, these powders were simply tamp packed in the rods. This powder also had been made by the sol-gel process.

7. A trefoil cluster was irradiated in an ORR pressurized-water loop operating at 500°F (260°C) and 1750 psi with a predicted thermal neutron flux of $2.67\text{-}3.26 \times 10^{13}$ neutrons/cm²-sec. The estimated peak heat flux was 330,000-400,000 Btu/hr-ft². The mechanically assembled bundle contained two rods that were clad with 0.460 in. OD x 0.015 in. wall Zircaloy-2 tubes, and the other was clad with type 304 stainless steel of the same geometry. The clad was sufficiently thin to expect collapse onto the fuel when the coolant was pressurized to 1750 psi, thereby assuring intimate contact. Each rod was spirally wrapped with a wire of the same material to assure that the rods did not bow

together. The primary objective of the test was to examine fuel-clad and clad-coolant interactions at elevated temperatures. This element has since been removed from the reactor due to a fuel rod failure.

Capsule Design

Three basic capsule designs utilized thus far in the program are illustrated in Figs. 5, 6, and 7. The fuel rod design for the cold process water MTR and NRX tests is schematically depicted in Fig. 5. Fuel rod lengths were 11, 22-1/2, and 39 in. To preclude bowing and stabilize the longer 39-in. rods (NRX Group III), stainless steel spring wire was helically wound along the length and fusion welded at the ends. The instrumented capsule design featured in the ORR poolside irradiations is shown in Fig. 6. Finally, a photograph of the tre-foil cluster for experiment L-1 is shown in Fig. 7.

Irradiation Behavior and Examination

Postirradiation examination of the first two MTR-irradiated rods has virtually been completed. Work on the twelve NRX-irradiated rods (Groups I and II) is complete except for metallographic examinations and burnup determination. These examinations included dimensional measurements, gamma radioactivity scans, fission-gas analysis, burnup measurement of the fuel, and metallographic examination of the fuel and clad.

The two MTR capsules (U-1, Z-5) behaved without incident and were removed according to schedule. Burnup analyses are shown in Table 4.

Table 4. Burnup Analyses for Capsules U-1 and Z-5

Capsule Number	Type of Oxide	Neutron Dose (nvt)	Burnup (Mwd/MT Th + U)			Specific Power (kw/kg)
			Cs ¹³⁷	Ce ¹⁴⁴	Mass Spectrograph	
U-1	Arc-fused	6.0x10 ²⁰	9,380	8,290	12,300	112
Z-5	Sol-gel E	7.0x10 ²⁰	14,800	12,900	14,000	127

Radiochemical and mass spectrometric burnup measurements on the fuel agreed fairly well with the neutron dose received by the stainless steel clad, which

Fig. 5 $\text{ThO}_2\text{-UO}_2$ Fuel Cycle Capsule for NRX and MTR Irradiations.

Fig. 6 Vertical Cross Section of Fuel Cycle; ORR Irradiation Capsule.

Fig. 7 Overall View of Trefoil Cluster for ORR Pressurized Water Loop Experiment L-1.

was determined by measurement of the cobalt activation.

No significant changes in the dimensions of the rods were found. Rod bowing was about the same as that before irradiation. Most of the observed diameter changes were increases, the maximum being 3 mils. Gamma scans reflected the neutron flux gradients along the rods, but did not indicate any significant shifting of the fuel.

Each rod was pierced for collection and analysis of the contained gases. The fission-gas-release fraction was determined by comparison of the Kr^{85} counting data with total Kr^{85} generation based on measured fuel burnup. Gas-release data are shown in Table 5. It may be noted from Table 5 that fission-gas release is nearly 4-1/2 times lower for the sol-gel $\text{ThO}_2\text{-UO}_2$ than for the arc-fused oxide. This effect is tentatively attributed to the structural differences between the two materials (see "Fuel Preparation" in this paper), but requires further experimental validation.

There was no evidence of sintering, grain growth, or central void formation in either rod, as attested in Figs. 8 and 9. Structurally, the oxide is characterized by a tightly packed fine powder surrounding the coarser fuel particles. The aforementioned metallic inclusions also were found in the irradiated material. There were more large granules of fuel in Z-5 than in U-1 and, consequently, less fine powder. The fuel had a speckled appearance due to uniformly

Table 5. Fuel Cycle Experiment Gas Data

Rod No.	Atoms Kr^{85}		Release (%)
	Total Released	Total Generated	
U-1	1.60×10^{17}	6.77×10^{18}	2.4
Z-5	3.91×10^{16}	7.77×10^{18}	0.50
A-1	9.3×10^{16}	4.0×10^{18a}	2.3
A-2	1.4×10^{17}	4.0×10^{18a}	3.5
C-3	2.0×10^{17}	4.0×10^{18a}	5.0
C-4	Gas lost	4.0×10^{18a}	-

^aBased on estimated burnup of 3500 Mwd/MT (U + Th).

(a) U-1 ~ 4X

(b) Z-5 ~ 4X

Fig. 3 Sections of Irradiated $\text{ThO}_2\text{-UO}_2$ Fuel Rods. (a) Transverse cut $3/5$ in. from bottom of capsule U-1; (b) transverse cut 1 in. from top end of capsule Z-5.

Fig. 9 Composite Photomicrographs Showing Typical Transverse Sections of Capsules U-1 and Z-5. Radial area from outside diameter of the cladding to center of the fuel.

distributed fine porosity; however, this phenomenon has been observed in unirradiated sol-gel oxide (Fig. 3b) and appears to be a characteristic of the material rather than the irradiation. There were no indications of reaction at the fuel-clad interfaces.

The eight NRX Group I capsules, which were irradiated in tandem, also performed satisfactorily in-pile. No deterioration was evident from visual examination. Dimensional measurements showed negligible changes as a result of irradiation.

Gamma scans of the rods did reveal an anomaly. The three capsules containing sol-gel A gave a normal scan with very few peaks and valleys. However, the five capsules containing sol-gel B exhibited an extremely erratic activity profile. This phenomenon is depicted in Fig. 10. Since all eight capsules were in one holder, these unusual effects apparently are related to the fuel itself. However, the cause of this anomaly is presently unknown and further examination is in progress.

No microstructural changes in the fuel and clad were apparent as a result of the irradiation, and there is no evidence of sintering or void formation.

The four NRX Group II specimens were prematurely discharged due to leakage of fission products from the holder that contained these rods. Since there were also 100 pellet fuel pins for the Power Reactor Fuel Reprocessing Program in the same holder, it was not known whether a compacted rod was responsible. Capsule C-3 was suspected because it presumably was stuck to the wall of the holder, apparently having bowed and created a hot spot on the cladding. However, subsequent visual, leak-test, and dye-penetrant examinations showed no indications of failure in any of the vibratory-compacted rods.

The results of the vacuum-leak-testing experiments conducted are summarized in Table 6. As a result of these tests, a rather interesting phenomenon was observed. The original hole made in each capsule at ORNL to measure fission-gas release was sealed with an epoxy resin and cured for a suitable length of time. Each rod was then punctured at the opposite end and the system pressure allowed to come to equilibrium. The leak rate was then measured and diffusion of gas

Fig. 10 Gamma Scans of Fuel Rods X-8 and O-3 Showing Regular and Erratic Profiles, Respectively.

Table 6. Leak Detection on NRX-II Capsules

Rod	Leak Rate ^a Through Cladding (μ /min)	Kr ⁸⁵ Activity Atoms Total	Diffusion ^b Rate Through Capsule (μ /min)	Measured Volume of Gas at STP (cc)
A-1	0.2	4.3×10^{13}	1.6	2.52
A-2	1.0	9.5×10^{13}	1.0	2.43
C-3	0.9	2.2×10^{14}	0.9	2.24
C-4	0.9	1.5×10^{14}	c	7.57

^aAfter system reached equilibrium.

^bBoth ends pierced.

^cRose to atmospheric pressure in 2 hr.

into the vacuum system was found to be insignificant (Table 6). This indicates that no leak was present that would permit diffusion of gas into or out of the capsules at room temperature.

A gas sample was then removed from each rod and analyzed for Kr⁸⁵ activity to determine whether the fission gases had been removed after the initial puncture. Despite the fact that the capsules had been punctured and exposed to the atmosphere for several months, a measurable quantity of Kr⁸⁵ remained (Table 6). The rods were then repunctured at the original end and the diffusion rate of air along the length of each rod was measured. As shown in Table 6, diffusion was unexpectedly slow except for capsule C-4. From these data, it would appear that gas diffusion was poor through these vibratory compacted rods. This situation warrants further investigation as the practical implications in terms of fuel element design may be profound.

As was the case with other rods examined, there was no evidence of sintering or void formation. The appearance of the fuel material was similar in each rod.

Preliminary effective thermal conductivity values for the ThO₂-UO₂ fuel in the two ORR poolside capsules were calculated on the basis of the measured parameters given in Table 7 and the nominal capsule dimensions (Fig. 6).

Table 7. Data on ORR Poolside Capsules

Capsule No.	Fuel Bulk Density (g/cc)	Neutron Flux (neutrons cm ⁻² sec ⁻¹)		Power Density (w/cc)	Temperature (°F)		
		Design	Actual		Clad	Center	Av Core
06-5	8.54	3.0x10 ¹³	2.5x10 ¹³	192	1000	2600	1815
03-5	8.60	3.0x10 ¹³	3.3x10 ¹³	253	1300	3500	2415

Two problems were encountered in the temperature measurements. First, in capsule 03-5, the thermocouple indicated a downward drift which presumably is a result of fuel sintering or a gradual change in thermocouple response. Second, occasional cladding temperature oscillations of $\pm 150^{\circ}\text{F}$ and $\pm 100^{\circ}\text{F}$ occurred for 03-5 and 06-5, respectively. These oscillations have been attributed to sporadic convective movement of the NaK surrounding the capsule.⁴

These conductivities include the gradient at the fuel-sheath interface and are averaged over the temperature gradient across the fuel. In performing the calculations, the following assumptions were made:

1. Uniform heat generation occurred in the fuel (neglect flux depression).
2. The internal thermocouple was in contact with the wall of the thermowell.
3. There was no temperature change across the wall of the thermowell.
4. The thermal conductivity of stainless steel was not significantly affected by the irradiation.
5. Energy release was 185 Mev/fission deposited locally, with no additional gamma heating.

The results are listed in Table 8 together with some comparative values from the literature for pressed-and-sintered bodies of ThO_2 and ThO_2 -10% UO_{2+x} . It is notable that the conductivities compare favorably. However, until burnup analyses are obtained and the flux more accurately determined, these conductivities must be regarded as estimates.

As previously mentioned, the trefoil cluster (L-1) was removed from the ORR pressurized-water loop when leakage of fission products was detected. The

Table 8. Thermal Conductivity of Thoria-Base Fuels

Source	Composition	Average Temperature		Thermal Conductivity ^a	
		(°C)	(°F)	(w/cm-°C)	(Btu/hr-ft-°F)
ORNL (06-5)	ThO ₂ -2.9% UO ₂	990	1815	0.025 ^b	1.44
ORNL (03-5)	ThO ₂ -2.9% UO ₂	1325	2415	0.024 ^b	1.38
Kingery ^c	ThO ₂	600	1112	0.046	2.66
Kingery ^c	ThO ₂	800	1472	0.036	2.08
Kingery ^c	ThO ₂	1000	1832	0.033	1.91
Kingery ^c	ThO ₂ -10% UO _{2+x}	600	1112	0.032	1.87
Kingery ^c	ThO ₂ -10% UO _{2+x}	800	1472	0.029	1.66
Kingery ^c	ThO ₂ -10% UO _{2+x}	1000	1832	0.025	1.44

^aData corrected to same density as vibrated ThO₂-2.9% UO₂ using the relationship $k_m = k_t (1-P)$ where P = pore volume fraction, k_m is the measured conductivity, and k_t is the value corrected to theoretical density.

