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Preface

This symposium was held at the request of the Atomic Energy Commission in order to provide an opportunity for people actively working in the field to exchange ideas and to be made aware of the problems of the entire thorium-U^{233} cycle. It also provided an opportunity for the AEC to define its position with regard to thorium in reactor technology.

I would like to acknowledge with thanks the help of F.T. Miles of Brookhaven, and of J. Fernandez of the AEC in organizing the program. I am grateful to the following Brookhaven personnel for acting as scientific secretaries: E. Weinstock, D.M. Richman, W.H. Regan, M. Steinberg, C.K. Klamut, and J. Powell. Credit is due Margaret Dienes for the painstaking editing of the papers. Finally, thanks are due to Mr. and Mrs. Howland Sargent (Myrna Loy) for their help in making this a memorable conference.

BERNARD MANOWITZ
Conference Coordinator

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Session I

GENERAL SESSION

The Thorium Team

CLARK GOODMAN
Division of Reactor Development, U.S. Atomic Energy Commission, Washington, D.C.

INTRODUCTION

This is a conference of technical people actively engaged in the thorium-U^{233} program. The specific objectives of the conference are threefold: 1) to define, in terms of accomplishments and planning, the AEC position with regard to thorium in reactor technology, 2) to provide an opportunity for an exchange of ideas between workers in this field, and 3) to develop a report which will be an up to date summary of the present thorium effort in the United States.

POSITION OF THORIUM

The present position of thorium in the field of power reactors is similar to that of a second string football team. It represents an important reserve which must be properly developed and equipped but which for the time being must sit on the sidelines while the first string, the uranium team, is on the field.

At the present stage of development the uranium team is certainly the stronger of the two. It has two members, U^{235} and Pu^{239}, which served during the war and several others that have seen military service since. Furthermore, these and other members of the first team have had several seasons of civilian training and experience. As a result many of their earlier weaknesses have been overcome. Despite these improvements, the uranium team still is not well seasoned. To date it has been unable to make much yardage against the powerful defensive team of conventional fuels. The novice nuclear team will do well to score even one touchdown in the next several seasons.

STRENGTHS AND WEAKNESSES

There are several areas of strength and weakness which account to some degree for the present position of thorium.

Let us consider the strength of thorium.

1) Thorium occurs quite widely in the earth. In common rocks thorium is more abundant than uranium. There are extensive, easily mined, alluvial deposits of monazite, the most common thorium-bearing ore, in a number of countries, notably India, Brazil, and Australia. Sizable deposits are present in South Africa, Indonesia, and the United States. Thorium also occurs in a number of mixed minerals now mined for their uranium content.

2) Thorium metal has fair tensile strength (20,000 to 40,000 psi at room temperature), good mechanical working properties, and machining characteristics comparable to those of mild steel. The oxide (ThO_2) is very stable, even at elevated temperature, as evidenced from the extensive use in gas mantles during the past half century.

3) Thorium is mono-isotopic (Th^{232} only). It absorbs neutrons to form Th^{233} which is relatively short-lived. Subsequent beta radioactivity results in the formation of long-lived U^{233} ($T_{1/2}=160{,}000$ years) which is fissionable with thermal neutrons in much the same manner as U^{235}.

4) The Th-U^{233} cycle is the only known way to breed in a thermal reactor. The number of neutrons emitted per fission, the fission cross section and absorption cross section of U^{233}, and the absorption cross section of Th are so balanced that in a properly designed reactor it should be possible to produce more U^{233} than is consumed during operation.

5) Thorium can be used in many ways as a fertile or blanket material in power breeder reactors. a) Thorium oxide slurries can be made which do not settle out of aqueous suspension and can be pumped through pipes, valves, and heat exchangers without undue settling or plugging. The proposed Pennsylvania Power & Light Company's circulating fuel reactor utilizes a thorium slurry in heavy water as the blanket. b) Thorium fluorides are very soluble in fluoride melts; hence thorium

can be used in eutectic mixtures in fused salt reactors such as the Aircraft Reactor Experiment (ARE) and others proposed at Oak Ridge National Laboratory. c) Thorium oxide may be used as a homogeneous mixture with uranium oxide in pin-type fuel elements such as those planned for the Consolidated Edison reactor now under construction at Indian Point, New York. d) Thorium oxide suspensions or slurries in liquid metals may be used in blanket materials for the liquid metal fueled reactor (LMFR) being developed jointly by Babcock & Wilcox and Brookhaven National Laboratory. These and other methods of arranging for thorium to absorb neutrons and thereby produce new fuel in power reactors will be discussed during this conference.

6) Another advantage of the application of thorium in reactors is that the operating temperature is not limited by allotropic transformation as is the case for uranium. This is significant since at this time there is a continuing reluctance to operate above the temperature at which uranium undergoes an alpha-beta phase change.

Another advantage of thorium appears in a rather negative way. Because of the nuclear properties of U^{233}, there should be less need for international inspection and security safeguards when thorium is used as the fertile element than when uranium (U^{238}) is used. In terms of our football analogy, we would not require as many referees in the game if the thorium team were on the international field.

Now we must consider the weaknesses of thorium.

1) Thorium absorbs neutrons, even thermal neutrons, only to a limited extent. As a result, large quantities of thorium are required as fertile material. The bulk is disadvantageous because it requires sizable volumes of reactor space and the handling of large quantities of thorium during chemical extraction of the U^{233}.

2) There are no chemical compounds of thorium sufficiently soluble to allow the use of aqueous solutions for the blanket in either fluid fuel or heterogeneous reactors. It is because of this limited solubility that so much attention has been given to the development of thorium slurries.

3) Neutron absorption in thorium is accompanied, under practical reactor conditions, by gamma radioactive by-products which interfere seriously with the fabrication of the main fissionable product, U^{233}. There is always some U^{232} formed by the fast neutron reaction $Th^{232}\ (n,2n) \rightarrow Pa^{231} + n \rightarrow U^{232}$ and $U^{233}\ (n,2n)$ when the quantity of U^{233} has built up to appreciable concentration in the blanket material. Being isotopic with the thermally fissionable U^{233}, the U^{232} cannot be separated by chemical means. Unfortunately, the U^{232} decays into a series of short-lived daughter products, some of which emit penetrating gamma-rays. Hence, the U^{233}, plus small amounts of U^{232}, grows to be gamma radioactive soon after chemical separation from the thorium in which it was generated. This gamma radioactivity interferes seriously with the fabrication of fuel elements from the U^{233}.

4) In addition to this gamma activity, U^{233} is also a very toxic material because of its relatively short half-life and alpha radioactivity. For this reason U^{233}, like Pu^{239}, must always be fabricated remotely. This complicated technique is only in its embryonic stage of development. We will hear from later speakers in detail about some of the methods being studied.

When we balance off these strengths and weaknesses of thorium against a similar list for uranium, it is difficult to understand why thorium has not received more attention. The explanation lies in the military might of plutonium, a derivative of uranium. Because of this the major U.S. atomic effort to date has been and continues to be in the production of plutonium. In fact, the emphasis on production has been so great that only recently have we been able to devote much attention to the use of plutonium as a fuel material for civilian power reactors.

As is clearly evident from the papers to be presented at this conference, the joint industry-government effort on thorium is very sizable and encompasses the full range of research and development problems which need to be solved to bring out the inherent capability of this material. I am sure you will agree that all that is needed is more push made possible by more reactor materials and financial assistance. I will indicate some of the major plans under consideration within the Commission at this time.

FUTURE DEVELOPMENTS

First as regards materials. There are several important reactor development projects going forward which employ thorium as fertile material

and require U^{233} as the fissionable material. There is a general need for a variety of critical experiments to be carried out in these programs over the next few years. Although some of the needed basic physics data are available from which to make approximate reactivity calculations, critical experiments are essential for each specific reactor type in order to confirm the assumptions in the calculations, especially at elevated temperatures.

A study recently completed by American Radiator and Standard indicates that 30 kg U^{233} are needed this year and 80 kg in 1960 to support the minimum thorium reactor development program. A really comprehensive program would require more than ten times this amount by 1960. Considerations are now being given to these needs, and it is hoped that the Commission will be able to produce sufficient material to satisfy these important requirements.

To date, no reactor has been operated on U^{233}; hence the actual feasibility of its use as fuel is not yet established. As a first step we are hoping to be able to operate the MTR with a full set of U^{233} fuel elements. As now planned the fabrication and use of these fuel elements will follow the already announced plan to operate the MTR on plutonium. These integral experiments should serve as valuable checks on the basic nuclear data as well as demonstrating in a limited way the feasibility of fabricating fuel elements containing these toxic materials.

Finally, there is the difficult problem of pricing these materials. As you know, the Commission has established a fair purchase price of $15 per gram for U^{233} in the form of uranyl nitrate and $30 to $45 per gram, depending on the Pu^{240} content, for domestic plutonium in the form of metal. Since it requires the absorption of one neutron to produce one atom of each of these fissionable isotopes, there is a strong economic incentive to produce plutonium for weapons as a by-product of producing power rather than producing U^{233} as a replacement fuel for the initial U^{235} used in the reactor. In fact, this pricing policy has caused several industrial organizations to consider seriously abandoning the thorium-U^{233} cycle in favor of the uranium-plutonium cycle.

In view of the long-term importance of thorium as a source of fissionable material, it is to be hoped that a pricing formula can be found that will be more favorable toward thorium but which will at the same time recognize the superior properties of plutonium for weapons purposes.

All that can be said at present is that the Commission is well aware of this problem. But no equitable pricing plan has yet been evolved which encourages the use of thorium in proper proportion to its fertility.

SUMMARY

In summary, the present international interest in thorium is large, and its use in the long run will certainly be essential to the world's conservation of fissionable materials. The United States has a vigorous long-range program of developing the thorium-U^{233} fuel cycle. This program includes the development of economic methods of recovering thorium from its ores, the utilization of thorium in the most suitable forms of fertile materials, the recovery of U^{233} and its economic fabrication into fuel by remote control means, and the development of power reactors which either have a high conversion ratio or actually breed. The pricing policy for U^{233} is not yet fully formulated, but despite this drawback the future of thorium continues to be bright.

The Thorium Cycle

F.T. Miles
Brookhaven National Laboratory, Upton, New York

The successful use of the thorium-U^{233} breeding cycle in a power reactor system depends on the solution of a number of problems. These problems involve nuclear physics, reactor design, metallurgy, chemistry, chemical engineering, and economics. At this conference we have the experts who know best where we stand on each of these. The real work of this conference will be done this afternoon when we split up into separate working meetings and attack each of the problems in detail. As an introduction I will give a very rough outline of the cycle and try to show what will be covered in the sessions and how they fit together.

To do this I have drawn up a chart or flow sheet of the thorium cycle (Figure1). The flow of thorium is shown by the black arrows, and the flows of other materials, uranium, protactinium, and fission products, are also shown. The widths of the arrows were chosen to indicate the relative rates of flow in grams per day. The width of each arrow is proportional to the cube root of the mass flow rate, based on some rough guesses about a typical reactor system.

There are, of course, alternate ways of arranging the cycle, but I have tried to make the chart applicable to different arrangements with obvious changes. For example, the chart shows a two-region reactor with a core and blanket, but it could also represent a reactor with a seed core or a single-region reactor. The reduction to metal step would be by-passed if oxide fuel elements or an aqueous solution fuel were used. The amount of burn-up achieved before processing will determine the mass flow rates and the widths of the arrows. High burn-up would show on the chart as narrower thorium-recycle streams for the same width of fission product stream.

Starting at the upper left of the chart, the thorium ore is concentrated, and then purified to fuel grade ThO_2. The stockpile of ThO_2 will supply a number of reactors, only one of which is shown on this chart. In many cases the next step will be the reduction to metallic thorium. The various processes through the reduction step will be discussed in Session III, "Thorium Crudes to Fuel Grade Thorium," of which Mr. Magoteaux is chairman.

The next step is fabrication of fuel, which is here taken to include fertile material. Depending on the particular reactor design, the fertile and fissionable material may be included in the same fuel elements or there may be separate fuel and blanket elements. The chart shows two regions,