^bBased on flux measurement during test.

^cW. D. Kingery, "Thermal Conductivity: XIV, Conductivity of Multicomponent Systems," J. Am. Ceram. Soc. 42(12), 617 (1959).

fuel rods were blanketed by a dark deposit which was loosely adherent and readily removed with steel wool and soap. After disassembling and scraping the rods, a failure was located on rod L-1B, approximately 2-1/2 in. from the top end. This area is situated midway along the length of the plenum, or about 1-1/4 in. above the top of the fuel column. The appearance of this area (Fig. 11) indicates that the failure occurred as a result of some corrosion reaction; it was also observed that a circumferential crack propagated around the surface of the rod. Diametral measurements at this location in comparison with the surrounding regions revealed that swelling up to 25 mils had occurred. Contrast dye-penetrant inspection of this area indicated a leak. An explanation, however, of the location and causes of this failure awaits further examination.

Fission-Gas-Release Studies

In conjunction with in-pile irradiation studies, neutron-activation (D')^{5,6}

Fig. 11 Defective Area Approximately 2-1/2 in. from Top End of Zircaloy-2 Clad Fuel Rod L-1B.

studies are under way to characterize fission-gas release from sol-gel and arc-fused oxide. Individual samples containing 0.2-0.6 mg of U^{235} were irradiated in the graphite reactor to an integrated dose of 6.77×10^{17} nvt, then vacuum-induction annealed and the release of Xe^{133} continuously monitored in a charcoal bulb.

In the case where diffusion is the primary release mechanism, several important relationships can be derived. After irradiation, the fraction of a stable isotope released during annealing under isothermal conditions may be expressed by

$$F = \frac{6}{\sqrt{\pi}} \sqrt{\frac{Dt}{a^2}} \quad (1)$$

where

F = fraction released,

D = diffusion coefficient (cm^2/sec),

t = annealing time (sec),

a = radius of equivalent sphere (cm).

The above equation is correct for small values of F . Because of uncertainties in measuring the equivalent radius, it is more convenient to determine the quantity D' ($=D/a^2$) which is the release-rate parameter. Equation 1 then becomes

$$F = \frac{6}{\sqrt{\pi}} \sqrt{D't} \quad (2)$$

For diffusion-controlled release, a plot of F vs $t^{1/2}$ at a given temperature will be linear and D' can be readily determined from the slope of the curve. Further, it is known that for a diffusion process, the temperature dependence on release rate will be given by the Arrhenius relationship

$$D' = D_0' e^{-Q/RT}$$

where

D_0' = a constant,

Q = activation energy for process (kcal/mole),

R = universal gas constant ($1.987 \text{ cal/g-mole-}^\circ\text{C}$),

T = absolute temperature.

By determining D' at several temperatures and plotting the $\log D'$ vs $1/T$, the activation energy can be determined from the slope of the plot.

Available data for sol-gel ThO_2 -5 wt % UO_2 , sol-gel ThO_2 -5.9 wt % UO_2 , arc-fused ThO_2 -4.5 wt % UO_2 , and arc-fused UO_2 are compiled in Table 9.^{7,8,9,10}

The fraction of Xe^{133} released as a function of temperature for the sol-gel oxide is shown in Fig. 12. Note that after an initial burst of gas, which has also been observed for UO_2 ,¹¹ the release mechanism was diffusion. Results for the arc-fused ThO_2 - UO_2 were comparable. Release was lower by a factor of ten for the coarse fraction than for the medium size fraction. Increased release with decreasing particle size was also noted for sol-gel S, which is the expected effect of decreasing particle size. It is also notable that whereas 30.6% of the Xe^{133} was released from the sol-gel ThO_2 - UO_2 at 2200°C after 25 hr, Xe^{133} was completely released from UO_2 at 1900°C for a comparable time and the UO_2 sample vaporized. This clearly illustrates the greater stability of ThO_2 - UO_2 compared to UO_2 , which is to be expected since the melting point of ThO_2 is 3300°C compared to 2750°C for UO_2 .

From the slope of the curve of $\log D'$ vs the reciprocal of the absolute temperature (Fig. 13), the activation energy for diffusion of Xe^{133} from sol-gel and arc-fused ThO_2 - UO_2 was calculated to be 75.9 kcal/mole and 25 kcal/mole, respectively. These values compare to 70-80 kcal/mole reported for diffusion of xenon from UO_2 .¹² The difference in activation energy between sol-gel and arc-fused ThO_2 - UO_2 may be due to the structural differences between the two materials (Figs. 2 and 3).

Since the NRX and MTR capsules ran at relatively low central temperatures, it would be expected that a significant portion of the fission-gas release occurred by a mechanism other than diffusion. This quantity can be estimated from the neutron-activation data by adding the fraction released during the low-temperature irradiation to the burst release upon subsequent annealing. This is being done for sol-gel S and will be conducted on other powders.

Table 9. Neutron-Activation Studies on Ceramic Fuel Powders

Material	Preparation	Particle Size (Mesh)	Test Temp (°C)	Total Fraction Xe ¹³³ Released (Cumulative)	Total Test Time (hr)	Release-Rate Parameter D' (sec ⁻¹)
ThO ₂ -5 wt % UO ₂	Sol-gel (similar to B)	Coarse chunks	1440	4.43 x 10 ⁻³	18.8	4.64 x 10 ⁻¹²
			1640	9.38 x 10 ⁻³	22.7	7.32 x 10 ⁻¹¹
			1760	1.23 x 10 ⁻²	19.6	1.10 x 10 ⁻¹⁰
			2015	3.47 x 10 ⁻²	48.0	1.27 x 10 ⁻⁹
			2200	3.06 x 10 ⁻¹	25.0	b
	Sol-gel S	10/16	Irrad. ^a	4.81 x 10 ⁻⁴	-	To be determined
			1000	2.30 x 10 ⁻³	2.0	
			1200	2.40 x 10 ⁻³	2.0	
			1400	2.56 x 10 ⁻³	2.0	
			1800	1.29 x 10 ⁻²	2.0	
			2000	1.30 x 10 ⁻²	2.0	
		-325	Irrad. ^a	1.86 x 10 ⁻²	-	
			1000	5.14 x 10 ⁻²	2.0	
ThO ₂ -4.5 wt % UO ₂	Arc fusion	70/100	1000	2.9 x 10 ⁻³	25.0	1.7 x 10 ⁻¹²
			1200	8.9 x 10 ⁻³	25.0	6.1 x 10 ⁻¹²
			1400	3.2 x 10 ⁻³	25.0	1.4 x 10 ⁻¹¹
			1600	3.94 x 10 ⁻²	25.0	3.5 x 10 ⁻¹¹
		10/16	1000	3.2 x 10 ⁻⁴	25.0	5.5 x 10 ⁻¹⁴
			1200	8.6 x 10 ⁻⁴	25.0	1.5 x 10 ⁻¹³
			1400	2.3 x 10 ⁻³	25.0	1.4 x 10 ⁻¹²
UO ₂	Arc fusion	70/100	1400	5.91 x 10 ⁻³	22.5	1.13 x 10 ⁻¹¹
			1600	1.67 x 10 ⁻²	24.5	2.66 x 10 ⁻¹⁰
UO ₂	Pellet fuel	-	1900	Complete	25.0	b

^aRelease on puncture after neutron activation.^bRelease not controlled by diffusion.

Fig. 12 Release of Xe^{133} from ThO_2 -5 Wt % UO_2 Prepared by the Sol-Gel Process. Results obtained by neutron-activation technique.

Fig. 13 Log D' vs $1/T$ for Various Oxide Fuels.

PLANNED EXPERIMENTS

The experiments currently in-pile (Table 3) provide comparisons and assessments in the following areas: (1) type of oxide, (2) content of fissile material, (3) fuel rod length, (4) irradiation temperature, (5) heat-generation rate, and (6) burnup. In addition to concluding this work, it is necessary that the scope of the program be broadened by embarking upon new areas of investigation.

Among the in-pile experiments under consideration are the following: (1) exposure at higher heat ratings; (2) variations in fuel chemistry, which includes testing fuel with a higher uranium content and a comparison of air-fired vs H_2 -fired sol-gel oxides; (3) irradiation of larger diameter specimens; (4) remote fabrication and irradiation of fuel rods and a large fuel rod bundle containing U^{233} ; (5) constant power irradiation tests; and (6) evaluation of new fuel systems. Finally, additional out-of-pile studies appear warranted in such areas as: (1) characteristics of sol-gel powder particles and the relation to irradiation performance; (2) sintering behavior of arc-fused and sol-gel oxide; (3) thermal conductivity; (4) neutron activation to evaluate fission-gas release; and (5) water-logging susceptibility.

SUMMARY AND CONCLUSIONS

Some of the conclusions which can be drawn from the results obtained thus far are as follows:

1. Sol-gel oxide performs well as compared to arc-fused oxide under irradiation.
2. Vibratory-compaction appears to be a suitable technique for fabricating ThO_2 - UO_2 fuel rods.
3. On the basis of the irradiations and examinations completed, there is no evidence that this type of fuel would not be suitable for use in thermal breeder reactors.
4. The work to date shows sufficient progress such that a vigorous program is warranted to examine additional parameters.

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Session VI
Paper 30

REACTOR IRRADIATION OF THORIA POWDERS AND PELLETS

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INTRODUCTION

The successful use of thorium oxide in a nuclear reactor requires that changes in its properties because of irradiation be predictable. Studies have been carried out to determine the stability of thoria powders and pellets under reactor irradiation at exposures up to 2.5×10^{18} fissions/g. Two of these studies are described in this paper: one involves the dry irradiation in aluminum capsules (air atmosphere) of thorium oxide powders fired at various temperatures; the other, the irradiation both dry and in D_2O of thoria pellets prepared by pressing and firing techniques.

Because of its crystalline similarity to UO_2 ,¹ which is particularly resistant to radiation damage, bulk ThO_2 should also resist radiation damage well. Experiments have already demonstrated that structural defects saturate in UO_2 at exposures of about 10^{15} fissions/g. At this point the UO_2 shows a slight increase in lattice dimension. From this exposure up to at least 10^{20} fissions/g damage does not appear to increase.² Hence, one would not expect to observe a great change in the structure of ThO_2 at exposures considered here. However, there are the possibilities of radiation-induced particle break-down and interaction in the case of powders and surface attrition processes in the case of pellets and it is primarily with these aspects of the problems that we are concerned.

RADIATION-INDUCED SINTERING OF THORIA POWDERS

Two series of thorium oxide powders, designated series C and series D, fired at 650, 800, 900, 1100, and 1500°C were irradiated dry in aluminum capsules for 16 and 22 months in the Low Intensity Test Reactor to an exposure in each case, because of a difference in neutron flux of 1.5×10^{18} fissions/g. During irradiation the 650, 800, and 900°C fired oxides sintered into hard, glossy red fragments. The 1100°C fired materials formed off-white, chalky plugs and the 1500°C fired oxides remained powders. Specific surface areas of the oxides fired at $\leq 1100^\circ C$ were markedly decreased by the irradiation although the estimated maximum temperatures of the powders during irradiation were less

than 900°C. Little or no sintering and some particle degradation occurred in the 1500°C fired powders.^{3,4}

Experimental

The thorium oxides were prepared by refiring 650°C fired D-16 thorium oxide⁵ in platinum crucibles in air for 24 hr at 650, 800, 900, 1100, and 1500°C. The D-16 oxide was a high-purity oxide⁶ prepared from thorium oxalate precipitated from thorium nitrate solution.