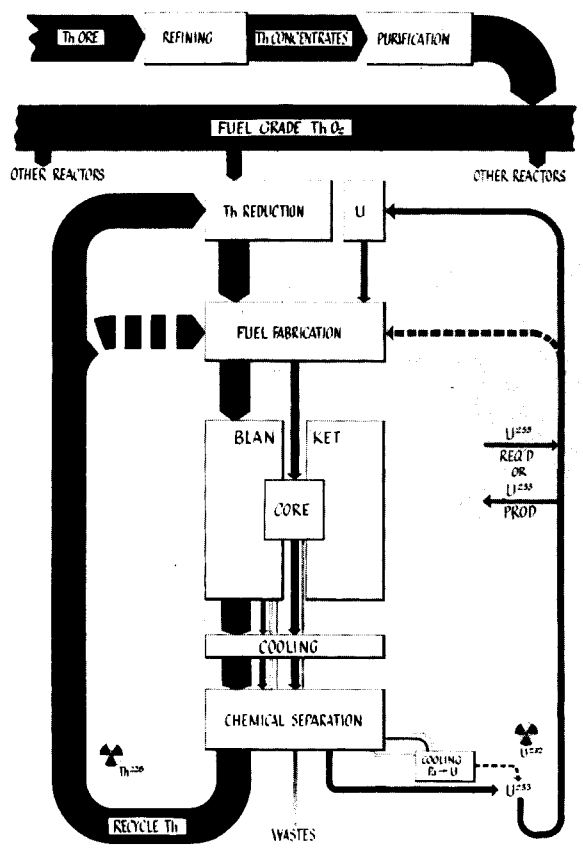
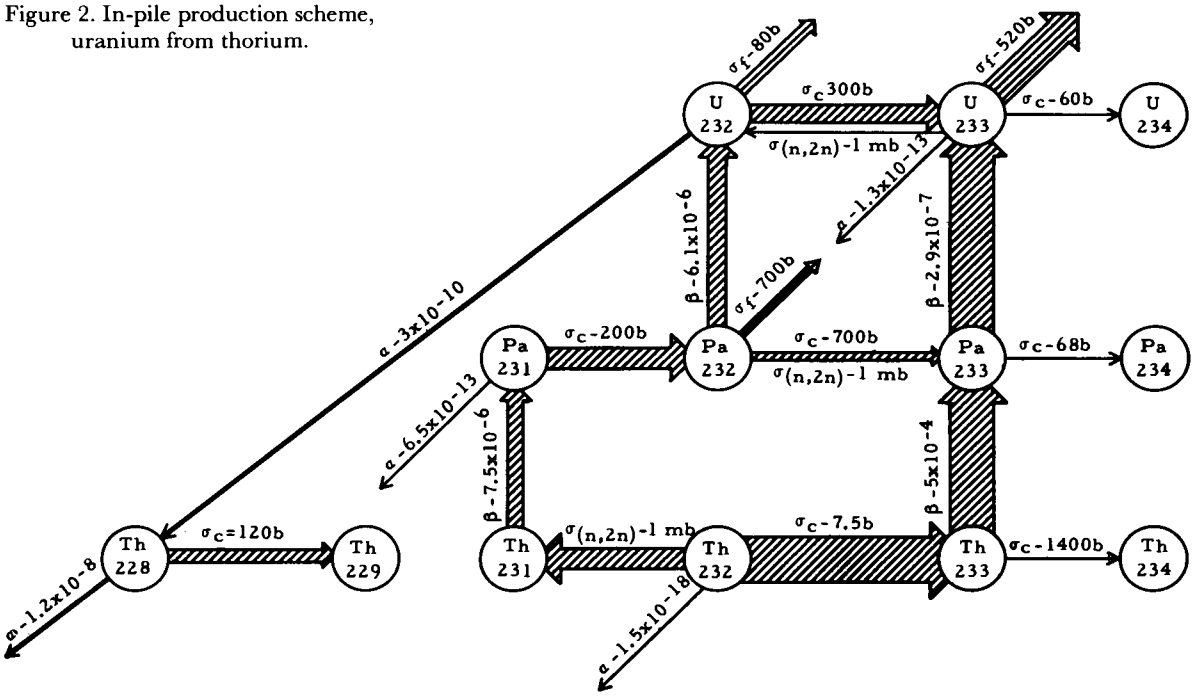


Figure 1. The thorium cycle.

Figure 2. In-pile production scheme, uranium from thorium.



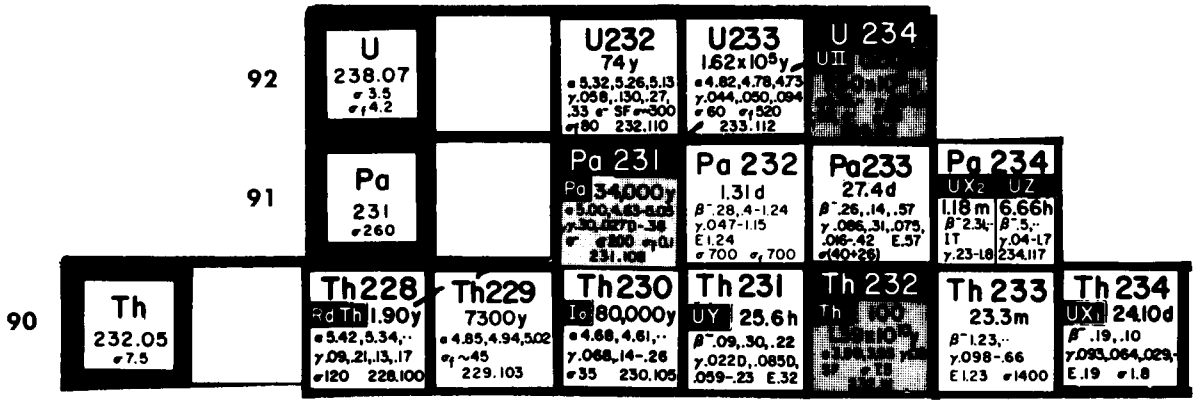


Figure 3.

but would apply with minor changes to a single-region reactor.

The two competing types of reactor fuels are, of course, solid and fluid. With the former an attempt is made to reduce costs by making the burn-up as high as possible, with resulting infrequent processing so that costs can be spread over many kwh. With the latter frequent or continuous processing is used, but the processing is made as simple and cheap as possible. The fabrication may consist of only the make-up and adjustment of a fuel solution. It will require long operating experience with both types to decide which of these approaches offers the best chance of economical power.

Among the solid fuel elements the leading contenders are metals and oxides. Metals show better heat transfer, while oxides have a better chance for long burn-ups. Both types will be discussed in Session IV, "Fuel Preparation and Radiation Experience – Solid Fuels," chaired by Mr. Schumar.

A number of fluid fuels have been suggested, of which the aqueous systems have received the most development. Others are fused salt and liquid

metal systems. These will be covered in Session V, on fluid fuel, conducted by Dr. Lyon.

After fabrication the fuel is put in the reactor. Here the primary questions are those of the basic physics, the values of the nuclear constants of U^{233} and thorium. The cross sections and particularly the neutron yields of U^{233} will determine how a reactor fueled with U^{233} will perform. These values will, therefore, have an important influence on the worth of U^{233} as compared with its competitors U^{235} and Pu^{239}. For example, they will largely determine under what conditions it will be possible to breed and whether the chart should show "U^{235} required" or "U^{233} produced." These and related questions are the subject of Session II, "Basic Physics," of which Dr. Redman is chairman.

One special problem related to the nuclear physics is the build-up of undesirable isotopes of uranium and thorium. Figure 2 shows the pertinent portion of the isotope chart, and Figure 3 shows the nuclear processes. The desired sequence is, of course,

$$Th^{232}(n,\gamma)Th^{233} \xrightarrow{\beta} Pa^{233} \xrightarrow{\beta} U^{233}.$$

Unfortunately, there are side reactions. Th^{233} and Pa^{233} capture neutrons and each such reaction results in a double loss, the neutron and the potentially fissionable atom. In addition $n,2n$ reactions followed by β decays and neutron captures form 74-year U^{232}. This decays to 1.9-year Th^{228}, radiothorium. Thus the recycled thorium and the uranium will become contaminated with isotopes of high specific alpha activity and will therefore be biologically poisonous. In addition the short-lived daughter members of the $4N$ decay chain have high gamma activities and will require shielding and special precautions in handling. Some of the radioactivity can be avoided in part. For example, it is possible to schedule the chemical separations and the decay of certain batches of Pa^{233} so that some isotopically pure U^{233} is produced. But this is a troublesome and expensive procedure which could only be applied to part of the U^{233} production.

The radioactivity in recycled thorium and U^{233} would seem to make remote reprocessing necessary, and this in turn seems to favor fluid rather than solid fuels. We must remember, however, that automatic manufacture of complicated machine parts has been highly developed in the automobile industry and that such procedures would be adaptable to remote control. Where it has been used, automation has generally reduced costs provided the production volume is large enough. Mr. Arnold's meeting, Session VII, "Fuel Recycle and Handling," will cover these problems in detail.

The chemical reprocessing plant completes the cycle. The type of process is, of course, influenced by the fuel element. There are two very general approaches to chemical processing which correspond to the two general types of fuel. One way is to process very infrequently but with complete decontamination. This allows for handling of recycled material (except as the Th^{238} and U^{233} may be limiting) and is suited to solid fuel elements. The other way is to process rapidly but with only enough decontamination to remove pile poisons and, possibly, to reduce the hazard of the fission product inventory. This way is suited to fluid fuels. Mr. Bruce is chairman of Session VI, in which the status of chemical reprocessing will be discussed.

This description of the thorium cycle has been very superficial. The details will come up in the special meetings when the experts will come to grips with the actual problems. I hope, however, that this rough account has shown the interdependence of the various parts of the cycle. Each step must be successful before the cycle will be practical. Let us hope that the experts will report back tomorrow that each part shows a good chance of success.

Advanced Thorium Reactor

SIDNEY SIEGEL
Atomics International, A Division of North American Aviation, Inc., Canoga Park, California

INTRODUCTION

In order to achieve a really high performance, we are convinced that a nuclear power system should satisfy at least three major requirements:

1) Operate at elevated temperature to maximize thermal efficiency.
2) Have a high conversion ratio to minimize fuel costs.
3) Be compact and have high power density to reduce capital costs.

In seeking directions in which the technology of the sodium-graphite system, with which we have been concerned for some years, could make substantial advances, the concept of a reactor utilizing the Th^{233} cycle, sodium cooled, having a neutron spectrum significantly above thermal, seemed worthy of exploration. Locally, we call this concept the Advanced Thorium Reactor, ATR. In it we attempt to retain, and improve upon, the desirable characteristics of the SGR and release some of the constraints imposed upon the SGR by its operating conditions.

SGR TECHNOLOGY

The use of sodium as coolant permits high operating temperature at low pressure; the materials present in the SGR are all essentially chemically inert with respect to each other. These characteristics provide a high degree of reactor safety, in addition to good thermal efficiency, and are retained in the ATR. Most of the constraints on the SGR arise from the limitations on materials which can be tolerated in a thermal reactor, and from the necessity to separate physically graphite from liquid sodium. To optimize neutron economy in a thermal spectrum, zirconium is the preferred material for sheathing the graphite. However, its poor mechanical properties at elevated temperature set limitations on the reactor temperature; in addition, zirconium is expensive.

Stainless steel is not attractive for use in the relatively large amounts required for graphite sheathing, and cladding of a high surface/volume fuel element configuration, because of its effect on the conversion ratio, required enrichment, and hence fuel costs. In the event of failure of the graphite sheath, carburization of stainless steel coolant structure by carbon carried over by sodium can occur above 1050°F, and this possibility sets another operating temperature limitation on the SGR.

The use of Be in place of graphite would obviate a number of these limitations, but in a thermal reactor so much expensive Be is required that its use is not economically justifiable at present prices. These considerations suggest that the release of constraints on the selection of reactor materials, and the freedom to improve power density by permitting more coolant in the core, may be achieved by going to a neutron spectrum which is faster than thermal.

NEUTRON PHYSICS IN THE INTERMEDIATE ENERGY REGION

A neutron spectrum in the 100 to 10,000-ev range, where structural and coolant cross sections are low, would permit the use of stainless steel for core components, a larger volume of coolant within the core with resultant higher power density, and the use of relatively modest amounts of Be for whatever moderation might be required.

The crucial questions upon which the reactor concept depends are the variation with neutron energy of η_{23} and of σ_a for the fission products. In Table 1 data by Spivak et al.[1] are listed for η vs neutron energy for U^{233}, U^{235}, and Pu^{239}. As is well known, η_{25} and η_{49} fall rapidly with increasing

Table 1

η for U^{233}, U^{235}, and Pu^{239} as a Function of Neutron Energy Between Thermal and 900 kev

Neutron energy region	U^{233}	U^{235}	Pu^{239}
Thermal neutron beam	2.28±0.02	2.06±0.02	2.03±0.02
0.5 ev	2.28±0.09	2.06±0.06	1.79±0.07
0.4 – 3 ev	2.24±0.05	1.6 ±0.04	1.79±0.04
0.6 – 6 ev	2.24±0.05	1.50±0.04	1.81±0.04
2.5 – 25 ev	2.28±0.05	1.52±0.04	1.79±0.04
8 – 130 ev	2.28±0.05	1.48±0.04	—
30 kev	2.25±0.07	1.86±0.04	2.01±0.05
140 kev	2.43±0.12	2.12±0.10	2.35±0.12
250 kev	2.45±0.12	2.21±0.15	2.60±0.18
900 kev	2.60±0.13	2.28±0.08	2.57±0.12

neutron energy above thermal. Breeding is not possible with U^{235} at any energy; in fast spectra Pu^{239} offers the best prospects, but the spectrum must be maintained above perhaps 10^5 ev. However, high power density designs may have difficulty in achieving an adequately fast spectrum. Breeding, or at least a good conversion ratio, appears possible with U^{235} at thermal energy, except for the material limitations discussed earlier. Of central importance to the ATR concept, hower, η_{23} remains nearly constant over the thermal to kilovolt range; this suggests that the conversion ratio achievable in the thermal region can be improved upon at higher energies where structural and coolant cross sections are low. Furthermore, there is no necessity for going to really fast spectra, where limitations on volume of structure and coolant again become important. While there is a significant gap in the data between 100 ev and 30 kev, it is likely that the major effects of resonances upon η occur in the region below 100 ev, and that no spectacular behavior will be found above that energy.

The information on fission product absorption vs energy is meager above the epithermal region. However, Greebler, Hurwitz and Storm[2] on theoretical grounds conclude that the variation of average fission product cross section varies with energy as shown in Table 2, which indicates a decrease in the relative importance of these poisons. In addition to the parasitic losses to fission products, absorption by Th^{233}, Pa^{233}, U^{234}, and other higher isotopes is of importance in this reactor concept, as well as any other reactor using the Th^{233} cycle.

POSSIBLE REACTOR CONFIGURATION

Some conceptual studies on a reactor based on these ideas have been carried out, primarily to size the plant physically and thermally. With the present cloudy state of information on neutron physics constants, such a concept is necessarily highly tentative at this time, particularly on such matters as critical mass, median fission energy, etc.

The core is relatively small, consisting primarily of pin-type fuel elements, coolant, and a modest volume of Be if moderator is required to achieve the optimum spectrum. Structure within the core is stainless steel. The core is surrounded by a Th blanket cooled by sodium, and thermalized by Be or by sheathed graphite. An active core 6.8 ft in diameter and 8 ft high can produce 900 Mw thermal, with sodium entering at 770°F and leaving at 1070°F. Under these circumstances the steam conditions are 1800 psia/1000°F/1000°F, with a resulting thermal efficiency of over 40%.

PROBLEM AREAS

Encouraged by the potentialities of this system if the assumed neutron physics data can be confirmed and an optimum practical design achieved, AI is about to undertake a development on this concept under the sponsorship of a group of investor owned electric utilities in the south, which have joined to form a nonprofit organization for this purpose, called the Southwest Atomic Energy Associates.