The oxide powders were canned (air atmosphere) in aluminum capsules, about 2-1/2 in. long, 1/2 in. OD, and 1/4 in. ID (Fig. 1), which contained cobalt flux monitors. They were irradiated 489 days in a modified fuel element in the C-52 lattice position in the LITR, after which the D series was removed and irradiation of the C series continued for an additional 170 days in the C-21 lattice position. The capsules were held upright in open-top aluminum cans, which permitted reactor cooling water to be in contact with the capsules. The maximum possible temperatures of the powders during irradiation were less than 900°C (Fig. 2).

The temperatures shown in Fig. 2 were calculated assuming a gamma heating of 1.5 w/g of gamma heating, a flux of 2×10^{13} n/cm².sec, a thorium capture cross section of 10 barns, a uranium-233 fission cross section of 530 barns, and 175 Mev deposited locally per fission. Natural convection cooling was assumed (40°C ambient temperature) and only radial heat transfer was considered. In the case of the lower fired materials ($\leq 900^\circ\text{C}$) which sintered, uniform shrinkage was assumed and temperature curves for assumed densities of 8 and 10 g/cc were calculated. It is seen that the maximum temperatures of the powders which sintered were certainly less than 900°C and probably between 700 and 800°C when sintering was complete. However, loss of surface and sintering must have begun at 300°C or less. The temperature of the 1100°C fired material was probably between 300 and 600°C; that of the 1500°C material about 300°C. The integrated radiation exposure for each series of capsules was about 1.5×10^{18} fissions/g. About 0.4% of mass-233 isotopes were produced in each series. The U²³³ which

Fig. 1. Aluminum capsules used in thorium powder irradiations.

Fig. 2. Calculated maximum temperatures in irradiated thoria powders as a function of irradiation time. Flux of 2.5×10^{13} n/cm²·sec; — sintered pellet density; --- bulk powder density.

fissioned corresponded to a burn-up of about 0.07% of the original thorium atoms. Figure 3 shows the 650, 1100, and 1500°C materials recovered from the series D irradiations (489 days).

Results and Discussion

Table 1 shows the surface areas of the irradiated powders and the average particle sizes of the 1100 and 1500°C materials. All the oxides fired at $\leq 1100^\circ\text{C}$ lost most of their surface, those fired at 900°C or less losing a higher proportion. The surface area of the 1500°C fired powder remained unchanged. The average particle size of the 1100 and 1500°C oxides was decreased by a factor of two. Particle-size distributions for the unirradiated and irradiated 1100 and 1500°C fired materials by a neutron-activation sedimentation method⁷ showed that more particle damage resulted from irradiation in the 1100°C fired oxide than in the 1500°C, particularly in the production of the size fraction less than $1\ \mu$ (Fig. 4).

Crystallite size measurements by x-ray diffraction line broadening were obtained on the series D powders as recovered and after annealing 4 hr at 900°C (Table 2). It is interesting to note that, unlike unirradiated oxalate-derived ThO_2 , the crystallite sizes of the irradiated materials show no correlation with the specific surface area data of Table 1 even in the case of the 1500°C fired oxide where a threefold decrease in crystallite size is not accompanied by a corresponding increase in surface area. Lack of change in the x-ray diffraction line broadening of the 1100 and 1500°C fired materials as a result of the 900°C annealing indicates that the line broadening did not result from strain. The 900°C annealing removed the blue color centers of the 1500°C fired oxide but did not change the color of the lower fired materials.

The radiation-induced sintering in the lower fired materials probably resulted from recrystallization processes and material transport induced by fission fragment irradiation. Absence of sintering in the 1500°C fired material shows that the effect was essentially confined to a volume of material of about $2000\ \text{\AA}$ diam. The recrystallization process is probably an interface phenomenon,

Fig. 3. Thoria powders irradiated dry in the LITR to an exposure of 1.5×10^{18} fissions/g. (a) Fired at 650°C, irradiated 16 months, maximum temperature 900°C; (b) fired at 1100°C, irradiated 16 months, maximum temperature 600°C; (c) fired at 1500°C, irradiated 16 months, maximum temperature 300°C.

Fig. 4. Size distribution of thoria powder, fired at (a) 1100°C and (b) 1500°C, irradiated dry. 1.5×10^{18} fissions/g; $nvt = 6 \times 10^{20} \text{ n/cm}^2$.

TABLE 1

LITR THORIA POWDER IRRADIATIONS

Maximum temperature: $<1000^{\circ}\text{C}$

Oxide Firing Temp, $^{\circ}\text{C}$	Thermal-Neutron Flux $\times 10^{-13}$		Average Particle Size, μ			Specific Surface Area, m^2/g		
			Before	After	After	Before	After	After
	Series D	Series C	Irradia- tion	489 Days, Series D	659 Days, Series C	Irradia- tion	489 Days, Series D	659 Days, Series C
650	2.6	-	2.4	-	1.3	28	1.0	<0.5
800	1.6	1.1	2.7	-	3.5	15	<0.5	<0.5
900	1.7	1.0	2.4	-	1.7	8	<0.5	<0.5
1100	1.5	1.1	3.1	2.9	1.4	3.3	1.9	0.6
1500	1.4	1.1	4.7	3.3	2.4	0.8	0.8	0.8

TABLE 2

EFFECT OF REACTOR IRRADIATION ON X-RAY CRYSTALLITE SIZE OF THORIA POWDERS

Irradiation time 489 days; exposure 1.5×10^{18} fissions/g

Oxide Firing Temp, °C	X-ray Crystallite Size, Å		
	Before Irradiation	After Irradiation	
		As Recovered	Annealed 4 hr at 900°C
650	120	255 ^a	390
800	220	400	446
900	500	560	440
1100	1140	540	570
1500	>2000	850 ^a	820

^aProbably low because of sample loading.

and the rate at which a given ThO_2 preparation approaches an equilibrium crystallite size may depend on the original crystallite size of the material and the relative number of surface events.

IRRADIATION OF THORIA PELLETS

Code P-82 thorium oxide pellets prepared from pressed powders with a final firing at 1650°C ^{8,9} had shown the highest wear resistance in attrition tests of any pressed pellet preparation.¹⁰ These were irradiated under D_2O and in D_2O vapor at $250\text{--}300^\circ\text{C}$ in stainless steel autoclaves and dry in aluminum capsules under a helium atmosphere for 3 months¹¹ and 12 months in the LITR to exposures of 7×10^{16} and 2.5×10^{18} fissions/g. While some minor weight losses were observed as a result of the irradiations there did not appear to be any significant structural damage. Pellets irradiated 12 months in the D_2O vapor phase rather than in the liquid showed significant weight losses as well as considerable surface and structural damage.

Experimental

The P-82 pellets were prepared⁸ from oxalate-derived thorium oxide modified by refiring at 1425°C followed by wet ball-milling in a steel mill, leaching

with HCl to remove abraded iron, mixing with 2% carbowax, prepressing to 15,000 psi, granulating and sizing to -35+100 mesh. Rounded-end pellets were pressed to green densities up to 6.3 g/cm^3 . Roughness formed at the juncture of the dome and the cylinder was removed by first firing the pellets at 1450°C , cooling and wet-tumbling. The pellets were then fired at 1650°C in air. As prepared the pellets had a pycnometric density of 9.16 g/cm^3 . Pellets exposed to high temperature water had densities of 9.6-9.7 before drying.

The materials irradiated dry lost <0.05% of their weight; those irradiated in D_2O , <0.4%; and the vapor phase material, 6.2%. During the 12 month irradiation about 0.6% of mass 233 isotopes was produced. The amount of U^{233} fissioned corresponded to a burn-up of 0.11% of the original thorium atoms.

Results and Discussion

Figure 5 shows pictures of the original P-82 pellets and those recovered from the 12 month irradiation experiment. The pellets irradiated under the D_2O and in the vapor phase were tan in color similar to the originals (but not glossy); those irradiated dry were gray-white. As was true with the 3 month irradiated pellets, other than the color change and an occasional chip at the flash the pellets irradiated dry and in the D_2O appeared undamaged. Those irradiated in the vapor phase showed sand-like surfaces and in the exposed interiors of the broken pellets a black peripheral layer just underneath the outer shell. Two of the vapor phase irradiated pellets were broken during a brief, relatively mild, wet stirring operation carried out to rid the surfaces of steel corrosion products. Extended stirring operations with the original pellets and liquid phase irradiated pellets did not produce any breakage.

Wear rates on the pellets were obtained in spouting bed tests (Fig. 6). Pellets prepared by the technique used in preparing the P-82 pellets ordinarily have a wear-resistant, vitreous-like surface layer. In the wear tests this layer is worn away in the first hour or two and then the wear rate increases. Both wet- and dry-irradiation appears to have enhanced the wear resistance of this layer (Tables 3 and 4). Once the surface layer was removed, however, wear

(a) P-82 thorium pellets

(c) Irradiated in D_2O

(b) Irradiated dry

(d) Irradiated in D_2O vapor

Fig. 5. The original P-82 thorium pellets and those recovered from the 12 months irradiation experiment.

Fig. 6. The spouted bed test for determination of attrition rates on ThO_2 pellets.

TABLE 3

WEAR RATES OF P-82 THORIA PELLETS

Irradiation exposure: 7×10^{16} fissions/g

Pellets	Weight Loss, %/hr					
	1st	2nd	3rd	4th	5th	6th
Original	0.06	0.08	0.07	0.17	0.15	0.43
D ₂ O-control	0.11					
Dry-irradiated	0.03	0.22	0.22	0.32	0.37	0.22
D ₂ O-irradiated	0.01	0.0	0.07	0.11	0.12	0.38

TABLE 4

WEAR RATES OF P-82 THORIA PELLETS

Irradiation exposure: 2.5×10^{18} fissions/g

Pellets	Weight Loss, %/hr					
	1st	2nd	3rd	4th	5th	6th
Original	0.20	0.74	0.71	0.72	0.76	0.69
D ₂ O-control	0.26	0.59	0.62	0.64	0.66	0.82
Dry-irradiated	0.05	0.25	0.22	0.48	0.50	0.46
D ₂ O-irradiated	0.15	0.34	0.41	0.41	0.44	0.49

rates of the 3 months irradiated pellets were comparable to those of the unirradiated pellets. Wear resistance of the 12 months irradiated pellets appears slightly enhanced for the duration of the test. The difference in wear rates of the original pellets in the tables results from the fact that two different experimental set-ups were used and the rates shown for the original pellets are in the nature of calibration tests. Figure 7 is a picture of the D_2O -irradiated pellets after the wear test. With the exception of an occasional pit wear of the dry- and D_2O -irradiated pellets appeared to be uniform and indicated little radiation-induced structural damage.

Table 5 gives the results of impact fracture tests on the original pellets, those from the 12 month D_2O -control experiment, and the irradiated pellets. No decrease in structural strength appears to have resulted from irradiation dry and in the D_2O . The pellet irradiated in the vapor phase is definitely weaker. This was also indicated by the breakage observed in the stirring operation mentioned above. The fracture test consisted in dropping a pestle down a loose fitting tube onto a pellet contained in a mortar. The pestle was dropped in a pattern of increasing heights until fracture was achieved. In all cases, the pestle was dropped normal to the cylindrical side of the pellet.

The interiors of the 12 month liquid phase irradiated pellets were similar to the unirradiated pellets. Those of the dry irradiated materials were black (Fig. 8). Heating at $400^{\circ}C$ for 1 hr in air failed to remove the black color but heating at $900^{\circ}C$ overnight restored the original color. No weight increase was noted as a result of the $900^{\circ}C$ heating and it is postulated that the black color results from a very slight oxygen deficiency.

To indicate that the production of radiation-stable thoria pellets is more an art than a science, Fig. 9 shows pellets prepared by what was considered a more promising technique⁹ than that used in preparing the P-82 pellets and the results of the 12 month irradiation dry and in D_2O at $250-300^{\circ}C$. Thirteen out of twenty pellets irradiated under D_2O were badly damaged or disintegrated the products sintering into the irregular shaped masses shown in the picture. The vapor phase irradiated pellets did not appear as severely damaged. The dry-

TABLE 5
IMPACT FRACTURE TEST ON P-82 THORIA PELLETS

Pellet	Instantaneous Impact Energy, in.-lb	Cumulative Impact Energy, in.-lb
Original	0.651 ^b	4.52 ^b
D ₂ O-control	0.893 ^c	8.14 ^c
7 x 10 ¹⁶ fissions/g		
D ₂ O liquid ^a	0.788	6.30
Dry He atmos.	0.683	4.78
2.5 x 10 ¹⁸ fissions/g		
D ₂ O liquid ^a	0.893	8.04
D ₂ O vapor ^a	0.342 ^c	1.34 ^c
Dry He atmos.	0.945	8.98

^aO₂ overpressure.

^bAverage of five tests.

^cAverage of two tests.

Fig. 7 D_2O irradiated pellets after spouting bed wear test.

(a) D_2O -irradiated

(b) Dry-irradiated

Fig. 8. D_2O - and dry-irradiated P-82 pellets after impact fracture test.

(a) As prepared

(b) Irradiated dry

(c) Irradiated in D_2O

(d) Irradiated in D_2O vapor

Fig. 9. Thoria pellets prepared by the pressed-cube technique as prepared and after 12 months irradiation.

irradiated pellets were black in color but appeared undamaged. These pellets were first formed into cubes with the aid of an organic binder and without firing abraded dry into spheres. The spheres were then fired at 1300°C, tumbled in water to polish the surfaces, and given a final firing at 1800°C in a molybdenum furnace and a hydrogen atmosphere. Final density of these pellets was 9.8 g/cc.

The marked stability of the P-82 pellets, as opposed to the above, appears to be associated with its tough surface shell. Failure of the shell to turn black during dry-irradiation may indicate that the shell contains some impurities introduced during preparation which may contribute to its strength.

SUMMARY

As a result of reactor irradiation crystallites in thorium powders degrade. Powders composed of small crystallites lose surface and sinter. The sintering effect becomes negligible as the x-ray crystallite size becomes $>2000 \text{ \AA}$. Particle degradation occurs in thorium powders fired at $\geq 1100^\circ\text{C}$. Thorium pellets which are not weakened and suffer negligible weight losses when irradiated dry in an inert atmosphere and in D_2O to an exposure of 2.5×10^{18} fissions/g can be prepared by pressing and firing techniques. Thorium pellets irradiated in D_2O vapor show pronounced surface attack and are structurally weakened.

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Session VI
Paper 31

IN-PILE TESTING OF CIRCULATING THORIA SUSPENSIONS

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IN-PILE TESTING OF CIRCULATING THORIA SUSPENSIONS

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Previous speakers have dealt with the qualities of bulk thorium oxide and the radiation behavior of such material when canned in various forms of fuel elements. Mr. McBride has discussed the radiation behavior of unclad thorium oxide pellets and powders, both dry and wet. Suspensions of fuel or fertile oxides in water, heavy water, liquid metals, including sodium potassium alloy and liquid bismuth, and other fluids, have been the subject of consideration in various laboratories, even prior to the Manhattan Project. These materials are still of interest as potential reactor fuels. However, a common problem to all proposals for suspensions which are to be moved through the reactor is this: What is the effect of extensive irradiation and fission damage on the properties of the moving suspension? It is hoped that the experiments that I will describe will be relevant not only to the water systems in which they were carried out but also to the other systems of suspended thorium and uranium oxides which are under consideration as potential fuel systems.

As may be seen in Figure 1, a number of potential problems exist with slurries. One of these is the problem of erosion or corrosion - of attack of the metals of containment by the circulated slurry. A second potential problem is associated with deposition on surfaces or caking which could lead to loss of material from circulation, resulting in poor heat transfer, and also possible heat generation due to fissioning in the cake. A third possible problem is associated with thickening of the slurry. This could lead to laminar rather than turbulent flow, poor heat exchange, and to certain relatively stagnant regions. Loss from the suspension may occur, and the thick slurry under some circumstances could plug annular and other regions.

1. EROSION OR CORROSION
2. CAKING OR DEPOSITION ON SURFACES
3. THICKENING: LAMINAR RATHER THAN TURBULENT FLOW:
POOR HEAT EXCHANGE, STAGNANT REGIONS, LOSS
FROM SUSPENSION, DIFFICULT RESUSPENSION,
PLUGGING

FACTORS AFFECTING ABOVE PROBLEMS

1. CONCENTRATION
2. ADSORBED OR DISSOLVED IONS
3. PARTICLE SIZE
4. SURFACE AREA
5. FLOCCULATION
6. CIRCULATION
7. RADIATION DAMAGE

Fig. 1. Potential Problems with Slurries.

Among the factors affecting these problems are the concentration of the slurry, the adsorbable ions or other materials which may react from the medium, the particle properties including size, surface area, etc., and the degree of flocculation of the slurry which results from particle properties and adsorbed materials. Circulation and radiation damage affect these characteristics possibly to a substantial degree as I will describe in the discussion below.

I would like to talk today about two actual slurry experiments which have been completed and a proposed experiment which has now been prepared for in-pile operation. Characteristics of these experiments are shown in Figure 2. The first of these experiments used thorium oxide coprecipitated with 0.4% enriched uranium oxide. Added uranium was used in order to simulate inbred uranium in a breeder blanket. Original average particle size was 1.7 microns. Palladium precipitated on finely divided thorium was added to serve as a recombination catalyst for radiolytic hydrogen and oxygen.

In the second experiment, pure thorium was used and uranium-233 was inbred by conversion from the thorium. This is also true of the third experiment. In all cases, concentrations of 900 to 1000 g of thorium per liter were employed at the beginning of the run. Flow velocities in the core of 6 to 8 ft/sec were employed. The first loop contained a core volume of about 300 ml, this was enlarged in the second loop to 815 ml and will be enlarged in the proposed loop to 1435 ml, resulting in a higher neutron efficiency. In each of the two earlier runs an in-pile circulation time of over 2000 hours was developed. In the first experiment which was carried out in the LITR at Oak Ridge, an effective average flux of about 2×10^{12} nv was developed. In the second loop a mean flux of about 1.5×10^{13} nv was developed. Although the first experiment did not develop nearly as great a conversion of thorium into protoactinium and U^{233} as did the second, a larger number of fissions were developed because of the originally added enriched uranium. Consequently, the first experiment was a deeper experiment as far as examining the effects of fission are concerned, if the characteristics of thorium with coprecipitated and inbred uranium are the same.

<u>EXP. NO.</u>	<u>L-2-27S</u>	<u>O-1-28S</u>	<u>O-1-29S PROPOSED</u>
<u>SLURRY</u>	THORIA - 0.4% ENR. URANIA, Pd	PURE THORIA	PURE THORIA
PARTICLE SIZE	1.7 μ	2.3	2.3
CONC., g Th/liter	980	937	1000
<u>LOOP</u>			
SLURRY VOLUME, ml	900	1344	1960
CORE VOLUME, ml	300	815	1435
CORE FLOW, fps	6	8	7
<u>OPERATION</u>			
IN-PILE HOURS	2200	2036	>5000
SLURRY CIRC. HOURS	3115	2360	----
AVG. (MAX) FLUX	0.22 (1.0) $\times 10^{13}$	1.5 (10) $\times 10^{13}$	>2 (10) $\times 10^{13}$
FISSIONS/GRAM SOLIDS	7 $\times 10^{16}$	2 $\times 10^{16}$	>10 ¹⁷
(Pa + U)-233, % Th	.015	0.07	>0.20

(LOOP MATERIAL, 347SS; LIQUID, D₂O; ATMOSPHERE, O₂; TEMPERATURE, 280°C)

Fig. 2. Parameters of In-Pile Slurry Loop Experiments.

It is desired in the third experiment called O-1-29S to operate as much as 5000 hours at somewhat improved fluxes (due to the larger core), and to develop substantially greater fission intensities and a substantially greater conversion to Pa and U. These conversions should approach levels which are actually of interest in processing uranium from thorium.

The first experiment was terminated by schedule. The second experiment was terminated as a result of the burning out of a pump current supply terminal in an external but radioactive region such that it could not be repaired. Consequently, the stoppage of the run was not in any sense a result of malfunction of the loop parts proper or of the slurry in the loop. This has lead us to believe that 5000 hours of circulation has a reasonable possibility of being developed in the third experiment. If this is achieved, we will end up with an appreciable quantity of thorium slurry which would have an exposure resembling that visualized in potential breeder blanket applications.

The radiation time was a little over 90 days in each of the first two experiments. Increases in the flux or in the irradiation time tend to develop proportionate thorium burnup. Increasing values of the flux tend to produce higher Pa levels. With present exposures fissions from inbred uranium increase roughly in proportion to the square of the time or of the flux.

It may be desirable to reach levels of thorium burnup in breeder reactors of the order of 2 to 5 grams per kilogram before processing. The equilibrium uranium-233 value has been cited as being about 15 grams per kilogram. Thus an experiment yielding a burnup of 2 grams per kilogram is regarded as highly relevant.

The flow pattern in the loops is as follows. A 5 gpm pump discharges the slurry through 3/8 inch stainless steel pipe past a sampling station, across a tubular filter into a coiled core. The core region has corrosion specimens in it at two different velocities of 8 and 22 fps. From the coiled tubing core the slurry passes over out-of-pile corrosion specimens into the pump suction. A stream of filtered water from the slurry section

passes into a heated pressurizer system and thence after cooling into the rear of the pump where it keeps slurry purged out of the pump.

A layout of the loop is shown in Figure 3. The forward end of the containment can at the core is very close to the tank wall of the Oak Ridge Research Reactor.

Figure 4 shows a material balance from the first loop experiment. First of all, it is noted that of the solids added at Y-12 a certain amount was withdrawn in samples during operation. The loop was transferred to X-10 for insertion in the beam hole. At this point, additional catalyst was added and in-pile operation begun. The sintered metal filter cracked and a certain amount of material leaked into the pressurizer and into the annular region of the tubular filter. Samples were removed readily throughout the course of the run. Finally after the completion of the experiment, the residues in the loop were drained into the slurry holdup tank and later were dried and totally recovered. The material balance shown in the figure seems to be reasonably good. I imagine that a little of the agreement is fortuitous but the numbers are as they were actually developed. It is indicated among other things that little or no material was held up in the loop in the form of cakes or otherwise.

The catalyst additions point out that we anticipated a radiolytic gas problem in this LITR experiment. We did not find any radiolytic gas, and we subsequently concluded that recombination due to the intensity of gamma irradiation was, at these temperatures, sufficient to entirely recombine the gas generated at this fission level.

The generalized corrosion experienced for this loop run is shown in Figure 5. Generalized corrosion of the loop was observed by oxygen consumption or by the analysis of corrosion products in samples of the slurry. No particular sustained increase in loop corrosion was observed as a result of the irradiation. In the examination of the corrosion specimens from this run, no radiation effects were observed on zirconium or titanium specimens. On stainless steel specimens, however, there was some indication of a mild radiation effect. A maximum corrosion rate of about 10 mils a year was observed.

Fig. 3. In-Pile Slurry Loop O-1-28S (Elevation).