The major uncertainties clearly lie in the neutron physics data. Analysis and experiments will

Table 2

Fission-Product Absorption Cross Sections

Type of cross section	Symbol	Unit	10^2 ev	10^3 ev	10^4 ev	10^5 ev	10^6 ev
Fission-product absorption	$\bar{\sigma}_p$	Barns per fission	15.4	2.8	0.49	0.10	0.09
U^{235} fission	σ_f	Barns per atom	23	8.5	3.7	1.7	1.3
	$\bar{\sigma}_p/\sigma_f$	—	0.67	0.33	0.13	0.06	0.07

be required to arrive at an optimum neutron spectrum and to determine the neutron economy, effects of fission products, actual variation in η, effective cross section of higher isotopes, etc.

Reactor control problems are accentuated by the low fraction of delayed neutrons from 23 fission products, the short neutron lifetime, and the low effectiveness of conventional absorber control materials. Some of these problems may be eased if the blanket is thermalized.

As with other high fuel-throughput reactors, chemical reprocessing and refabrication will pose substantial problems. In all likelihood remote reprocessing and refabrication will be necessary, and the design will have to include provision for the requirements of the reprocessing system.

It is expected that the development and feasibility investigations will encompass about four years of effort. The first year will be primarily devoted to improving the physics data, preparing a conceptual design for evaluation, and exploring some problems relating to fuel element handling. If these results continue to be encouraging, a critical experiment and component development program will be undertaken. When and if final feasibility is established, it is hoped that a large-scale version of the system will be constructed by one or a group of the members of the SAEA.

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Circulating Homogeneous and Fluid Fuel Thorium Breeding Reactors

R.N. Lyon
Oak Ridge National Laboratory, Oak Ridge, Tennessee

Advantages of Fluid Fuel Reactors

1) No fuel rod damage due to radiation or burn-up.
2) No fuel rod fabrication.
3) No fuel dissolving problems.
4) May permit continuous removal of Xe and other fission product gases.
5) Simple methods of fuel removal and addition.
6) Eliminates need for control rods and associated electronics.
7) Uniform irradiation of fertile material.

Disadvantages

1) External circulation of fission products (external complexity).

Homogeneous reactors have increased internal simplicity without marked increase in external complexity. Two-region systems with fertile blanket, and possibly with some additional fertile material in the core, provide greater neutron economy.

Aqueous homogeneous and molten salt homogeneous reactors are being studied at Oak Ridge National Laboratory. The Pennsylvania Advanced Reactor Program is directed toward development of a single-region aqueous homogeneous system by Westinghouse and the Pennsylvania Power and Light Company.

Since this is a technical meeting, I will concern myself with an outline of some of the technical problems which occur in the utilization of thorium in circulating homogeneous reactors. I will not indulge here in comparing the assumptions which we use to demonstrate that homogeneous reactors will produce cheaper power than heterogeneous reactors with the assumptions made by the advocates of heterogeneous reactors, by which they arrive at exactly the reverse conclusion.

I will first outline the status of the molten salt system. Two fluoride salt systems have been studied as vehicles for thorium and uranium in a reactor, the NaF-ZrF_4 system and the LiF-BeF_2 system. The former was used in the Aircraft Reactor Experiment which was operated in November 1954 with a solid stationary matrix of BeO as a moderator.

In that experiment UF_4 dissolved in the NaF-ZrF_4 mixture was circulated through serpentine tubes of nickel alloy entering at 1200°F and leaving at 1500°F. Sodium cooling was used in the BeO moderator. This experiment proved several important points: The expected high negative temperature coefficient of reactivity was demonstrated; it was found possible to maintain a system of this complexity at a high enough temperature to prevent freezing of the salt; and finally no important increase in corrosion of the nickel alloy tubes occurred as a result of the intense fission density in the core.

The current studies are directed toward a Th breeding commercial power reactor of 600-Mw heat and between 250 and 300-Mw electrical output.

By using a LiF-BeF_2 mixture as the vehicle for UF_4 and ThF_4, sufficient moderation occurs in the fluid itself. The eutectic is at about 50-50 mole % and melts at 680°F, but BeF_2 tends to produce a viscous melt and therefore a compromise is made between high viscosity and power moderation with higher melting point. A BeF_2-LiF mole ratio of 37-63 has been chosen which melts at about 840°F. With 13% additional ThF_4 the melting point is raised to about 980°F. In such a two-region system it is expected that a conversion ratio of 0.6 will be obtained; if a graphite moderator can be used with the salt directly in contact with the graphite, a conversion ratio of about 1.0 is believed to be possible.

Nickel alloys appear to offer adequately low corrosion at temperatures up to 1300°F. Centrifugal pumps will be used, and advantage can be taken of the high melting point to provide freeze

points to supplement stop valves. High pressure is not required in the primary blanket or core system.

Removal of U^{233} from the irradiated blanket melt is to be accomplished by oxidation with full fluorine. After removal of UF_6 by vaporization, the mix is returned to the blanket system.

The aqueous homogeneous thorium breeder uses a slurry of ThO_2 in heavy water at a pressure of about 2000 psi. In a reactor with a UO_2SO_4 solution core the temperature of the blanket is limited at the present time to about 560°F because of the temperature instability of UO_2SO_4 solutions. If, however, some ThO_2 is used in the core as well, this limitation is removed, and the new limitation is the pressure at which it is economical to build a circulating fluid system.

Studies with $Th(NO_2)_4$ have shown that this compound is not stable enough either to temperature or to radiation to be used as a fertile material in a reactor. To this must be added the fact that naturally occurring nitrogen has too high an absorption cross section; thus reconstruction of the nitrate would require very low nitrogen loss and negligible exchange for atmospheric nitrogen.

Slurries of ThO_2 vary widely in properties, a fact which has hampered the formulation of useful generalizations and the development of system components. Some ThO_2 slurries are prohibitively abrasive, while on the other hand clear solutions of ThO_2 have been made which are no more abrasive than water.

Some ThO_2 slurries form hard scale on the inside of pipes and components; some slurries, even at low concentration, become a thick plastic mud; some slurries are converted into a full flowing, rapid settling suspension of relatively large (up to 4 or 5-mil diameter) balls of ThO_2 particles.

Abrasion has qualitatively been identified as being due to large particles, the shape of the particles, and other ions present in the slurry.

The flow properties and the cake and ball forming tendency of ThO_2 slurries have been attributed to the relatively greater influence of the surface properties of very fine ThO_2 particles. It is believed currently that if all the ThO_2 particles were in the range of 0.5 to 1 μ, or possibly larger if the particles were spherical in shape, the surface properties would not exert a strong influence, and the attack rate on stainless steel would not be severe.

Now that the HRT is in operation, studies are being made with the objective of completing a 60-Mw heat two-region aqueous breeder in 1962.

Problems posed by the slurry which require special development, as opposed to the problems of a solution system, are largely associated with sedimentation and abrasion. For example, special flushing is required to keep the bearings in the motor end free of abrasive ThO_2. Pipe taps for pressure measurements are easily plugged or filled with plastic slurry which interferes with accurate indication of pressure. Because of the danger of sedimentation, velocities in all pipes must be held above a given value, even after the pumps have stopped. Sedimentation in the blanket vessel could conceivably produce an increase in reactivity of as much as 20%, and only an emergency dump could prevent a serious increase in core temperature as a result.

Continuous monitoring of the concentration of the circulating slurry, while not essential, is very desirable, as an indication that serious sedimentation has not occurred.

More evidence is needed to support the generally held belief that fission does not seriously increase the corrosion or abrasion of zirconium in contact with a ThO_2 slurry which contains uranium.

And finally, clearer specifications are required for the specific ThO_2 which is to be used, and methods for producing the ThO_2 to meet these specifications must be developed.

The problems of molten salt systems and those of the aqueous homogeneous system do not appear to be particularly comparable, even though the reactors using these two concepts share many advantages over heterogeneous systems. We at Oak Ridge feel that neither system presents obstacles which in the semidarkness of our current ignorance appear to be insurmountable. What is needed now is the development of some real reactors of a practical size from which on the one hand more realistic economic information can be obtained, and on the other hand the technical problems can be evaluated in a realistic fashion.

Thoria Boiling Reactors

J.A. THIE
Argonne National Laboratory, Lemont, Illinois

INTRODUCTION

Current interest in thoria reactors at Argonne stems from reasons originating in several fields of reactor technology:

1) Metallurgy: Ease and cheapness of fuel element fabrication.
2) Chemistry: Inertness of oxides in water.
3) Economics: Utilization of thoria by thermal breeding.
4) Physics: Extension of boiling reactor safety and stability data to nonmetallic fuel.

It was this combination that early in 1956 led to the decision to construct the first thoria boiling reactor, BORAX IV.[1] Since this was essentially a core change in the BORAX III power plant,[2] the resulting facility is characterized by natural circulation, direct cycle, boiling light water.

A longer range thoria boiling reactor program envisions the possible use of thoria and heavy water in EBWR.[3] The breeding potentialities are better realized with heavy water, although the small size of EBWR would not allow their full realization. A preliminary study of this reactor type has shown that by forced circulation boiling it may be possible to achieve power densities as high as 400 kw per liter of coolant. The THUD or ZPR VII critical program at Argonne has as one of its objectives the accumulation of information pertinent to the design of such a core.

The information presented here, however, will be that from BORAX IV in view of the fact that it has already progressed from the design to the operating stage. Design and core fabrication were done during 1956, and criticality took place December 3, 1956. The design philosophy was conservative, the goal being a workable reactor suitable for intermittant experimental operation for a year or so. It therefore should be emphasized that this core is not necessarily an optimized prototype of a large power reactor.

REACTOR DESCRIPTION

Figures 1 and 2 show the reactor building and turbine building respectively. Up to 2 Mw electrical power can be generated in the latter and is disposed of, according to law, in a water rheostat at the extreme left of Figure 2. This power plant has already been adequately described.[2]

The fuel element is shown in Figures 3 and 4. Aluminum with 1 wt % nickel is the clad and structure with lead being the bond. One of the 48 positions is available for optional insertion of a boron steel rod. Fuel element characteristics are listed in Table 1.

Figure 5 shows the core loading used most of the time. The 59 elements contain a total of 16.7 kg U^{235}. Table 2 shows volume fractions.

PHYSICS

The lattice constants from two-group theory appear in Table 3 for two 300-psig conditions, 0 and 10% average voids in the water volume. Comparison of these k_{eff}'s leads to a theoretical void coefficient of about -0.3% reactivity per percent void.

A quantity of interest, though perhaps academic, is the conversion capabilities of the reactor. Because of its small size, this design was never intended to be an efficient converter. The conversion ratio of Table 4 is defined as atoms U^{233} formed per atom U^{235} destroyed. By the end of 1957 the reactor had produced 300 megawatt days of heat.

Figure 6 shows the reactivity loss. The principal effects contributing to the total loss are U^{235} burn-up, U^{233} production, and fission products (other than xenon).

PERFORMANCE

The initial set of experiments concerned itself with obtaining information on the inherent shut-

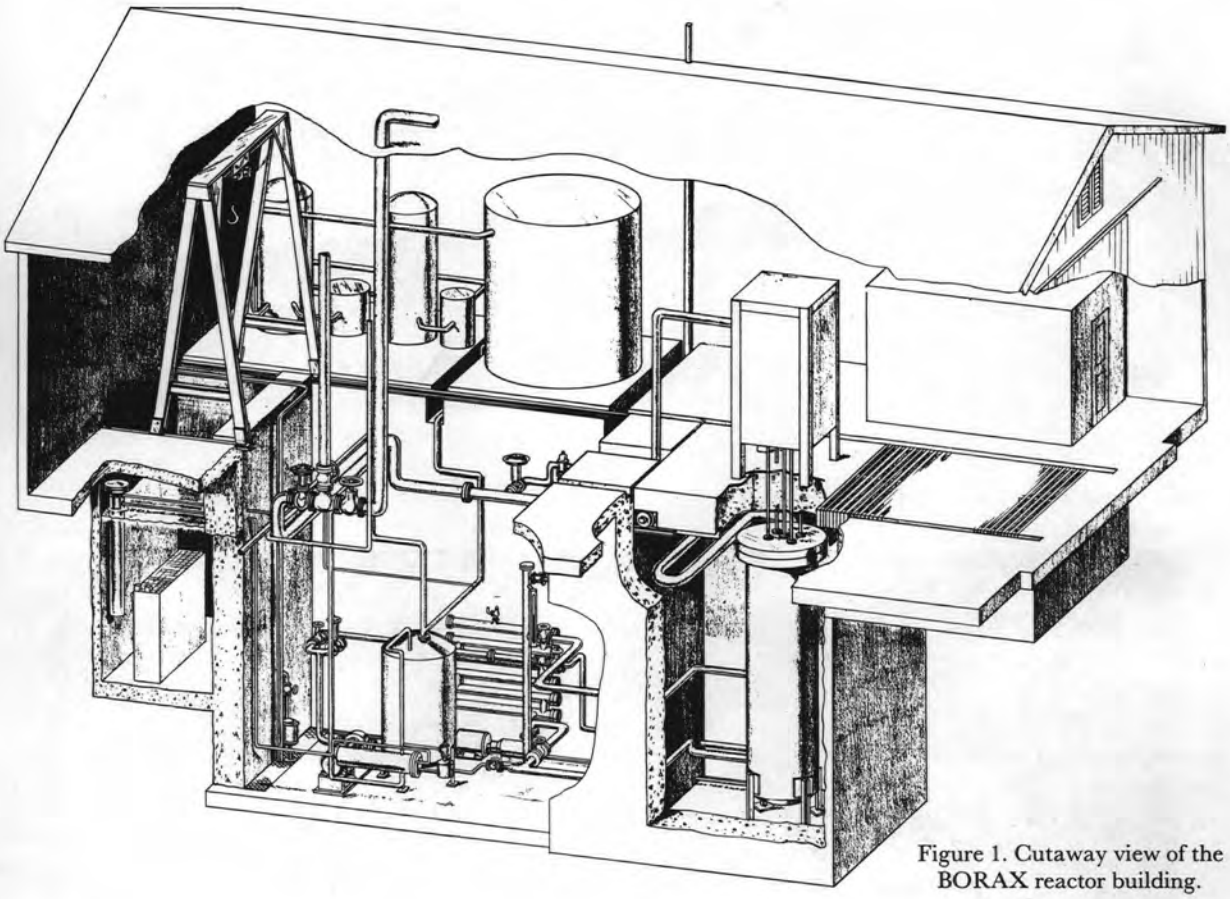

Figure 1. Cutaway view of the BORAX reactor building.