	<u>INPUT,</u> <u>GRAMS SOLIDS</u>		<u>RECOVERY,</u> <u>GRAMS SOLIDS</u>
	<u>Y-12</u>		<u>Y-12</u>
DT-22 THORIA URANIA	1395.4		
CATALYST SOLIDS	167.3		
CORROSION PRODUCTS	5.	SAMPLES	451.1

Y-12 SUBTOTALS:	(1567.7)		(451.1)
NET TRANSFERRED TO X-10	(1116.6)		

	<u>X-10</u>		<u>X-10</u>
CATALYST SOLIDS	6.6	FILTER ASSEMBLY	86.
CORROSION PRODUCTS	7.	PRESSURIZER	268.
TRACER SOLIDS (AFTER SHUTDOWN)	9.0	SAMPLES	293.5
		SLURRY HOLDUP TANK	481.

TOTALS	1590.3		1579.6

Fig. 4. Slurry Solids Material Balance (L-2-27S In-Pile Loop).

Fig. 5. Generalized Corrosion in Slurry In-Pile Loop L-2-275.

Samples of the slurry were removed from this run and examined from time to time. Figure 6 illustrates one of the examinations of this material. Electron microscope photographs of slurries from this run are shown after various amounts of radiation were received. As may be seen across the top from left to right, and across the bottom from left to right, there appeared to be a chipping away at the edges of the particles, with development of fines, ultimately a considerable disintegration of the particles is seen to have occurred.

It is possible, but by no means certain, that some agglomeration into somewhat larger particles occurred. Such large particles may be seen in some of the lower pictures.

In Figure 7 particle diameters are shown graphically as a function of the total fissions. The size distribution was determined by gravitational sedimentation. Material below about .6 of a micron was determined by centrifugal separation techniques.

Let me direct your attention first to the L-2-27S data which sweep across the chart. There seems to have been a fairly small but definite change in the fraction of material above 90%. The 50% fraction size limit decreased regularly, changing a factor of 10 in 7×10^{16} total fissions per gram. The 10% fraction appears to have decreased even more sharply but possibly is leveling off slightly at the right. However it must be noted that 10% of the material at the end was below .03 of a micron. Only slight extrapolations, if any, were involved in smoothing the data to cover the size limit of the 10% fraction. The general indication of this chart is that fines were produced by the spallation of a number of small chips from large particles rather than the splitting and resplitting of particles into successive halves.

For the experiment with pure thorium, experiment O-1-28S, not quite 2×10^{16} fission/gm of solids were developed and consequently a less extensive look at the trends is available. Clearly degradation had begun to occur. It appears likely that the degradation was a bit less severe here than was the case with the uranium containing material. However clear trends

0 hr IRRAD
831 hr CIRC

155 hr IRRAD
1076 hr CIRC

448 hr IRRAD
1412 hr CIRC

608 hr IRRAD
1579 hr CIRC

1042 hr IRRAD
2110 hr CIRC

1460 hr IRRAD
2617 hr CIRC

Fig. 6. Electron Photographs of Slurry From In-Pile Loop L-2-27S.

Fig. 7. Particle Diameter at 90, 50 and 10% Undersize vs Total Fissions in In-Pile Slurry Loop Experiments.

either in agreement or disagreement with the -27S data are not distinguished because insufficient fissions were developed in this run.

The effect of circulation is shown in Figure 8 by comparison with an in-pile autoclave experiment. Material similar to that placed in experiment L-2-27S was operated in an in-pile slurry autoclave which gently sloshed rather than pumped the material. The autoclave experiment revealed no particle size changes. The data from the loop experiment (shown in the left hand column) clearly indicate particle size changes, attributable to the combined effects of circulation and fissioning. Radiation exposures, temperatures and atmospheres in the two experiments were similar. Surface areas at the same exposures in the loop and autoclave experiments were in agreement, and the crystallite size changes were found to be similar. Therefore, it was concluded that fissioning tended to produce changes within the particle but that the general breaking up of the particles required the additional element of circulation.

Figure 9 shows changes in crystallite size of thorium in the two in-pile experiments as a function of total fissions. Crystallite size was determined by x-ray line broadening. A regular degradation in crystallite size was observed in the first experiment, with a final value of about 220 Å being observed. In the second experiment with pure thorium crystallite size degradation appeared to be less. After an initial drop, little further change is noted.

Figure 10 compares surface areas developed in the two loop experiments as a function of total fissions. The lower line represents, for experiment L-2-27S, an essentially linear increase in surface area with total fissions. In the case of the experiment with pure thorium, O-1-28S, the line is not in disagreement with the -27S data but perhaps represents a somewhat steeper slope. More surface area appears to have been developed in the pure thorium experiment by a given amount of total fissions.

In an effort to determine the nature of the surface area, in experiment L-2-27S, pore volume determinations by BET techniques were carried out using the automatic equipment developed by P. Dake and others. Three samples are represented showing the distribution of pore volume as a function of pore radius in Figure 11. The original material without catalyst, the material

Fig. 8. Effect of Irradiation on Particle Size Degradation in Loop and Autoclave Experiments.

Fig. 9. X-Ray Crystallite Size vs Total Fissions.

Fig. 10. Surface Area vs Total Fissions.

Fig. 11. Distribution of Pore Volume as a Function of Pore Radius, In-Pile Slurry Loop Experiment L-2-27S.

which contained catalyst and had been circulated but not irradiated, and the irradiated material are shown.

These pore volume distribution data were used to calculate the distribution of surface areas with pore radius. This permitted a comparison with the surface area determined by straight BET techniques. As may be seen in Figure 12, which shows the distribution of surface area with radius, the agreement between the two techniques in all three cases is reasonably good. Furthermore, it is seen that a great proportion of the surface area is associated with pores of quite small radius. More than half the area was in pores of less than $45 \text{ \AA}$, radius, and an appreciable amount was in pores of $10 \text{ \AA}$ or less radius.

The external surface area corresponding to the particle size distributions amounts to about $5 \text{ m}^2/\text{g}$. Crystallites of average size of $220 \text{ \AA}$ would have a surface area of about $25 \text{ m}^2/\text{g}$.

Thus we can interpret the surface area observed in the first experiment as being about $5 \text{ m}^2/\text{g}$ external, $20 \text{ m}^2/\text{g}$ internal pores, and about $10 \text{ m}^2/\text{g}$ excess which may be associated with material not showing the crystal pattern of ThO_2 . This could be material which was removed by fission fragment effects, possibly evaporation.

In the second experiment much less degradation of particle size and crystallite size was observed. Surface area on the other hand was a bit higher at similar dose than in the first experiment. So the patterns of degradation in the thorium-uranium and pure thorium experiments differ somewhat. It is hoped that a long irradiation of pure thorium in the third loop experiment will be able to clarify the extent of these differences.

The settling characteristics of irradiated slurry from experiment L-2-27S were examined as shown in Figure 13. Original and unirradiated pumped material settled substantially more rapidly than the irradiated slurries. The final settled bed was more dense in the case of the unirradiated material. The settled beds from the irradiated samples were very easily picked up and were not very mud-like. The irradiated slurries thus appear to be somewhat more flocculated in the sense that they contained a larger proportion of water to solids.

Fig. 12. Distribution of Pore Areas as a Function of Pore Radius, In-Pile Slurry Loop Experiment L-2-27S.

RADIATION HOURS	0*	155	1460
CIRCULATING HOURS	0-810	1076	2712
ORIGINAL VOL. % SOLIDS	11.2	9.4	5.4
SETTLING RATE, cm/min x 10 ³	52	33	0.8
SUBSIDENCE HALFLIFE, min	19	28	120
FINAL SETTLED BED, v/o SOLIDS	20	21	7

***MIXED Y-12 SAMPLES**

Fig. 13. Settling Characteristics of Irradiated Slurries.

It was of interest to examine the viscosity of the irradiated material and to compare it with similar unirradiated material. After the completion of the first loop experiment, material was recovered from the dump tank, which consisted of slurry which was recovered from the rinses for various samples and the final draining of the loop. This material had a particle size of .76 microns and it had a surface of about 33 square meters per gram. Thus, it would correspond roughly to the material taken about 3/4's of the way through the irradiation. The viscosity of this material was determined in a capillary viscometer at room temperature at 3 concentration levels, from 500 to 1000 gms of thorium per liter. Similar tests using unirradiated thoria were made on the same instrument and on another instrument. From the viscosity determinations under various stresses it was possible by using the Bingham plastic model to deduce values of the yield stress of the material at each concentration.

Figure 14 shows the yield stress data that were obtained. Theory indicates that the yield stress should be proportional to the cube of the volume fraction solids and possibly should be inversely proportional to a diameter squared. This correlation applying to thoria and other slurries was developed particularly by Dr. D. G. Thomas of Oak Ridge National Laboratory. It appears first of all that the original thoria-urania slurry gave results in reasonable agreement with this particular theory when tested at several different concentrations and on the two different viscometers. Tests of the yield stress of the irradiated material are seen to be in reasonable agreement with theory as regards dependence on concentration, and in fair agreement with what might have been expected for such a particle size. It is to be noted however that not quite as much yield stress was developed as the theory predicted. The final particle size of the loop experiment was of the order of .3 micron and theory predicts yield stresses of somewhat higher values there.

Figure 15 shows the effect of yield stress on the transition velocity, at which the change from laminar to turbulent flow occurs, for various yield stresses. It is to be noted at a yield stress of about 1/2 lb/ft², the critical velocity is about 7 fps and this goes up, as indicated by the formula there, with the square root of the yield stress so that to get up to 14 fps

Fig. 14. Observed and Estimated Yield Stresses of Slurries Prepared from Solids from In-Pile Slurry Loop Experiment L-2-27S.

Fig. 15. Effect of Slurry Physical Properties on Transition Velocity.

it would be necessary to have a yield stress of 2.

One point remains: to estimate what kinds of viscosity effects might be anticipated for highly irradiated pure thorias. This means that we are interested in a thorium burnup of 0.5%, and total fissions of about 100×10^{16} per gram of solids. This is a factor of about 15-20 beyond the range of our present tests.

First of all: the log diameter - total fission correlation cannot be extrapolated linearly very far without leading to ridiculously untenable diameters. The surface area is of interest for extrapolation for two reasons. The response to total fissions was essentially linear. This is compatible with a spallation or bombardment model, so that there is a reasonable basis for linear extrapolation.

Secondly, the yield stress is believed to be a function of surface area rather than particle diameter for particles of high internal surface. In a somewhat sponge-like particle the thickness or dimension of the crystalloid ligaments is measured inversely by the surface area. In our viscosity measurements above, the yield stress varied with the $1/2$ to $1/4$ power of surface area. In the "theoretical" equation cited above, variation would be with the first power of the surface area.

In any event, the changes in yield stress at the ultimate exposure would be limited though substantial. Their effect might be mitigated considerably by adjustment of concentration.

Insofar as the effects are the results of spallation by fission fragments, they may well be expected in all liquid media, in which the high energy spallation fragments cannot readily return to the parent particle.

Provided the pure thoria slurry experiment now in preparation can be operated to produce a sufficient number of fissions, it should be possible to determine whether behavior resembles that observed for the thoria-urania slurry, and to arrive at reliable models and data to estimate the characteristics of fully irradiated thoria slurries. It is hoped that the generalization will prove appropriate for various liquid media.

Session VII
Paper 32

THORIUM FUEL CYCLE ECONOMICS

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The thorium fuel cycle can be started with either highly enriched uranium or plutonium, the choice depending on the availability and the relative prices of the two fuels. Since neither the availability or relative prices of plutonium are firmly known today, this discussion will be limited to the case in which highly enriched uranium is used as the feed material. The first cycle in a Spectral Shift Reactor would use highly enriched uranium-235 mixed with thorium in the form of oxide fuel. After discharge from the reactor the core would be reprocessed and the uranium recovered for reuse.