Figure 2. BORAX turbine building with reactor building in the background.

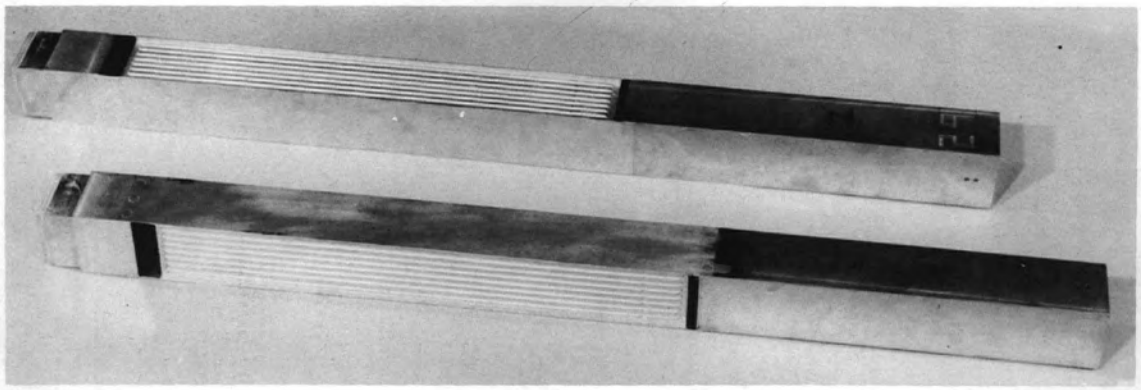

Figure 3. BORAX IV fuel elements.

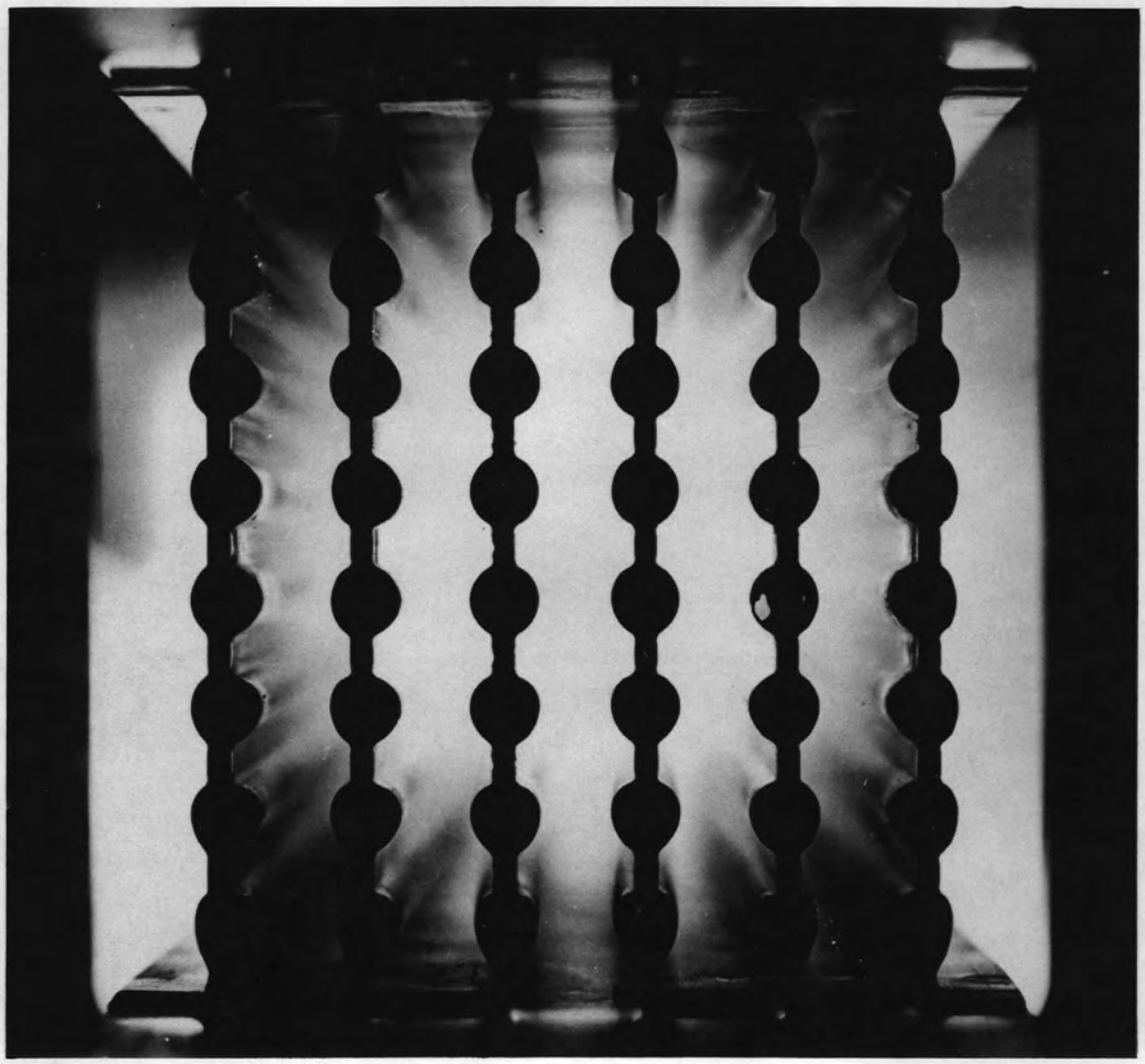

Figure 4. End view of fuel element showing six extruded aluminum plates containing the oxide pellets.

Table 1

Characteristics of the Fuel Element

Over-all length	56.6 in.
Fuel length	24.375 in.
Cross section	3.875×3.828 in.^{2}
Fuel plate spacing	0.604 in.
Oxide diameter	0.230 in.
Weight of $UO_2 + ThO_2$ per assembly	5.425 kg
g U^{235} per g ThO_2	0.0556

Table 2

Volume Fractions at Room Temperature

Al + 1% Ni	0.1750
$ThO_2 + UO_2$	.0903
Pb	.0555
Steel	.0006
Borated steel (2% by weight)	.0004
H_2O	.6782

Table 3

Lattice Constants at 300 psig for Fission Product Free Conditions[4]

% Voids in coolant channels	0	10
η_{235}	2.053	2.053
U^{235} Absorptions + total absorptions	0.683	0.693
p	0.969	0.965
ε (estimated)	1.011	1.011
k_∞	1.374	1.390
t in cm^2	61.47	72.65
L^2 in cm^2	6.10	6.81
Reflector savings in cm	8.79	9.53
B^2 in cm^2 (all control rods out)	0.004016	0.003902
k_{eff} (from preceding)	1.048	1.019
k_{eff} (experimental)	1.058	—

Table 4

Conversion Characteristics

	Initial conversion ratio	Grams U^{233} formed in 300 Mwd
Thermal	0.172	53.9
Resonance	.055	17.2
Total	.227	71.1

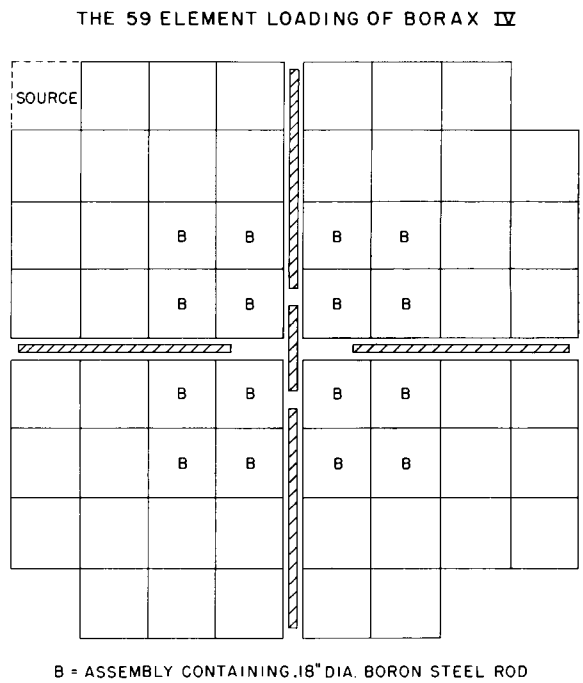

Figure 5. Top view of reactor core.

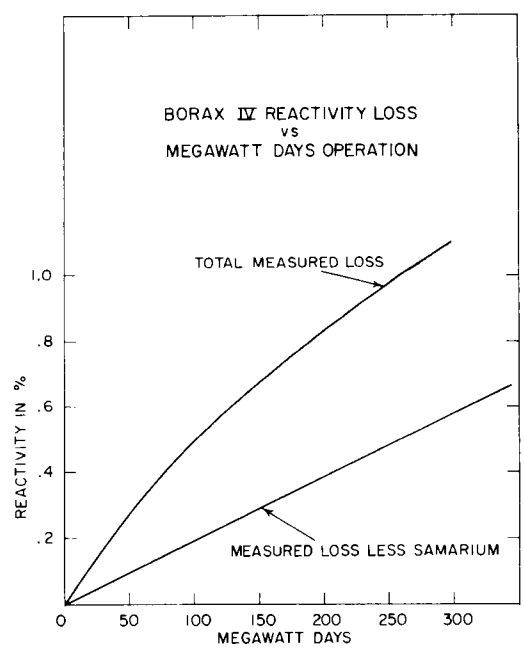

Figure 6. Reactivity loss resulting from reactor operation during 1957.

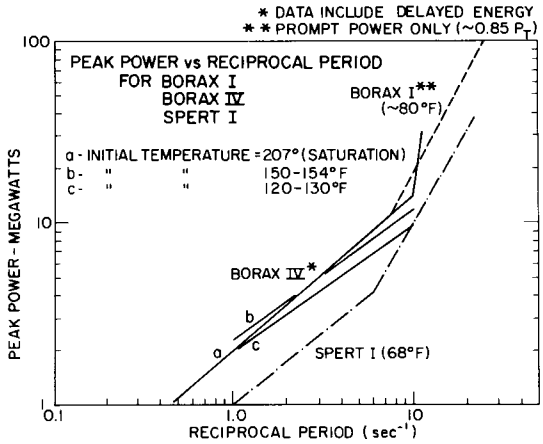

Figure 7. Comparison of BORAX IV's peak power in rod ejection experiments with other reactors.

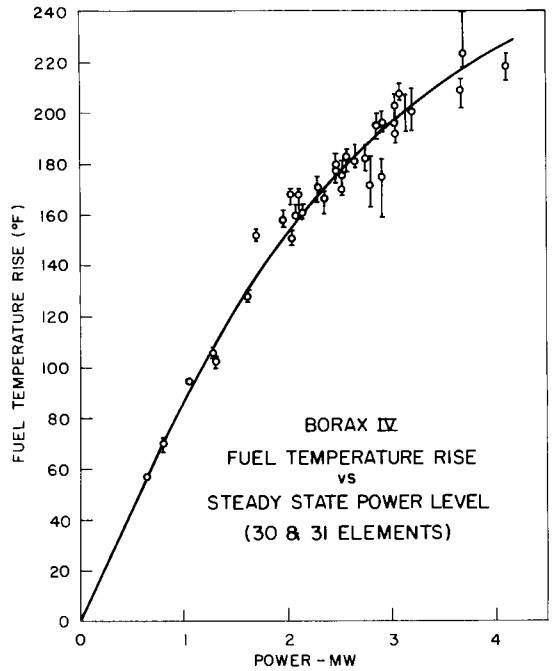

Figure 8. Maximum central fuel temperature during steady boiling.

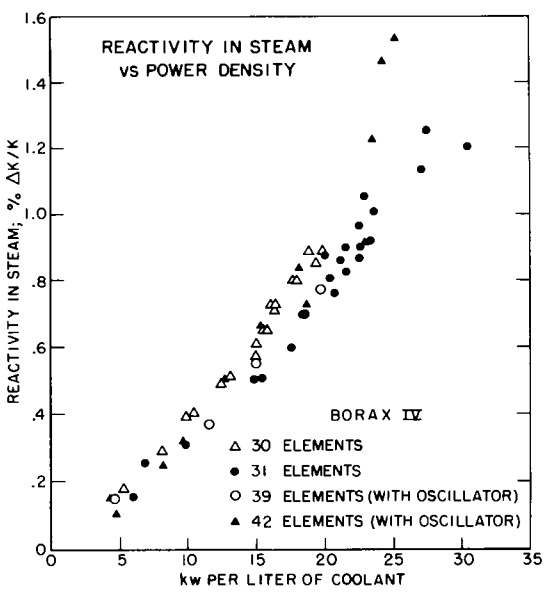

Figure 9. Reactivity in steam voids at atmospheric pressure steady boiling.

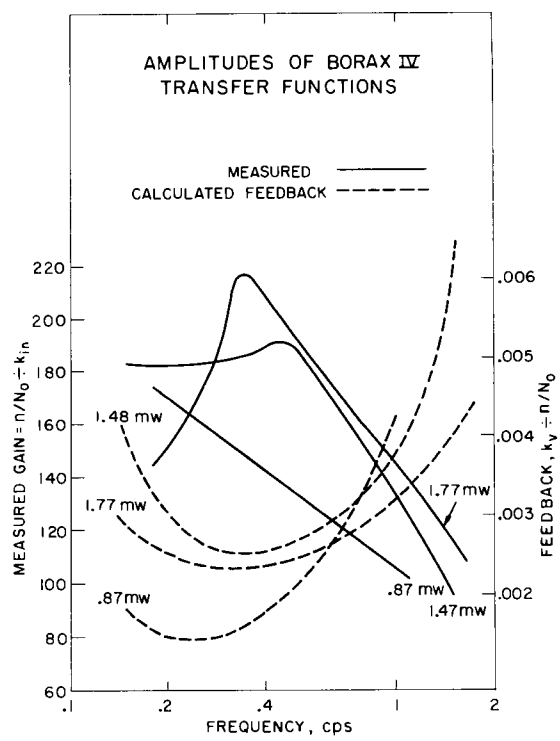

Figure 10. Reactor transfer function at various power levels at atmospheric pressure

down mechanisms coming into play after the rapid ejection of a control rod. Figure 7 shows results of these tests and displays trends comparable to those already found in reactors having much faster fuel. The significant difference of this oxide fuel element and previous BORAX and Spert fuel elements is the former's long thermal time constant, 0.9 sec. This leads to higher fuel temperatures before shutdown of short reactor periods.