The U-233 recycle flow chart is given in Figure 1. Starting with the reactor the spent core is sent to a chemical reprocessing plant where the uranium is separated from the thorium and the fission products. The uranium recovered after several cycles will contain several thousand ppm of uranium-232 which decays by alpha emission with a half life of 74 years to thorium-228. The thorium-228 is the precursor of several radioactive decay products, two of which, thallium-208 and bismuth-212 emit high energy gamma rays. The time constant for the series is essentially determined by the half life of the thorium-228 (1.9 years). Since the gamma radiation associated with the decay of U-232 and Th-228 is very weak, it is possible to handle the uranium for a limited period of time after reprocessing with minimal shielding requirements. Only the uranium will be recycled, thereby avoiding the need for a completely remote fabrication plant. The thorium is sent to storage for a period of approximately 12 years to permit the thorium-228 to decay. It can then be recycled in the fabrication plant. This does not involve a very severe economic penalty. Assuming that the thorium has zero value upon being sent to storage, the economic penalty is only 0.06 mills/Kwhr.

The uranyl nitrate from the reprocessing plant is sent to a feed materials preparation plant where mixed thoria-urania powder is then loaded into fuel tubes in the core fabrication plant, the fuel rods assembled into bundles and the core sent to the reactor completing the cycle.

The thoria-urania powder will be produced using the sol-gel process developed at Oak Ridge National Laboratory. This is a very simple and inexpensive

Fig. 1. U^{233} Recycle Flow Chart.

process which produces powder of high density and having the proper particle distribution required for vibratory compaction of the powder in the fuel tubes. Fuel tubes can be filled to 90% of theoretical density by vibratory compaction using the powder produced by the sol-gel process.

In Figure 2 the material flow chart for the two top boxes in the previous figure has been expanded. The recycle fabrication plant will receive UF_6 make-up from the diffusion plant, thorium nitrate from a raw material production plant and uranyl nitrate from the reprocessing plant. The uranyl nitrate is processed in a small ion exchange unit to strip the thorium-228 and its daughter products which have built up in the uranium during the time interval between reprocessing and receipt of the material at the recycle fabrication plant.

The total time required in the process from the time that the uranyl nitrate is cleaned up in the ion exchange unit to the time that the fuel element is assembled is less than four days. The process will have several parallel lines. Cleanup and maintenance of the equipment will be scheduled weekly to prevent the accumulation of fuel at any part of the process line. This will permit direct maintenance and repair of equipment.

Some shielding of the feed material process equipment is required. The filling of the fuel tubes, however, since only a small amount of uranium is contained in a single fuel tube, can be done directly without shielding. The final assembly of the fuel element will require some shielding and will be done mechanically under water.

Based on a preliminary design of a recycle fabrication plant using these processes, the fuel fabrication costs are estimated to be \$80/kg of fuel. This cost is for the plant operating at half-capacity which is sufficient to serve three large reactors (400-500 Mw electric each). A breakdown of the cost is shown in Table I.

These costs are based on existing prices that are being quoted in the United States for thorium and Zircaloy and prices for services as given in the

Fig. 2. U^{233} Recycle.

TABLE I

COST BREAKDOWN SSCR THORIUM FUEL CYCLE

	<u>\$/Kg Fuel</u>
Fabrication	
Thorium	15
Zircaloy	22
Labor and Markup	40
Miscellaneous	<u>3</u>
Subtotal	80
Reprocessing	21
Transportation and Insurance	<u>12</u>
Subtotal	33
TOTAL	113

United States Atomic Energy Commission's "Prices for Nuclear-Reactor Materials and Charges for Fuel Processing Services." If the plant were operated at full capacity the increase in throughput would reduce the recycle costs by about 20%.

We have investigated the thorium fuel cycle for two types of water reactors which may prove to be important in the generation of electricity during the next 20 years. They are the pressurized water reactor with Spectral Shift Control and the pressurized water reactor with soluble poison control.

The thorium fuel cycle offers the potential of the lowest fuel cost in the SSCR. The high value of η (neutron regeneration factor) of uranium-233 leads to very high conversion ratios in the SSCR, which in turn results in significantly reduced fissionable material requirements. The average conversion ratio and the uranium-235 make-up in grams per megawatt day of heat for the equilibrium cycles are shown as a function of fuel exposure in megawatt days per metric ton of fuel in Figure 3. For example, with an average exposure of 25,000 MWD/MT the conversion ratio is almost unity. Note also the very small fissionable material make-up requirements. The equilibrium make-up requirements are less than 0.05 gram/MWD. This should be compared with 1.25 grams/MWD

Fig. 3. Conversion Ratio and U^{235} Requirement vs Fuel Exposure.

of heat from uranium-235. In other words, by conversion of thorium to uranium-233 and recycle of the bred uranium, the fissionable material cost is reduced by a factor of 25 as compared to a uranium-235 burner. The fissionable materials costs are accordingly very low, being less than 0.1 mill/Kwhr using highly enriched uranium-235 feed.

Thorium fuel cycle costs have been calculated for a 1355 MW thermal reactor that is reflected by a 3-inch thorium blanket. The blanket elements are reprocessed to recover the uranium-233 at the end of each cycle. The core is batch loaded. Operating parameters for the core are given in Table II.

TABLE II
OPERATING PARAMETERS FOR SSCR

Thermal Power (MW)	1355
Net Electrical Power (MW)	407
Fuel Cycle (days at full power)	1000
Active Core Height (in.)	116
Active Core Diameter (in.)	103
Lattice Metal-to-Water Ratio	0.8
Blanket Thickness (in.)	3.0
Fuel Pin O.D. (in.)	0.42
Plant Factor	0.80

In the first cycle the fuel is highly enriched uranium-235. Successive cycles use the fuel recovered from the previous cycle. The uranium-235 make-up per cycle rapidly approaches equilibrium as shown in Table III. After four cycles each of average fuel exposures of 30,000 megawatt days per metric ton of fuel, the uranium-235 make-up is nearly constant.

The fuel enrichment, or more exactly, the average initial isotopic ratio of uranium-235 and uranium-233 to thorium for the equilibrium cycle are given in Figure 4. The fuel is loaded in four radial and two axial zones according to the pattern shown in Figure 5 to reduce the peak to average power ratio to

Fig. 4. Fuel Enrichment at Beginning of Cycle vs Fuel Exposure.

⊕

$E = 2.56$	$E = 2.69$	$E = 3.58$	$E = 5.38$
$E = 2.23$	$E = 2.34$	$E = 3.12$	$E = 4.68$
$E = 2.56$	$E = 2.69$	$E = 3.58$	$E = 5.38$

⊕

Fig. 5. Core Radial and Axial Zone Enrichments (E = Average Zone Enrichment, wt % U^{235}).

2.0. The fuel enrichment for the first cycle lies in the range of 3 to 4% for average fuel exposures in the range of 20,000 to 40,000 MWD/MT. The fuel enrichment is decreased by about 30% for the equilibrium cycle.

TABLE III
URANIUM-235 MAKE-UP - SSCR
(30,000 MWD/MT Exposure per Cycle)

Cycle	1	2	3	4	Equilibrium
U-235 (kg)	-	42	78	89	91

The mass balances for the first and fifth or equilibrium cycles are shown in Table IV. The average fuel exposure is 30,000 MWD/MT which results in nearly minimum fuel costs.

TABLE IV
MASS BALANCE OF SSCR, (kg)

	<u>First Cycle</u>		<u>Fifth Cycle</u>	
	<u>Initial</u>	<u>Final</u>	<u>Initial</u>	<u>Final</u>
U-235	1,638	537	225	134
U-233		615	1,039	874
U-233 Blanket		119		139
Total Fuel (Oxide)	45,500		45,500	
Average Conversion Ratio	0.79		0.92	

In order to estimate the fuel costs for the thorium cycle it is necessary to establish a value for uranium-233. In the absence of both a supply and fuel market for uranium-233, a reasonable approach is to determine the fuel value of uranium-233 in the SSCR. The fuel value is determined by making the fuel value at the beginning of each cycle constant. This determines the value of uranium-233 relative to highly enriched uranium-235. The value varies from \$14.65 per gram to \$16.50/gram depending on the cycle. The average over a large number of cycles is \$15/gram and is used in the fuel cost estimates presented below.

Fuel costs for an average fuel burnup of 30,000 MWD/MT in the SSCR with the blanket are shown in Table V. The fuel inventory includes all the inventory charges during power operation at 80% load factor, reprocessing, fabrication, shipping and cooling at 4.75% interest rate. A relatively conservative allowance for the time required for cooling, shipping, reprocessing and fabrication (740 days) has been assumed to reflect the higher inventory charges that would apply with less than three reactors in operation. After several reactors are in operation the inventory charges would be reduced by about 0.1 mill/Kwhr. The other cost components are those shown in Table I for the equilibrium cycle. The fabrication cost for the first cycle is slightly higher due to the cost of converting a large quantity of highly enriched UF_6 to UO_2 .

TABLE V
SSCR FUEL COSTS

	<u>Mills/Kwhr</u>	
	<u>First Cycle</u>	<u>Fifth Cycle</u>
Fabrication	0.51	0.45
Fuel Inventory Charge	0.50	0.46
Uranium-235 Burnup	1.36	0.11
Reprocessing Cost	.11	0.11
Transportation and Insurance	.05	0.05
Uranium-233 Credit	- <u>1.16</u>	<u>----</u>
Total Fuel Cost	1.37	1.18

The variation of fuel cost with exposure for the equilibrium cycle is shown in Figure 6. The fuel inventory and uranium-235 burn-up costs increase with exposure to offset the declining costs due to fabrication, reprocessing and shipping. The minimum fuel cost is 1.18 mills/Kwhr at about 30,000 MWD/MT.

Fuel cycle costs have been estimated for a PWR using a neutron absorber which is soluble in water such as boric acid for shim control. Both batch and partial reloading with shuffling of fuel have been considered. The reactor power in both cases is the same as the SSCR (1355 MW thermal).

Fig. 6. Fuel Cycle Costs vs Average Fuel Exposure.

In the batch loaded core, zone-loading of fuel similar to that for the SSCR is used to obtain a peak to average power ratio of 2.0. The other reactor parameters are the same as those listed in Table II for the SSCR, except for the omission of a blanket. Since the neutron leakage in the case of the PWR is smaller, a blanket does not appear to offer any economic advantage.

The shuffled core has three fuel zones. At the end of each cycle the central third of the core is removed, the outer two zones moved to the center and new fuel elements placed in the outer zone. The fuel loading increases from inner to outer zone, resulting in substantial power flattening. However, due to shuffling of fuel, the peak to average power ratio is about 30% higher than for the batch-loaded core. Thus, to obtain the same power under identical conditions of thermal design the core must be 30% larger.

The mass balances for the batch core with a cycle of 30,000 MWD/MT average exposure and a reshuffled core with a cycle of 7,750 MWD/MT average exposure are shown in Tables VIa and VIb, respectively.

TABLE VIa
MASS BALANCE (KG) OF PWR BATCH CORE

(45,500 kg Oxide Fuel)				
	<u>Cycle 1</u>		<u>Cycle 5 (Equil)</u>	
	<u>Initial</u>	<u>Final</u>	<u>Initial</u>	<u>Final</u>
Uranium-235	1959	727	1030	475
Uranium-233	----	503	800	778
Average Conversion Ratio	0.59		0.65	

TABLE VIb

MASS BALANCE OF PWR SHUFFLED CORE, KG
(62,900 kg Oxide Fuel)

		Cycle 1		Cycle 2			
	<u>Zone</u>	<u>Initial</u>	<u>Final</u>	<u>Initial</u>	<u>Final</u>		
Uranium-235	Inner	504	309	334	221		
	Middle	553	334	486	297		
	Outer	653	486	654	478		
	TOTAL	<u>1710</u>	<u>1129</u>	<u>1474</u>	<u>996</u>		
Uranium-233	Inner	0	122	128	200		
	Middle	0	128	86	185		
	Outer	<u>0</u>	<u>86</u>	<u>0</u>	<u>91</u>		
	TOTAL	<u>0</u>	<u>336</u>	<u>214</u>	<u>476</u>		
		Cycle 3		Cycle 4		Cycle 7	
	<u>Zone</u>	<u>Initial</u>	<u>Final</u>	<u>Initial</u>	<u>Final</u>	<u>Initial</u>	<u>Final</u>
Uranium-235	Inner	297	200	293	202	158	115
	Middle	478	295	330	207	255	159
	Outer	464	337	391	276	307	224
	TOTAL	<u>1239</u>	<u>832</u>	<u>1014</u>	<u>685</u>	<u>720</u>	<u>498</u>
Uranium-233	Inner	185	236	186	236	288	302
	Middle	91	186	187	242	265	289
	Outer	<u>136</u>	<u>187</u>	<u>213</u>	<u>241</u>	<u>280</u>	<u>289</u>
	TOTAL	<u>412</u>	<u>610</u>	<u>586</u>	<u>719</u>	<u>833</u>	<u>880</u>

The fuel costs using the same cost factors as for the SSCR are given in Table VII.