Figure 8 shows the internal fuel temperature during steady boiling at atmospheric pressure. A number of these open-vessel boiling experiments were done with cores containing fewer than 59 elements. Another result of such tests is Figure 9, which gives the reactivity compensated by steam voids.

Of major interest on this core was some quantitative measure of its stability, since it was assumed that the long fuel time constant would surely influence the amount of stable power obtainable. For this reason an oscillator control rod was installed for the purpose of measuring the reactor transfer function at atmospheric pressure. Typical results obtained during stable operation are shown in Figure 10. To assist in understanding the mechanism causing the resonance, the feedback transfer function,[5] $kv+n/N_0$, was calculated from the measured transfer functions, G_0 and G, at zero power and at power respectively:

$$G=\frac{G_0}{1-(kv+n/N_0)G_0}.$$

Possibly of more practical interest are the stable power capabilities of this core at 300 psig, since it is well known that stability improves markedly with pressure. The 59-element loading has made 14.4 Mw with 5.5% reactivity in steam voids and corresponding to 36 kw per liter of core or 56.5 kw per liter of coolant.

ACKNOWLEDGMENTS

The BORAX IV reactor experiment was conducted by M. Novick, R. Wallin, O.A. Schulze, and B. Maxon, with the assistance of many from the Idaho Division of Argonne National Laboratory.

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Liquid Metal Fuel Reactor

CLARKE WILLIAMS
Brookhaven National Laboratory, Upton, New York

The U-Bi Liquid Metal Fuel Reactor systems were originally conceived as a Th-U^{233} breeder power reactor system. While various kinds of LMFR's have been studied, such as U^{235} or Pu burners, we believe that in the long run LMFR's will be economically successful only if they convert Th to U^{233} at about a one to one ratio. Consequently a number of studies have been made on various breeder blanket schemes for LMFR. Recently J.R. Powell of the Brookhaven Nuclear Engineering Department has recalculated the breeding potentialities of the four most complete LMFR designs made so far, using the most recent available nuclear data. Taking into account the present information on processing losses, the effect of higher isotopes, fission product poisoning, etc., the value for breeding ratio, while lower than in the original calculation, falls in the allowable range of 0.95 to 1.01. All the above designs are based on separate core and blanket regions. There may be possible advantages to a single-region system in terms of processing costs, although the breeding ratio will definitely be smaller.

Since it was felt that the most essential part of the LMFR system was the core, at least until a satisfactory fuel system were developed, the major effort at BNL has been applied to core problems. Research and development on the blanket is not nearly so far advanced. Now that the fuel is well established, it is possible to seek compatible blanket systems.

The most promising moderator and core structure material is graphite. In order to achieve a good neutron economy for core and blanket, the structure, except for the outside container, must have a low absorption cross section and would be constructed entirely of graphite. It appears impossible in the present state of the art to guarantee that such a structure would separate the blanket completely from the core. Leaky seals, seepage, possible cracking, etc., are always a possibility and therefore a fluid blanket which can be tolerated in small amounts in the fuel or vice versa seems highly desirable. Unfortunately thorium is much less soluble in bismuth than uranium, and as the neutron economy calls for considerably higher ratios of Th to Bi in the blanket than U in the fuel, we had to look at the possibility of developing a dispersion. A dispersion of a thorium-bismuth compound in bismuth appeared most promising and most of the work to date has been on this system.

If thorium is dissolved in Bi at high temperature, around 1000°C, and allowed to precipitate by cooling, it forms platelets which are impossible to circulate. If the Th is reacted with Bi at temperatures around 500° to 600°C, it exfoliates in roughly equiaxed particles of $ThBi_2$ of around 50 μ maximum dimensions. Up to 10 wt % Th (25 volume % $ThBi_2$), the dispersion is quite fluid with a viscosity of about three times that of liquid Bi. Such a dispersion has a settling velocity of about ¾ mm/sec and hence must be circulated. However the circulating velocity required for heat removal is much greater than that needed to keep the dispersion in suspension and this should be no problem. The metallic compound is completely wetted at all times by the Bi and it is readily resuspended at any time.

As $ThBi_2$ is soluble in Bi at all temperatures down to the freezing point, it was necessary to study the rate of growth and possible sintering of the particles. Under thermal cycling between 350° and 550°C, a greater ΔT than anticipated in the reactor designs, the particles increased from 50 μ to 100 μ in 500 hr and then showed no appreciable growth over the next 1000 hr. At more rapid cycling time the size reached was somewhat greater. However, in neither case were any platelets observed. As the processing cycle reduces the size of the particle to 50 μ, this should be sufficient. However, addition of Te reduces the growth rate markedly, and could be used if required.

At the operating temperature 99% of the thorium and hence the bred Pa and U^{233} are in the

solid state. The bred products diffuse out to the liquid extremely slowly. However, by raising the temperature of the dispersion to around 1000°C, they can be put in solution. On cooling about one half go back with the Th to the solid state. Separating the liquid Bi from the solids would separate an appreciable fraction of the bred materials from the Th. They can be removed by suitable oxidation or slagging processes for use in the fuel. While the Th originally precipitates in the form of small platelets, if quenched rapidly and then held at around 800° to 900°C, the platelets thicken and approach equiaxed shape. Preliminary investigations indicate that ultrasonic agitation may be applied to prevent the formation of platelets and to break up large particles.

The problem of material corrosion and containment appears to be very similar to that for the fuel. However, much more engineering development has to be done to determine whether or not this dispersion can be used in the LMFR. We are now constructing several pumped $ThBi_2$ in Bi loops comparable to those used in our fuel testing, and it is hoped that in a year or two we will have the same confidence in this blanket system that now exists for the fuel system.

Probably the next best blanket system to the $ThBi_2$ in Bi is the suspension of ThO_2 in Bi. The ThO_2-Bi slurry appears compatible with graphite and other materials in the reactor. The ThO_2 is wetted by the liquid if some Th is in solution in the Bi. This allows sufficient Th to be suspended in the fluid (27 volume % ThO_2). The separation of the ThO_2 from the liquid for processing could be achieved by evaporation of the Bi or by mechanical means. The oxide can be processed by Thorex. We are also investigating some pyroprocessing methods. However, at present processing costs for the blanket based on present methods appear to be excessively high. ThO_2 might have advantages in a single-region reactor where the lower breeding ratio and somewhat greater fuel inventory inherent in the design might be offset by not requiring any processing of the mixture for anything other than some of the fission products.

We are also constructing a pumped slurry loop of several gal/min capacity for circulating the oxide slurry as well as the intermetallic compound.

Other liquid metal blankets might be feasible, such as thorium fluoride or thorium carbide, or possibly other thorium compounds, suspended in Bi. The thorium-magnesium eutectic is another possibility. If we were forced further afield, solids, pebble beds, and other gas-cooled blankets are conceivable but do not at the moment appear very attractive. However, as indicated earlier, the most promising attack is the $ThBi_2$ in Bi dispersion. We intend to push this system to the utmost, with a greatly increased emphasis on the blanket than in the past. And we are convinced that in the long run the many advantages of the Liquid Metal Fuel Reactor system with built-in processing will prove to be the most economical way of burning thorium.

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The Consolidated Edison Thorium Reactor

FRANK WARD
The Babcock & Wilcox Company, New York, New York

INTRODUCTION

The Consolidated Edison Company of New York is erecting a nuclear steam electric generating station on the Hudson River 24 miles north of New York City. The station will have an ultimate electrical capability of 275 Mw, 163 Mw from the reactor and 112 Mw from two oil-fired superheaters.

The Atomic Energy Commission issued a construction permit to the Consolidated Edison Company on May 4, 1956. At this time, January 1958, the design of both the conventional and nuclear portions of the station is progressing rapidly and Consolidated Edison and Babcock & Wilcox Co. have ordered most of the major reactor and electric station equipment. The Vitro Engineering Co. is actively rendering design and architectural services on the project.

A broad research and development program on fuel materials and fuel elements, in-pile loop irradiations, critical experiments, and plant component testing is under way in the laboratories of The Babcock & Wilcox Co. and its subcontractors.

Initial site clearing and excavation work at Indian Point started in December 1956. It is expected that the core will be installed in the reactor in the fall of 1960 and initial critical operations will be attained in December 1960.

PHYSICAL LAYOUT OF STATION

The general layout of the station is shown in Figure 1 and follows the general arrangement used for the company's conventional steam plants, with the nuclear reactor replacing the conventional boiler. The arrangement provides for the addition of future generating units while still permitting economical use of common items such as the turbine room crane, control room, and general service facilities.

STEAM THERMAL CYCLE

The station heat balance diagram is shown in Figure 2. To develop an ultimate electrical output of 275 Mw, 2,200,000 pounds of steam per hour generated in the boilers at 420 psia and heated to 1000°F in two half-size superheaters will be introduced into the turbine generator at 370 psia and will be exhausted to the condenser at a pressure of 1.5 inches of mercury and a temperature of 84°F.

Condensate will be returned to the boilers after being heated in a string of three closed heaters, an economizer and a high-pressure deaerator. The condensate flowing through the three closed heaters and the deaerator is heated by bleed stream from the turbine and receives additional heat from the economizer which in turn is heated by combustion gases passing from the superheaters to the stack. From the deaerator, the boiler feed pumps will return the condensate to the boilers of the nuclear steam generator at a temperature of 332°F.

The heat rate of the steam cycle, exclusive of reactor efficiency, is 10,700 Btu/kwh.

DESCRIPTION OF NUCLEAR STEAM GENERATOR

The nuclear steam generator comprises chiefly the reactor and its heat transfer system containing valves, piping, pumps, boilers, and pressurizer; reactor safety and control systems; safety containment vessel and auxiliary equipment; primary and biological shielding; reactor service facilities containing laboratories and auxiliary equipment; fuel element charging, discharging, and storage facilities; waste disposal facilities for collection, storage, and disposal of solid, liquid, and gaseous wastes; coolant treatment and make-up systems.

An artist's conception of the nuclear steam generator is shown in Figure 3, and the principal reactor design and performance characteristics are shown in Table 1.

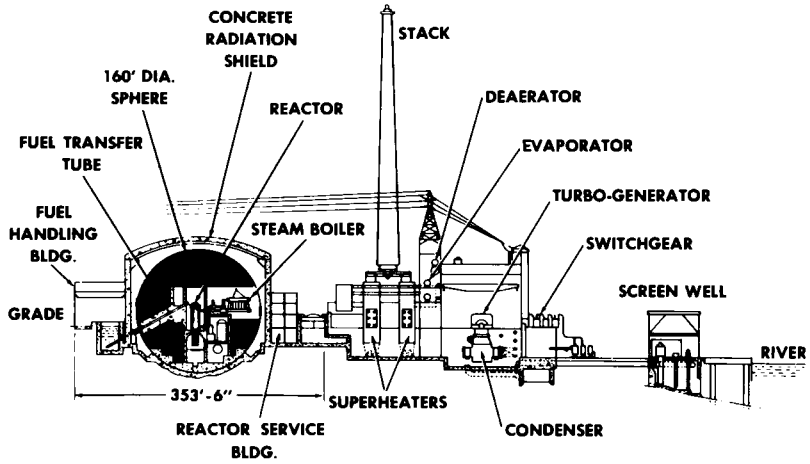


Figure 1. Elevation of Indian Point station.

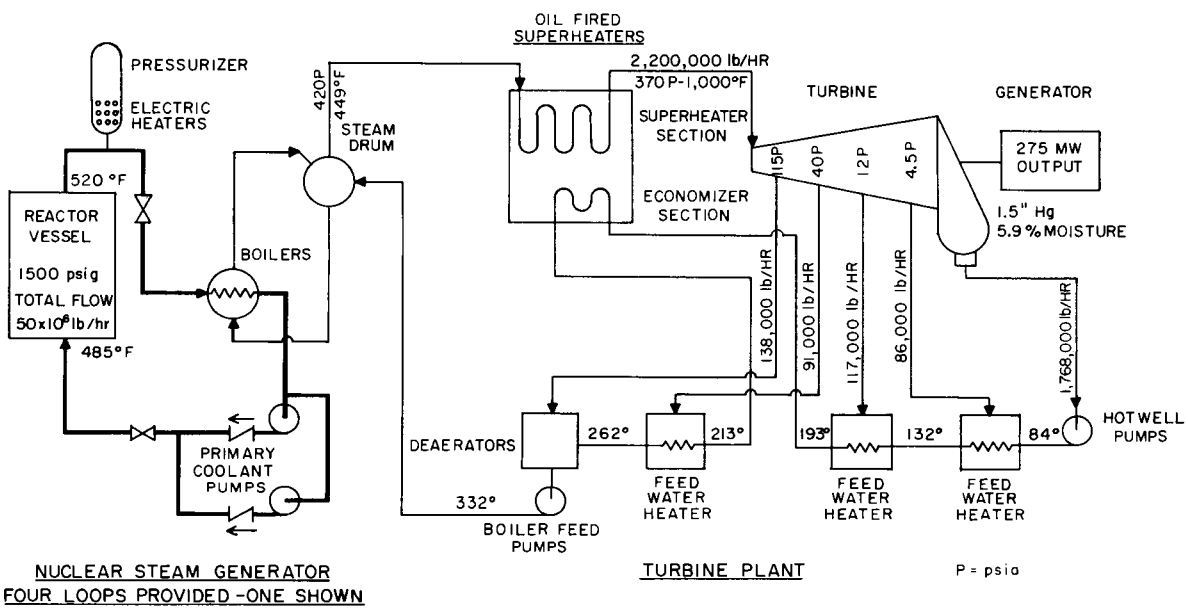


Figure 2. Indian Point heat balance, 275-Mw nuclear plant.

The reactor core is an internal thorium converter. It is cooled, moderated and reflected by pressurized light water and operates in the thermal neutron range. The reactor utilizes fully enriched uranium as the base fuel in the form of uranium oxide (urania) and utilizes thorium oxide (thoria) as the fertile material. The two materials are homogeneously mixed and incorporated in pin or rod type fuel elements clad with stainless steel.

Thoria was chosen as the fertile material on the basis of 1) its favorable ability to supplement the base fuel by the production of fissionable U^{233}, 2) its radiation stability, 3) its high resistance to corrosion in high-temperature water, and 4) its compatability with UO_2 and stainless steel.

The reactor operates at 1500 psia and is cooled by the circulation of water in four coolant loops operating in parallel. 126,000 gpm of coolant enter the reactor at 481°F and leave at 510°F to transfer the heat of the nominal reactor plant rating of 500 Mw. This results in the generation of 1,890,000 lb/hr of saturated steam at 405 psig and 449°F.

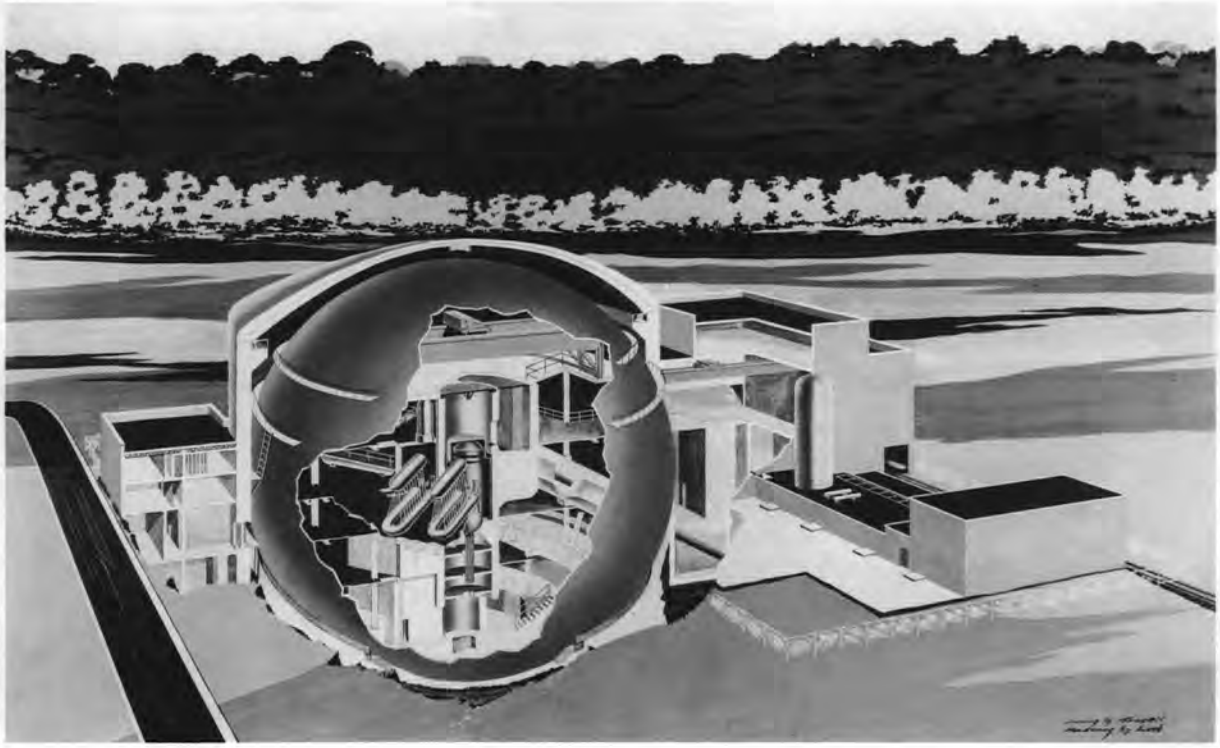


Figure 3. Artist's conception of nuclear steam generator.

The reactor and its auxiliaries are being designed to have an ultimate thermal capability of 585 Mw, which will produce 2,200,000 lb/hr of steam at the above conditions and produce the ultimate station design capability of 275 Mw of electricity.

The first core, composed of 120 fuel elements, will have an expected life of approximately 600 full power days.

General Layout and Arrangement

Figures 4 and 5 show the general layout and arrangement of the five principal portions of the nuclear steam generator: 1) safety containment vessel, 2) radiation shielding, 3) reactor service building, 4) fuel handling building, and 5) waste disposal building.

1) The ***Safety Containment Vessel*** is provided to eliminate the possibility of dispersing radioactive vapors over the area surrounding the station. The vessel is designed to withstand a maximum internal pressure of about 27.5 psig and a maximum external pressure differential of 1.0 psi. The maximum internal pressure is based upon an assumed maximum credible incident consisting of the instantaneous release and expansion of the entire primary system water (237,400 lb) and the expansion of the secondary water from one primary coolant system boiler (22,761 lb). The maximum external pressure differential is assumed to take into account combined increases in barometric pressures and decreases in ambient temperatures within the vessel.

The vessel is designed in accordance with ASME Boiler and Pressure Vessel Code, Section VIII and all existing applicable code cases. The vessel requires ASME Code stamping and will be given a pneumatic test in accordance with paragraph UG-100 of the ASME Unfired Pressure Vessel Code.

The vessel is a 160-ft-diameter sphere and houses the nuclear reactor proper and all the high-pressure, high-temperature coolant and auxiliary system equipment. The sphere is constructed of carbon steel plate approximately ⅞ in. thick. Suitable penetrations for electrical, steam, instrument, water, and ventilation lines will be provided, as well as a 40-ton gantry crane for handling equipment.

The selection of equipment for installation inside the sphere and the shielding requirements for this equipment have been based on the criterion that

Table 1

Station and Reactor Plant Design Parameters

Reactor type	Internal thorium converter	
Neutron energy	Thermal	
Station electrical output, Mw	275 (236)	
Reactor heat output, Mw	585 (500)	
Steam flow, lb/hr	2.2×10^6 (1.9×10^6)	
Steam conditions:		
from reactor	405 psig, 449°F	
from superheaters	355 psig, 1000°F	
Reactor primary coolant	Pressurized light water	
Temperature, °F	(481.5 in), (510 out)	
Flow, gpm	126,000	
Pressure drop, psi	41 core, 116 total	
Pressures, psia	1800 design, 1500 operating	
Coolant loops	Four 304 SS loops 2 pumps/loop; 1 boiler/loop	
Reactor core		
Life full power days	600	
Loading, kg	Initial	Final
ThO_2	17,400	17,100
U^{235} (f.e. oxide)	850 (1035)	517 (630)
U^{233}	0	146
Over-all conversion ratio	0.55	
Power density, kw/l	66	
Metal/water ratio	1.12	
Core size, ft	6 d×8 h	
Av. heat flux, Btu/hr-ft.^{2}	112,000	
Fuel elements		
Total	120	
Pins/element	1236	
Pin clad	20 mils SS	
Pin o.d., in.	0.3125	
Pin length, in.	16	

(Based on first core nominal rating of 500 Mw)

there will be no access into the vessel during normal plant operation.

The vessel will have cooling, ventilating, spray, and pressure control auxiliary systems.

2) The ***Radiation Shielding*** consists of a reactor primary shield, a biological shield (part of which serves also as accident shield protection), and localized shielding of other sources throughout the plant.

The primary shield consists of an annulus of light water surrounding the reactor pressure vessel. The thickness of this water layer is 49 in. and is sufficient to reduce the neutron flux from 10^{10} to less than 10^4 neutrons/cm^2-sec. The primary shield serves also to attenuate the core gamma spectrum during operation and the fission product decay gamma flux after shutdown. During refueling operations the water level in the primary shield tank is raised to obtain permissible radiation levels from the fission product decay gamma flux.

Outside the primary shield tank of the reactor, there is a small air annulus and a 3.0-ft-thick ordinary concrete shield. This concrete serves as the inner biological shield, reducing the gamma dose rate during reactor operation to approximately 700 mr/hr at its surface and further attenuating the neutron flux to insignificant levels. With the reactor shut down, this inner shield serves to reduce the core decay gamma dose rate to levels low enough to permit safe personnel entry. Other parts of the biological shield within the containment include a 2.0-ft slab concrete floor at an elevation of 108 ft situated above the reactor and primary loops, and a concrete walled, water-filled storage pool for reactor internals. The slab floor shield is primarily to protect operating personnel from corrosion and fission product activity in the primary loop during fuel transfer and similar operations.

The concrete wall surrounding the containment sphere is the outer biological shield. It is designed to attenuate further the core gamma dose during full power operation so that, together with the dose rate from $O^{16}(n,p)N^{16}$ water activation gamma from the primary loops, the total dose rate is less than 0.75 mrem/hr at the outer shield surface. The outer shield wall is also designed to offer adequate protection to personnel in the Fuel Handling Building, Reactor Service Building, and other nearby locations following the postulated maximum credible accident, in which 25% of the inert gases and halogen fission products and 1/16 of the remaining fission products are released into the containment vessel. The maximum dose adjacent to the outer shield surface following this incident in the first 40-hr work week is less than 100 mr.

Concrete and lead shielding about the spent fuel transfer tubes and localized shielding for such items as decay heat coolers, primary loop sampling coolers, primary vent system separators, filter units, and deionizers are also included in the plant shield design for the protection of operating personnel.

Miscellaneous shielding in the reactor system would include the spent fuel storage pools where

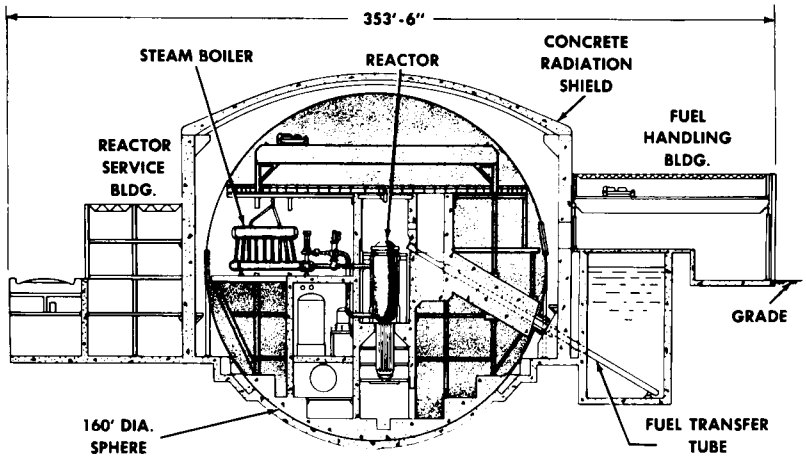


Figure 4. Elevation of nuclear steam generator.

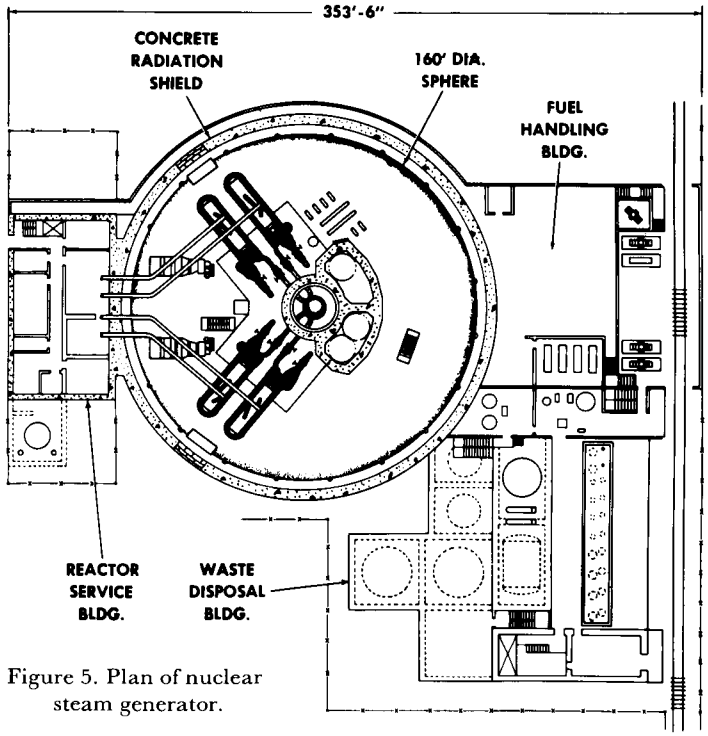


Figure 5. Plan of nuclear steam generator.

water depth is sufficient to attenuate fission decay product gammas, and spent fuel shipping casks where the lead thicknesses are sized to permit shipment at the end of the storage period in accordance with ICC regulations.

The shield wall outside the containment sphere is constructed of ordinary concrete about 6.0 ft thick up to 135 ft above grade, and the completely self-supported trussed concrete roof is about 3.0 ft thick.

The space between this wall and the outside of the containment vessel will be ventilated to the superheater stack.

3) The ***Reactor Service Building*** is immediately adjacent to the west side of the external radiation shield wall. This 4-story structure contains offices, laboratories, counting rooms, and certain auxiliary systems equipment.

4) The ***Fuel Handling Building*** is immediately adjacent to the east side of the external radiation

shield wall. This structure is used to store, handle, and ship both new and used fuel elements, control rod elements, etc. Provisions are also made for inspection and maintenance of the reactor vessel closure and internal components and for maintenance and decontamination of other reactor equipment and apparatus removed from the containment vessel.

The canal is sized to provide for the cooling and storage of 2.4 spent cores.