TABLE VII
FUEL COSTS - PWR
(Mills/Kwhr)

	<u>Batch Core</u>	<u>Shuffled Core</u>			
	<u>Equilibrium Cycle</u>	<u>1st Cycle</u>	<u>2nd Cycle</u>	<u>3rd Cycle</u>	<u>7th Cycle</u>
Fabrication	0.46	1.46	0.52	0.49	0.48
Fuel Inventory	0.56	0.65	0.67	0.68	0.69
Uranium-235 Burnup	0.68	1.79	1.47	1.25	0.49
Reprocessing	0.10	0.13	0.13	0.13	0.13
Trans. & Insurance	0.05	0.10	0.07	0.07	0.07
Uranium-233 Credit	----	1.29	1.00	0.76	----
	1.85	2.84	1.85	1.86	1.86

The minimum fuel cost for a PWR with soluble poison shim control occurs at lower fuel exposures than the SSCR. The fuel costs for both the batch and shuffled cores have broad minima in the range of 20,000 to 25,000 MWD/MT exposure of the discharged fuel. Since the calculations for the above cores were performed for different fuel exposures (30,000 vs 23,200 MWD/MT) a correction should be made for the batch core. Reducing the fuel exposure to 23,000 MWD/MT for the batch core reduces the fuel inventory 13% or 0.07 mills/Kwhr and reduces the fuel burnup by 0.14 mills/Kwhr. Offsetting this reduction is an increase of 0.16 mills/Kwhr for all other costs giving a net reduction of 0.05 mills/Kwhr. Thus, for all practical purposes the above cases are sufficiently close to their respective minima to permit direct comparison.

The fuel cost for shuffled cores, except for the first cycle, is very nearly the same as for a batch core. The theoretical advantage of shuffling is largely offset by the increase in power peaking factors resulting from shuffling which leads to a substantial increase in core size. The energy cost from pressurized water reactors using either spectral shift or soluble

poison for shim control is lower for batch loaded cores. The larger size of the shuffled core results in higher capital cost of the reactor, since the pressure vessel and primary system are larger. The plant availability is also higher for the batch core, since fewer shutdowns for refueling are required.

Session VII
Paper 33

ORNL Studies of Thorium Utilization Economics

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Introduction

At the present time, most nuclear power experts believe that slightly enriched pressurized or boiling water reactors plus fast breeders will form the backbone of the future nuclear industry. These same experts regard the development of thorium fueled reactors as superfluous, since as they put it, "You can satisfy all of mankind's future energy needs with natural uranium as the source material; therefore, why develop thorium reactors, or even thermonuclear power?"

Such an attitude toward thorium utilization is understandable for a number of reasons. First, known reserves of low cost thorium ore are only about one-third as great as reserves of low cost uranium. Second, the thorium fuel cycle needs U^{235} or Pu to get it started; therefore, it is initially dependent on natural uranium. Third, the development of thorium fueled reactors is not as advanced or been demonstrated on such a large scale as UO_2 fueled systems. Finally, economic methods of fabricating U^{233} -thorium fuel elements necessary for recycle of the U^{233} remain to be developed and demonstrated. To overcome these barriers, the thorium utilization program must establish not only a sound technical base but also prove that there is both a short term and long term economic justification for thorium fueled reactors. Studies have been carried out at ORNL during the past few years with this objective in mind; namely, to evaluate the economics of thorium utilization in current generation reactors and the long range potential of thorium breeders or high neutron economy converters. This paper summarizes the results of these studies, which thus far, have dealt with the reactors listed in Table 1.

TABLE 1

REACTOR TYPES CONSIDERED IN THORIUM-FUEL CYCLE COST STUDIES

<u>Current Technology</u>	<u>Longer Range Systems</u>
Pressurized Water (Yankee)	Aqueous Homogeneous (AHBR, ASCR)
Boiling Water (Dresden)	Molten Salt (MSBR, MSCR)
Sodium Graphite (Hallam)	Liquid Metal (LBRR)
Gas Cooled (GCR-2, HTGR)	Gas Cooled (GGBR, PBR)
Heavy Water (CVTR, CANDU)	Heavy Water (DGBR)
Spectral Shift	

The reactors listed under "current technology" in Table 1 represent most of the reactor types being developed for central station power production. A few types, such as the organic moderated reactor, are not included since the fuel cycle characteristics of these are similar to those studied. Similarly, the longer range systems listed are believed to be representative of most of the types having long term potential.

Fuel Cycle Costs in Current Technology Reactors

Interest in the use of thorium in current reactors stems from the high value of η for U^{233} in the thermal and intermediate neutron spectrum. This leads to higher conversion ratios, longer reactivity lifetimes, and greater return of byproduct fissile material than is possible in thermal reactors using U^{238} based fuels; however, the influence of these nuclear advantages on net fuel cycle costs is not clear. In particular, the "values" of U^{233} and plutonium as recycle fuels are still uncertain since they depend on the relative costs of

refabricating fresh and recycle fuel elements which are unknown. Consequently, it was necessary to make arbitrary assumptions regarding these costs as shown in Table 2 along with other cost bases used in ORNL fuel cost studies.

TABLE 2
BASES FOR FUEL COST STUDIES

Utilization Factor, %	80
Preirradiation Holdup Time, days	210
Postirradiation Holdup Time, days	180
Shipping Costs, \$/kg	19
Processing Costs, \$/day	17,000
Uranium Use Charge, %/yr	4-3/4
Working Capital Interest Rate, %/yr	12
Value of Plutonium as Nitrate, \$/g	8
Value of U ²³³ as Nitrate, \$/g	12
Value of U ²³⁵ Based on July 1962 Schedule	12

FABRICATION COST, \$/kg

<u>Reactor</u>	<u>Fresh Fuel</u>	<u>Recycle Fuel</u>
BWR	105	165
PWR	95	155
GCR	25	88
SGR	55	120
HWR	80	145

The Influence of Reactivity Lifetime on Fuel Cycle Costs

The incentive for using U²³⁵ and thorium instead of slightly enriched uranium is that for a given enrichment (i.e., percentage of fissile to

fissile and fertile material) one achieves a longer reactivity lifetime. This is illustrated in Figure 1 which shows that for the GCR-2, Dresden and Yankee reactors, above certain enrichments, longer reactivity lifetimes are possible with the thorium fuel cycle. It is noted here, however, that the lines cross, which indicates that at low enrichments, the U^{238} fuels have an advantage. This implies that the reactors whose fuel costs minimize at high enrichments and long burnups tend to favor the thorium cycle whereas the converse is true for low enrichment reactors. In the case of Dresden and Yankee type reactors, optimum enrichments with the given fabrication and other cost bases used are quite high, as shown in Figure 2. With these enrichments, reactivity lifetimes are longer with U^{235} -thorium fuels.

The advantage of longer reactivity lifetimes with U^{235} + thorium; however, tends to be offset by the higher cost of highly enriched U^{235} compared to slightly enriched U^{235} . This is shown in Figure 3 in which reactivity lifetime is plotted against the value (or cost) of the initial fuel mixture. Again it is seen that the lines cross; however, until one gets to very high initial fuel values the slightly enriched fuels have an advantage. The crossover points correspond to enrichments considerably above the optimum which means that, for given inventory costs, reactivity lifetimes will be less for U^{235} -thorium fuels than for slightly enriched uranium.

One factor which may compensate for the lower reactivity lifetime per dollar invested in fuel inventory is that the "value" of U^{233} as recycle fuel in thermal reactors may be 50% higher than that of plutonium. This is the basis for the existing AEC buyback credits for U^{233} at \$12/gram

Fig. 1. Reactivity Lifetime Vs. Enrichment.

Fig. 2. Fuel Investment Costs Vs. Enrichment.

Fig. 3. Reactivity Lifetime Vs. Initial Fuel Value.

and plutonium at \$8/gram which have been used in the ORNL studies. These fissile material values may not hold up in a free market economy; nevertheless, they do tend to favor the thorium fuel cycle. The net result of all of these factors is that total fuel cycle costs are approximately the same for both fuel cycles as shown in Figure 4. The slightly enriched U fuels appear to have somewhat lower fuel cycle costs in the case of the BWR, whereas, the U^{235} - thorium fuels seem to be preferable for the more highly enriched PWR.

Fuel Cycle Costs in Pebble Bed Reactors

Fuel cycle costs in advanced gas-cooled reactors such as the Pebble Bed Reactor should be lower for the U^{235} -Th cycle because minimum fuel costs occur at very high burnups as shown in Table 3.

TABLE 3

FUEL CYCLE COSTS FOR 330 MWE PEBBLE BED REACTOR

Bases Used

Fuel Fabrication Costs, \$4.10 per 2-1/2" Diameter Ball

Present AEC Ground Rules

Carbon/ U^{235} Atom Ratio = 3024

Thorium/ U^{235} Atom Ratio = 10.1

Fueling Cycle	<u>Once Through</u>	<u>Graded Exposure</u>	<u>Batch</u>
Conversion Ratio	0.60	0.62	0.56
Fissions/IFA	1.36	1.41	0.92
Fuel Cost, mills/kwh	1.13	1.09	1.41

It is seen in this table that minimum fuel costs occur at an exposure of 1.4 fissions per initial fissile atom which correspond to about 100,000 MWD/MT. Unfortunately, fuel cycle costs for a slightly enriched UO_2 fueled

Fig. 4. Fuel Costs Vs. Enrichment.

PBR are not available for a direct comparison; however, intuitively one would expect these to be very high because of the buildup of Pu^{240} at the high exposures involved.

Influence of Important Cost Parameters on Thorium Fuel Cycle Economics

Two important cost parameters which may change in the foreseeable future are the cost of enriched uranium and the annual charges on fuel inventories. The former may drop through improvements in diffusion plant technology and reductions in the cost of natural uranium and the latter may rise as a result of private ownership of nuclear fuel. The influence of these factors on thorium fuel costs was examined and the results are summarized in Table 4.

TABLE 4

MINIMUM FUEL CYCLE COSTS FOR REDUCED U^{235} PRICE SCHEDULE

<u>Basis</u>	Feed Cost	= \$15/kg Nat. U	
	Separative Work Cost	= \$20/kg U	
	U^{235} Cost	= \$7.80/g at 90% Enrichment	
	Pu Value	= \$4.50/g as Nitrate	
	U^{233} Value	= \$8.60/g as Nitrate	
	Reactor Power	= 500 MwE Net	
		<u>Fuel Cost, mills/kwh</u>	
<u>Reactor Type</u>	<u>Annual Inventory Charge, Percent</u>	<u>Slightly Enriched U</u>	<u>$\text{U}^{235} + \text{Th}$</u>
BWR	4-3/4	2.13	2.14
BWR	12	2.51	2.87
PWR	4-3/4	1.88	1.76
PWR	12	2.32	2.48

It is seen in Table 4 that changes in the cost of enriched uranium (and corresponding credits for byproduct fissile material) will have little influence on the relative merits of the two fuel cycles. Private ownership of nuclear fuel, however, will tend to penalize the thorium fuel cycle more than the U^{238} fuel cycle because of the higher inventory costs at optimum enrichments.