5) The ***Waste Disposal Building*** is immediately adjacent to and south of the Fuel Handling Building. This structure houses the equipment for the Chemical Process System. The functions of this system are 1) to collect, contain and treat the various solid, liquid and gaseous wastes from the nuclear reactor plant and its auxiliary systems; 2) to provide decontaminated waste water for reuse in the primary coolant system; 3) to reduce the rate of radioactivity build-up from the deposition of long-lived isotopes on primary system surfaces; 4) to maintain the concentration of soluble corrosion products below the point where their activity would interfere with access to the plant after shutdown; 5) to maintain primary coolant water impurities of less than one ppm total solids to prevent radioactivity build-up and to minimize fouling of heat transfer surfaces; 6) to supply primary coolant water of sufficient quality for various apparatus mechanical seals such as the control rod drives and decay heat cooling pumps; 7) to provide a means of reducing the activity of the primary coolant water following limited fuel element failures.

An estimated average daily rate of wastes to be processed is as follows: 22,500 lb liquid, 50 lb solid, and 50 scfh gaseous.

Reactor Description

1) ***Reactor Core and Fuel Elements*** - The Consolidated Edison reactor is fueled with a mixture of thorium oxide and fully enriched uranium oxide contained in stainless steel tubes. The active portion of the reactor core approximates a right circular cylinder 8.0 ft in height and 6.5 ft in mean diameter. It is composed of 120 box-type fuel elements, each approximately 6 in. sq. (see Figure 6).

Full load operating conditions to deliver the nominal heat rating of 500 Mw are fulfilled by the circulation of 50×10^6 lb/hr (126,000 gpm) of water

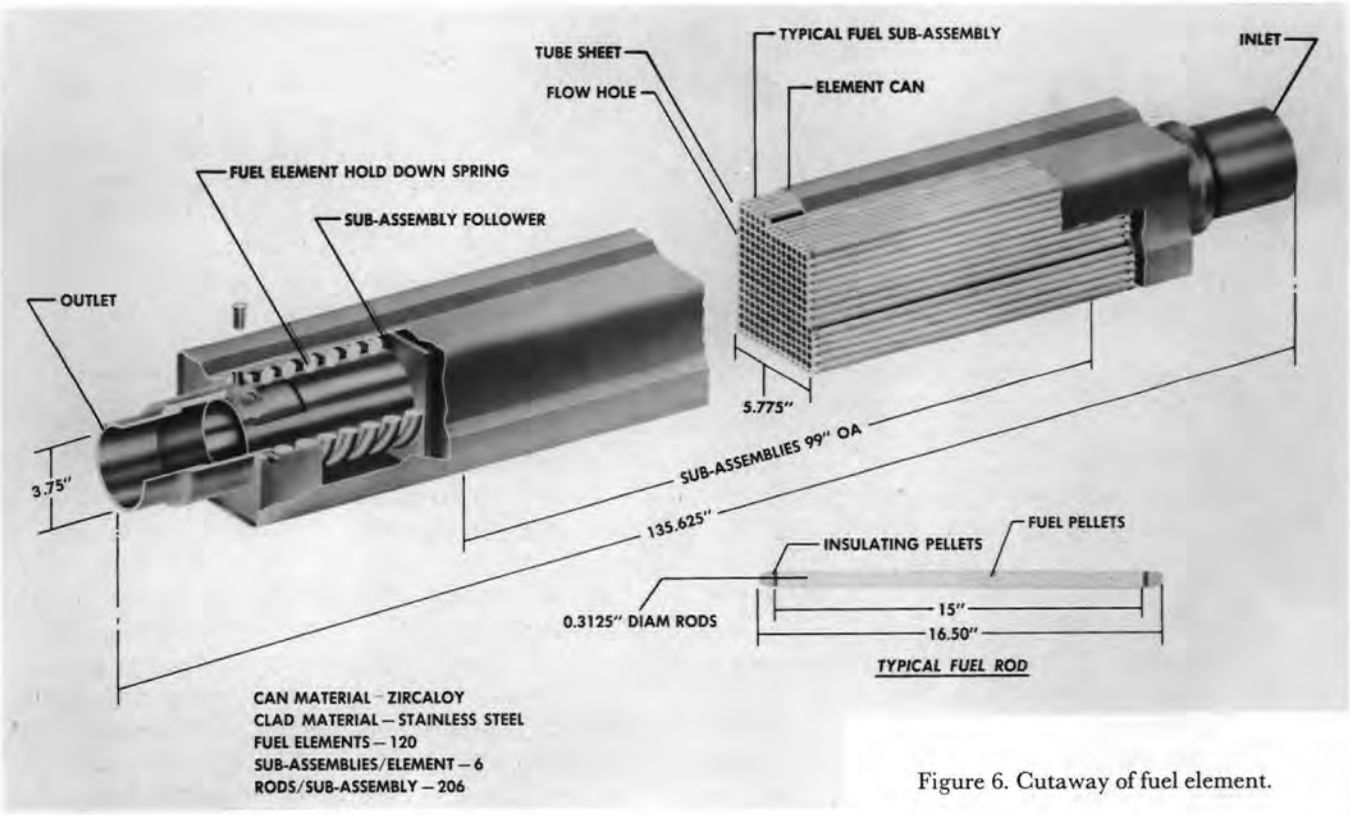
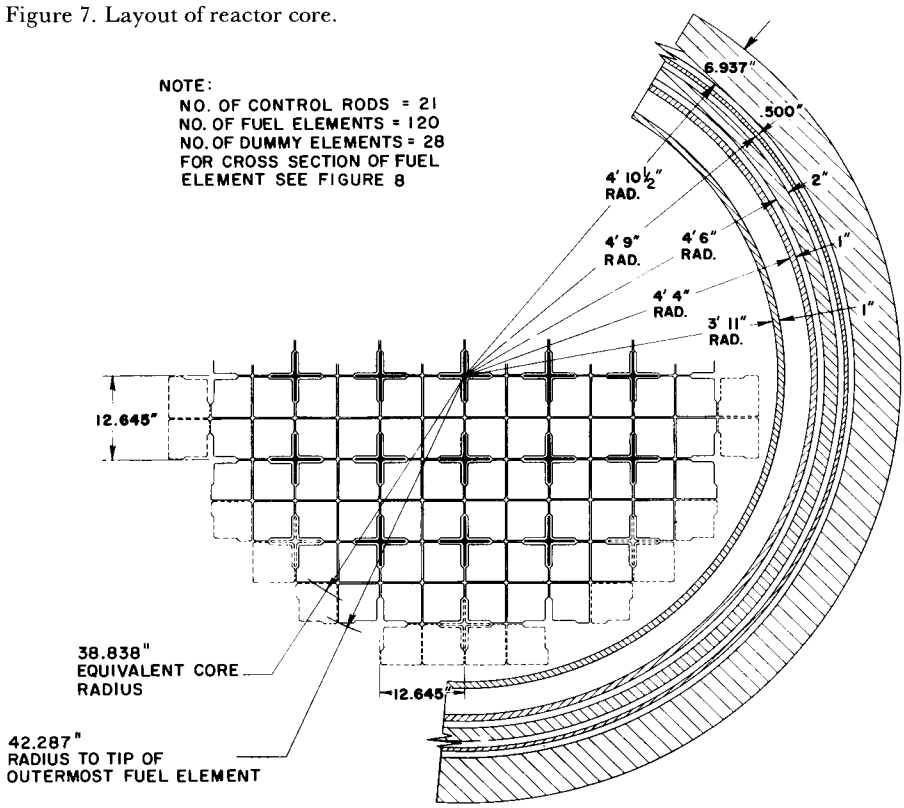


Figure 6. Cutaway of fuel element.

Figure 7. Layout of reactor core.



at a pressure of 1500 psia; average reactor water temperature at the inlet is 481°F and at the outlet is 510°F. Approximately 85% of the total one-pass reactor flow is available for heat transfer from the fuel elements. The remaining flow is diverted past the control rods and through the reflector and thermal shields. A conical shaped lower plenum baffle with properly sized orifices insures correct flow distribution to the core section and thermal shields. The upper plenum baffle is also orificed for the discharge of the coolant from the core to the reactor outlet nozzles.

The core is designed so that a structural failure will not occur as a result of any normal operational procedure. Because of the high specific power of this reactor, close tolerances must be placed on the manufacture of the fuel elements, control rods, and reactor vessel structural and support internals.

The composition of the core is determined by the requirements of heat transfer, structural integrity, excess reactivity for adequate life, and the need for an adequate negative temperature coefficient. Approximately 72% of the core volume is required for coolant flow and the inventory of approximately 18,000 kilograms of uranium oxide-thorium oxide mixture. The remaining core volume is stainless steel and Zircaloy-2.

Between the core and the pressure vessel, four alternate layers of stainless steel and water serve as a neutron reflector, and as thermal shields to reduce the effects of neutron bombardment and gamma radiation on the pressure vessel walls. The thermal shields are open-ended cylinders arranged between the core and the pressure vessel so as to form a series of concentric cylinders.

The core layout showing placement of fuel elements, thermal shields, and reactor vessel wall is shown in Figure 7. The core is designed in such a manner that the total number of fuel elements may be increased from 120 to 148 should this prove to be desirable in the future. This would only necessitate replacing the 28 dummy elements by active fuel elements.

The fuel elements are 136⅝-in. over-all length with a net active fuel height of 90 in. The fuel region of each element consists of six fuel subassemblies each 16.5 in. long and approximately 6 in.^{2} in cross section. These subassemblies are stacked end-to-end in a Zircaloy-2 can, positioned transversely by dowels and loaded axially by a spring.

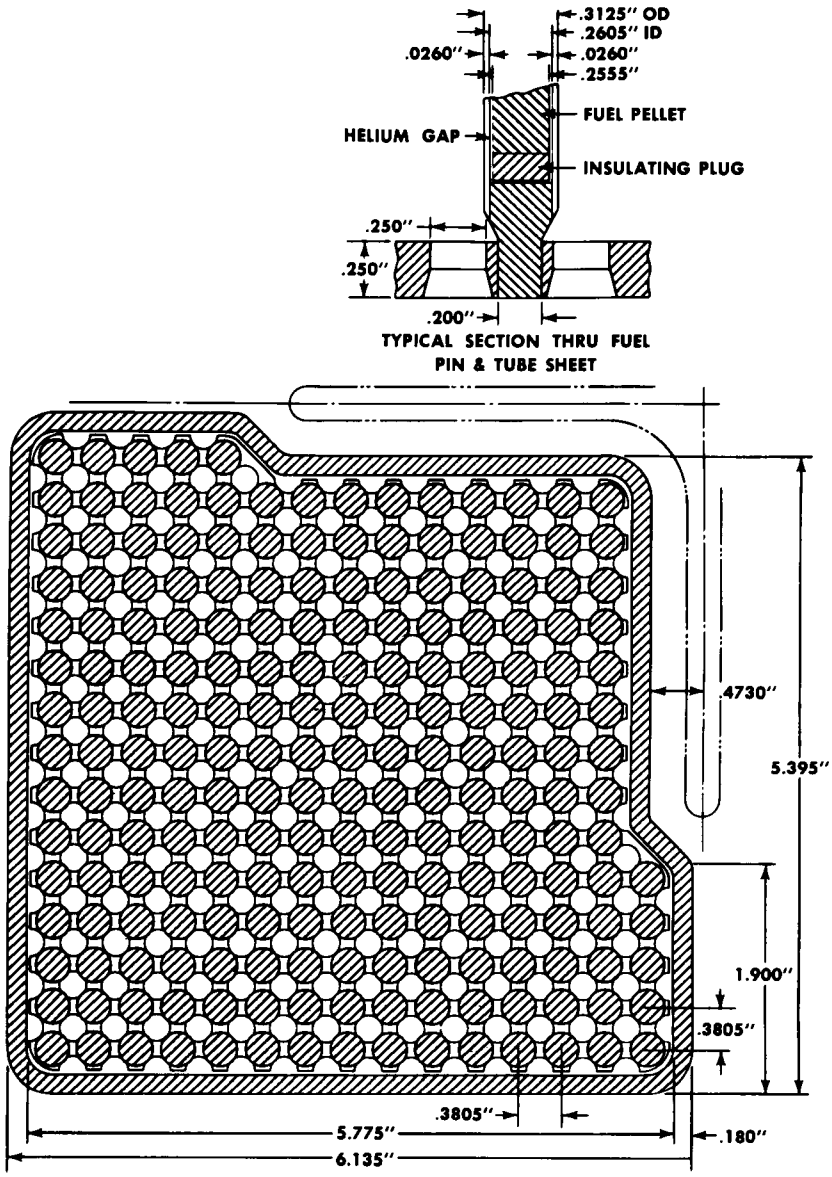


Figure 8. Cross section of fuel element.

Each subassembly consists of 206 fuel pins arranged in a square lattice with a pitch of 0.3805 in. The fuel pins consist of 0.3125-in.-o.d. $\times$0.020-in.-thick stainless steel tubes, which are loaded with fuel pellets. A cross section through the fuel element is shown in Figure 8.

The fuel is a mixture of UO_2 and ThO_2 (approximately 5.3 wt % UO_2) in the form of high density pellets of close dimensional tolerances. When the fuel pellets are loaded into the tubes, they form a fuel column 15 in. long. Sufficient longitudinal and transverse clearance is provided between the pellets and cladding to allow for assembly and differential expansion.

The fuel element can is made of Zircaloy-2 sheet, 0.180 in. thick, formed to the same contour as the tube sheets. The formed sides are welded along longitudinal seams to make a can 115⅜ in. long.

End adapters are made of type 304 SS and the bottom adapter is riveted to the can. The top adapter is held in the can by means of a spring loaded bayonet lock. The top adapter may be

easily removed for remote refueling without injury to the subassemblies or can.

The design permits the use of an Inconel-X spring to lock in the top end adapter, provide fuel element hold down against hydraulic forces, and allow for differential expansion between the subassemblies and can.