Comparison of U^{233} and Pu Recycle

Studies at Hanford and ORNL have indicated that the value of a mixture of plutonium isotopes as recycle fuel in thermal reactors is of the order of \$8.00 per gram total plutonium relative to the July 1962 AEC Enriched U^{235} Price Schedule. The comparable value of U^{233} as shown in Table 5 ranges from \$12 to 14 per gram for the assumed fuel management schemes and economic ground rules.

TABLE 5

FUEL VALUE OF U^{233} IN CURRENT REACTORS

July 1962 Economic Ground Rules

$$\Delta FAB^* = \$60/\text{kg Thorium}$$

<u>Reactor</u>	<u>MwE</u>	<u>Fueling Cycle</u>	<u>U^{233} Value, \$/gr</u>		
			<u>1st Cycle</u>	<u>2nd Cycle</u>	<u>3rd Cycle</u>
Dresden	180	Uniform Batch	12.30	12.80	12.90
Yankee	110	Uniform Batch	13.60	13.90	13.80
CVTR	17	Uniform Batch	12.30	12.70	13.20
CANDU	203	Countercurrent	13.60	13.20	12.30
Hallam	75	Countercurrent	14.50	14.10	14.10
GCR-2	225	Countercurrent	14.20	13.80	13.20

*Differential fabrication cost of recycle fuels.

These results lend credence to the assumed value of \$12/gram used in fuel recycle cost comparisons. The studies were performed for the purpose of establishing the feasibility of recycling fuel in one's own reactor. The results summarized in Table 6 show that fuel cycle costs remain constant with U^{233} recycle, whereas, recycle of plutonium leads to increasing fuel costs. This means that U^{235} -thorium fuel cycle costs do not depend on the sale of U^{233} to other reactor types, and a thorium based nuclear power system can center around a single reactor type. A U^{238} based fuel system, on the other hand, requires a combination of two or more reactor types (presumably thermal Pu converters and fast Pu users) for a balanced power economy. In summary, it appears that thorium utilization has little to offer to current technology reactors as a first cycle fuel; however, it provides a more direct path to a balanced power economy than the combination of thermal and fast reactors required with the U^{238} -Pu fuel cycle.

TABLE 6

FUEL COSTS IN THORIUM AND URANIUM SYSTEMS WITH EQUILIBRIUM FUELING, AND FINITE AMOUNTS OF RECYCLE FUEL AVAILABILITY*

Reactor Type	Initial Fuel Cycle	Fuel Costs, mills/kwh(e)					
		U^{235} -Th			Uranium		
		1st	2nd	3rd	1st	2nd	3rd
BWR		2.3	2.2	2.2	2.3	2.5	2.7
PWR		2.1	2.0	2.0	2.2	2.4	2.6
GCR		2.5	2.4	2.5	1.9	2.2	2.3
SGR		2.9	2.9	3.0	2.4	2.5	2.6
HWR**		2.3	2.2	2.2	2.3	2.7	2.8

* Based on 4-3/4% fuel inventory charge; a plutonium value of \$8/g and a U^{233} value of \$12/g; out-in fueling for BWR and PWR, and countercurrent fueling for GCR, SGR, and HWR.

** Includes 0.8 mill/kwh(e) for D_2O inventory charges and losses.

The Importance of Thorium as A Long Term Energy Source

The short term objective of the civilian power program; namely to reduce nuclear power costs to the point where nuclear energy is generally competitive with fossil fuels, provides a clean-cut economic criterion for evaluating proposed short term reactor types; however, the longer term objective of "making fullest use possible of the energy latent in uranium and thorium" is somewhat ambiguous. This has led to the use of various criteria such as conversion ratio or breeding ratio, doubling time, fuel yield versus fuel costs, etc., for evaluating longer range systems. As a result of this diversity no one at the present time has a clear idea of what constitutes an "ideal" long range reactor type. The long term objective, of course is identical to the short term objective of finding the cheapest mode of nuclear power production; however, the energy source must be sufficiently abundant to provide significant amounts of power for an appreciable length of time. Thus the determination of what constitutes best mode of production depends on the magnitude and cost of various sources of nuclear fuels relative to the magnitude of future energy needs.

This can only be guessed at; nevertheless, guesses are sufficiently to define what sources will be most important during the next hundred years or so. The consensus of projections of future nuclear capacity, as shown in Figure 5, indicates that complete conversion of the U. S. electric power industry to nuclear power may occur by AD 2050. Corresponding nuclear fuel requirements using such a projection as a basis are shown in Figure 6. In this figure, uranium consumption is given as a function of overall net conversion ratio (i.e., grams fissile material produced per cycle per gram

Fig. 5. Nuclear Electric Capacity Required for 100% Conversion of System by AD 2050.

Fig. 6. Reserves and Requirements of United States Nuclear Service Materials.

U²³⁵ consumed) and total inventory requirements are given as a function of specific power (i.e., kilograms of U²³⁵ (or equivalent) per MWE installed capacity). The presently known important sources of both high and low cost uranium and thorium are also shown on Figure 6 along with estimated recovery costs. It is seen that, regardless of conversion ratio and specific power (within the limits shown), there is little likelihood low-cost uranium will be exhausted before the year 2000 while the thorium and uranium in the Conway granites should last till 2100. Thus one can set lower and upper limits on the probable cost of uranium and/or thorium during the next 150 years or so. This provides a basis for defining the long range objective of the nuclear power program in terms of economic rather than nuclear criteria. More specifically, the objective should be to develop nuclear reactor types capable of achieving power costs no greater than present conventional power costs while utilizing nuclear fuels costing up to \$80/lb uranium or thorium. At this cost of raw material and using the assumptions given in Table 7, the uranium burnup costs in mills/kwhr are equal to 6.0 times $(1 - C_R)$, and the inventory charges in mills/kwhr are equal to 0.4 times (kg/MWE). It is obvious that, under these conditions, current technology reactors

TABLE 7

BASES USED TO DEFINE LONG RANGE ECONOMIC OBJECTIVES

Load Factor, %	80
Thermal Efficiency, %	33
Annual Charges on Fuel Inventory, %	7
Separative Work Cost, \$/kg	20
Natural U Cost, \$/kg	176
Value of U ²³⁵ , Pu ²³⁹ , U ²³³ , \$/gram	40

which have average conversion ratios less than 0.75 and fuel inventories of the order of 5 kg fissile/MWE would encounter excessively high inventory plus burnup costs. If one assumes that economically competitive nuclear power will require fuel cycle costs of the order of 1 mill/kwhr, and that half of this cost will be absorbed by fuel cycle costs not associated with the cost of nuclear source material, it will be necessary to keep these latter costs at 0.5 mill/kwhr or less, regardless of the cost of ore. This is the basis used in Figure 7 which shows inventory and conversion ratio requirements to achieve competitive power costs with ore at present prices, \$30/lb U or Th, and \$80/lb U or Th, respectively. Inventories and conversion ratios of typical high neutron economy reactors are also shown on Figure 7 for the purpose of comparing these reactors from the standpoint of the previously stated long range economic objective. Specific reactors are identified by name in Table 8. It is seen in Figure 7, that only the two-region breeders are capable of achieving the long term economic objective of utilizing \$80/lb material; the HTGR, MSCR and ASCR are probably capable of achieving economic fuel costs with \$30/lb U or thorium; while the Candu, PBR and SSCR types, insofar as present designs are concerned, appear to be less attractive with high cost ores.

TABLE 8

<u>Designation</u>	<u>Name</u>
PBR	Pebble Bed
Canduth	Thorium Fueled Candu
Candu	Canadian, D ₂ O moderated
SSCR	Spectral Shift Converter
HTGR	High Temperature Gas Cooled Graphite
MSCR	Molten Salt Converter

Table 8 (cont.)

<u>Designation</u>	<u>Name</u>
ASCR	Aqueous Slurry Converter
LBRR	Liquid Bismuth Breeder
GGBR	Gas-Graphite Breeder
MSBR	Molten Salt Breeder
DGBR	D ₂ O-Gas-Breeder
AHBR	Aqueous Homogeneous Breeder
FTB	Fast Thorium Breeder
FOB	Fast Oxide (U ²³⁸) Breeder

Fig. 7. Conversion Ratio Vs. Fissile Inventory for 0.5 mill/kwh Burnup and Inventory Costs.

Other Criteria for Evaluating Breeder Type Reactors

The evaluation of advanced reactor types relative to a specific economic objective has the weakness that the cost assumptions and other bases used are somewhat arbitrary and subject to change, and such changes can easily invalidate the conclusions reached. The discovery of large amounts of low cost uranium, for example, would tend to de-emphasize the importance of achieving high conversion ratios. Increases in annual charges on fuel inventory as a result of private ownership, on the other hand, would put a premium on higher specific powers and/or higher conversion ratios. Finally, the disappearance of the market for byproduct fissile material would downgrade the importance of achieving breeding ratios above 1.0.

In view of these uncertainties, it seems expedient that advanced reactor types should also be evaluated on the basis of how sensitive fuel cycle costs are in each case to changes in ore costs, fixed charge rates and credits for bred fuel. Reactors which are least sensitive to changes in cost bases should be most desirable to develop, assuming of course that they are equally competitive under present ground rules. Thus one should look for reactors which have simultaneously low fuel costs, high fuel yields and high specific powers. The evaluation of thorium breeders shown in Figure 8 represents an attempt to compare reactors on this basis; however, the use of the fuel yield versus fuel cost criterion does not take into consideration the possible effect of loss of market for byproduct fuel. This aspect is shown in Figure 9 which plots fuel inventories against conversion ratio for the various breeder reactor types and at the same time shows lines of constant fuel yield. Reactors with highest fuel yields are least sensitive to fixed charge rates while those with lowest fuel inventories are least sensitive to the market for byproduct fissile material. Thus the

Fig. 8. Thermal Breeder Evaluation.

Fig. 9. Conversion Ratio, Fissile Inventory and Fuel Yield.

"ideal" long range reactors should have inventories as low as 1 kg fissile/MWE and fuel yields as high as 7% to 12% per year. The only types that seem to fit these requirements are the AHBR and the MSBR. The FOB has an adequate fuel yield; however, the economics of the oxide breeder are very dependent on the sale of plutonium. Lacking a market for plutonium, such a reactor could not compete if only the higher priced source materials were available.

Summary

On the basis of the fuel cycle studies carried out at ORNL, it has been shown that the use of U^{235} thorium instead of slightly enriched UO_2 in current technology reactors does not offer significant fuel-cost savings. The reason for this is that fabricating and processing cost reductions resulting from the longer achievable reactivity lifetimes tend to be offset by the higher fuel-inventory charges associated with the use of highly enriched U^{235} . Subsequent recycle of the U^{233} in one's own reactor, however, can be done at no cost penalty, whereas, recycle of plutonium leads to higher fuel costs with each successive cycle.

The evaluation of reactor systems on the basis of the longer term criteria of (1) competitive fuel costs at present natural uranium costs, (2) economic burnup and inventory costs at higher ore prices, and (3) fuel costs which are insensitive to rising ore costs, inventory charge rates and the market for bred fissile material, indicates that of all of the systems studied, the aqueous homogeneous breeder and molten salt breeder are most promising.

Thus the development of these reactors plus the development of U^{233} recycle processes appears to be the best way to insure that the large amounts of thorium found in low grade sources can be economically utilized.

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