The arrangement of the 21 control rods in the reactor core is indicated in Figure 7. The cruciform shaped rods travel through slots which are provided by offsets in adjacent fuel element cans. The over-all width of each rod is 7.5 in. with a thickness of 5/16 in. These rods are attached to their drive mechanisms through control rod followers of Zircaloy-2 which prevent the formation of water spaces in the reactor when the control rods are withdrawn. Rod guides are provided for the control and follower rods above and below the core grid plate. To minimize coolant leakage flow, stainless steel dummy rods are placed in those cruciform slots at the outer edge of the core which are not occupied by control rods.

The selection of control rod material will be based on the results of the critical experiments being conducted at the Babcock & Wilcox Critical Experiment Facility. Three materials are at present being considered: boron stainless steel, cadmium-indium-silver alloy, and hafnium. Twenty rods will be "black" to thermal neutrons and the remaining rod, the regulating rod, will be "grey."

The control rod drives, a combination electromechanical-hydraulic type, are being designed, tested, and manufactured by the General Electric Company. These mechanisms are similar in design and operation to the control rod drive mechanisms at present being used in the General Electric Boiling Water Reactor at the Vallecitos Laboratory. The regulating rod drive mechanism operates in a manner similar to the 20 shim drive mechanisms, but minor design changes are incorporated to improve the operating speed and efficiency. The control rod drives are mounted in the vertical position directly below the pressure vessel. The control rod extension shafts penetrate the bottom hemispherical head of the pressure vessel through the control rod nozzles. Leakage from the primary system in minimized by the use of buffer seals for the control rod extension shafts. A shut-off valve is provided to seal positively the control rod penetration when the rod is moved to the maximum downward position. The drive mechanism enclosure is designed to contain the design pressure (1800 psia) of the primary system. Should a failure develop in the buffer seal and shut-off valve, isolation valves in the hydraulic supply and drain lines are closed and the mechanism enclosure is pressurized with primary water. Control rod position is indicated continuously on the reactor control panel.

Major thermodynamic characteristics of the CETR core are determined by the requirements of heat transfer, hydraulics, mechanical and optimum nuclear performance for steady state operation.

A comprehensive analysis has been made which includes temperature distributions, local boiling and two-phase flow pressure drops, and burn-out characteristics for the hot channel. Burn-out characteristics of the hot channel limit the maximum safe power at which the reactor can operate. In this assembly, burn-out occurs in the two-phase flow region where flow is reduced, due to two-phase pressure drop considerations, as heat flux increases. At sufficiently high power, this combination of increased heat flux and decreased flow can cause a failure of the heat transfer mechanism resulting in burn-out.

Existing data and correlations resulting from burn-out tests performed at various universities, national laboratories, and other AEC sponsored facilities have been used in determining the burn-out heat flux. Scattering of experimental data, with respect to both local boiling and boiling with net steam generation, makes it difficult to predict the exact burn-out heat flux. Based on the most conservative data available and with the most adverse combination of all power distribution and manufacturing tolerance factors, it has been determined that burn-out will not occur before 131% full power is attained.

The following thermal design criteria have been established for the CETR core:

a) No local boiling in a nominal channel at 100% power.
b) No net boiling in a nominal channel at 125% power.
c) The maximum fuel central temperature must not exceed the melting temperature (5800°F) at 125% power in the hottest pin.

These criteria limit the bulk water temperature, clad surface temperature, and internal fuel pin temperature.

A comprehensive fuel element testing and development program is under way at The Babcock & Wilcox Company Alliance Research Laboratories to verify mathematical analyses and to proof test design features which are not amenable to calculation. These tests will be conducted to insure a safe, practical fuel element for any foreseeable condition which may arise during reactor operation.

2) ***Nuclear Design*** – As mentioned previously in this paper, the reactor is classed as a pressurized water, internal thorium converter. The fertile material, thorium, in the form of the oxide, does not undergo appreciable fission. It absorbs neutrons and subsequently decays to U^{233} which does fission *in situ* to produce heat energy. During the estimated core life of 600 full power days, approximately 49 kg U^{233} are burned as supplementary fuel and approximately 146 kg U^{233} and 15 kg Pa^{233} remain in the spent core.

The initial core contains about 17,400 kg thorium oxide and about 1035 kg uranium-235 oxide. At the end of life, the spent core will contain approximately 17,100 kg thorium oxide and 630 kg uranium-235 oxide.

The critical mass of the cold clean core has been calculated to be 490 kg uranium-235 oxide. In addition to this, enough excess fuel must be placed in the core to provide reactivity for temperature rise, build-up of neutron absorbing fission products, burn-out of fuel, and other miscellaneous effects. The sum total of these effects dictates the initial fuel loading of 1035 kg.

The total excess reactivity for operation of the reactor over the reference life is calculated to be of the order or 21.2%. In addition to the 20 shim control rods, it will be necessary to incorporate into the core a burnable poison, such as boron-10, and to incorporate in the primary coolant a soluble poison, such as boric acid.

The estimated over-all conversion ratio is 0.55, and the core burn-up approximately 17,200 Mwd/ton of thoria.

Since the reference core is somewhat developmental in nature, the principal nuclear characteristics require experimental verification. An extensive experimental physics program has been undertaken in The Babcock & Wilcox Company Critical Experiment Laboratory in Lynchburg. The experimental program has as its principal objective the precise measurements of core nuclear parameters such as critical mass, worth of control rods, temperature coefficient of reactivity, etc., so as to allow an accurate prediction of the effective multiplication prior to manufacture of the first core.

An important part of the core experimental work, namely the measurement of the effective thorium resonance integral and the thorium Doppler coefficient, has been completed at the Pennsylvania State University research reactor.

Primary Coolant System and Components

1) ***Primary Coolant System*** – The primary coolant system consists of four parallel loops which circulate demineralized light water between the reactor vessel and the steam generators at a total design flow rate of 128,000 gpm. The system normally operates at a pressure of 1500 psia and at an average coolant temperature of 495°F with a design heat transfer rate of 1.7 billion Btu/hr. Each loop consists of two canned-motor pumps, two 18-in. swing check valves, two 24-in. electric motor operated gate valves, a steam boiler, and connecting piping. The design conditions for all components are 1800 psia and 650°F. The components of the primary coolant system are designed in accordance with applicable sections of the ASME Boiler and Pressure Vessel Code and the ASA Code for Pressure Piping. The principal material of construction for all components coming in contact with coolant water is type 304 SS (see Figure 9).

2) ***Primary Pumps*** – The primary coolant pumps are vertical shaft, canned-motor, single speed centrifugal type with a capacity of 16,000 gpm of 480°F water at 125 psi head. The pumps have single cast volutes, guide vanes, and double thrust bearings. Each loop has two pumps operating in parallel. The pumps are mounted on the head of the steam generator and supported by the piping alone. Water is provided for cooling pumps during normal operation; however, the pumps are required to operate without cooling water for 3 minutes at maximum pump delivery of hot-loop water with no injury to any mechanical or electrical parts. Idle pumps with no cooling water supply must be capable of withstanding hot-loop temperatures indefinitely without damage to the pump motor unit. The pumps are being designed, manufactured, and tested by the Westinghouse Electric Corporation.

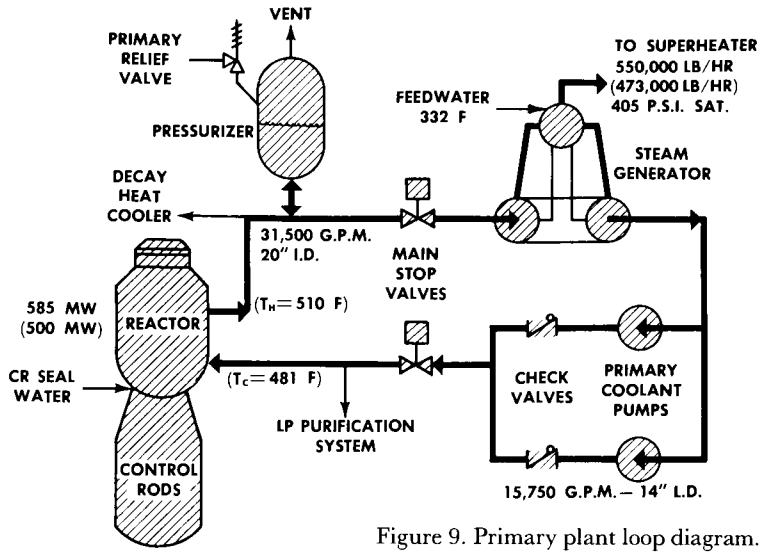


Figure 9. Primary plant loop diagram.

3) ***Check Valves*** – Each loop has an 18-in. swing check valve located downstream of each pump to prevent gross recirculation of flow through an idle pump. In the event of a boiler tube failure, these valves prevent excessive loss of water from the reactor while the slow acting gate valves are closing. To permit natural circulation through the loop, the check valves allow a small forward flow with the disc in the vertical position. To provide for warming up a cold loop, the check valves permit reverse flow with the disc in the vertical position. A ⅛-in. hole in the body or disc of the valve permits a small reverse flow to keep the idle section of 18-in. piping near operating temperature when only one pump in a loop is running.

4) ***Main Stop Valves*** – The two motor operated 24-in. gate valves in each loop serve to isolate the steam boiler, pumps, and check valves of each loop from the reactor and the remaining loops of the primary coolant system. These valves will normally be operated full open or full closed, providing no flow control. The valve located in the reactor outlet piping is designed to close in 30 sec to permit rapid isolation of a loop. The second gate valve located in the reactor inlet piping is designed to open in 4 min to minimize the rate of cold water flow into the reactor if the valve is opened accidentally with the idle loop cold and the pumps operating. This valve is equipped with a by-pass line and globe valve for equalizing pressure in the idle loop during start-up and for limited flow through the loop for gradual warmup. Normal closing pressure differentials on the valves are 175 psi; however, these valves are capable of closing with emergency pressure differentials of 1800 psi. The stuffing box on the valve is designed to prevent leakage from the gland to the atmosphere by means of a double packing with an intermediate drain.

5) ***Steam Boilers*** – The steam boiler in each coolant loop consists of a U-tube lower heat exchanger drum, a straight upper separator drum, and connecting risers and downcomers. The tubes are 1-in.-o.d. type 304 SS and are rolled and welded into SS clad tube sheets. The upper drum is located above and on the centerline of the lower drum and is connected to the lower drum by risers and downcomers capable of creating natural circulation of the secondary steam-water mixture. The normal steady state output of each steam boiler is 125 Mw with 117% maximum steady state overload capability. Normal steam flow (saturated) at the upper drum outlet is 472,500 lb/hr at 405 psig and 450°F. The steam boilers are capable of enduring the maximum normal load change at the rate of 11% of full power per minute for an unlimited number of cycles. This increase may occur at any power level in the range between 15% and 117% of full power for a duration not to exceed 5 min. In addition, the steam boilers are designed to endure 1000 cycles of the following emergency transient conditions:

a) Instantaneous increase of 22% of normal full power capacity at any power level in the range between 25% and 95% of full power.

b) Power decrease from 100% to 2% of full power in 10 sec.

The steam boilers are being manufactured by The Babcock & Wilcox Company.

6) ***Primary Piping*** – The primary system piping is of all welded construction, predominantly 24-in.-o.d. with short sections of 18-in.-o.d. for the parallel pump circuits. The piping will be ultrasonically tested, all welds will be radiographed, and the piping and welds will be dye penetrant checked. A check analysis will be required on each heat, and each length of pipe and each fitting is to be analyzed for the main identifying elements. The piping is being designed and will be fabricated by the M.W. Kellogg Co.

7) ***Pressurizer System*** – The function of the pressurizer system is to establish and maintain primary coolant system pressure within prescribed limits during warmup, steady state operation, load changes and shutdown. The pressurizer system consists primarily of a pressurizer tank, heaters, surge line, spray line, and spray head. The design conditions are 1800 psia and 650°F. Normal operating conditions are 1500 psia and 596°F.

The pressurizer tank, a cylindrical vessel with hemispherical top head and ellipsoidal bottom head, is installed vertically and normally contains saturated water in the lower portion and saturated steam in the upper portion. The water provides a reserve for sudden increases in primary coolant system density, and the steam provides a cushion and surge volume for sudden decreases in density. The tank is designed in accordance with ASME Boiler and Pressure Vessel Code, Section I.

Removable cartridge-type electric heaters are installed vertically in heater wells in the bottom head of the tank. The heaters are provided to heat the system on start-up and to generate and maintain a steam head necessary to maintain the primary cooling system at normal operating pressure.

A surge line penetrates the bottom head of the pressurizer and is connected to the reactor outlet leg of one primary coolant loop between the reactor and the main stop valve. The surge line carries water between the primary coolant system and the pressurizer system when there is a change in primary coolant density. Pressurizer water level is controlled by regulating the net blowdown or make-up to the primary coolant system.

The spray line penetrates the upper portion of the pressurizer and is connected to the reactor inlet leg of one primary coolant loop between the reactor and gate valve. The spray line is equipped with a control valve which is designed to pass a small quantity of water for retarding pressure rise on an insurge during normal operation and for reducing pressure when shutting down. The spray line is equipped with an orifice to limit the spray line flow should the control valve stick in the open position. The control valve in the spray line is also regulated by a temperature controller installed in the surge line so that a small flow is maintained to prevent development of a cold leg in the surge line. The spray head is installed within the upper head of the pressurizer and is designed to distribute the water from the spray line in a solid cone pattern without striking the pressurizer walls. The pressurizer tank is being manufactured by The Babcock & Wilcox Company.

Reactor Pressure Vessel

The general arrangement of the reactor pressure vessel consists of a cylindrical shell 9 ft×9 in. i.d. Carbon steel plate, SA-212 Grade B, is utilized, clad on the inner face with 0.109-in. type 304 SS. Four inlet connections with a minimum inside diameter of 20⅛ in. are located in the bottom hemispherical head and four similarly sized outlet connections are located in the upper portion of the shell. Twenty-one penetrations for control rod nozzles are located in the bottom hemispherical head. The top closure head of the reactor pressure vessel is secured by means of fifty studs of 5½ in. diameter. The closure head and vessel are seal welded to a semitoroidal shaped stainless steel seal which will insure leak tightness. Two auxiliary gaskets are provided to prevent water leakage during the seal removal operation.

Concentric, cylindrical, stainless steel, thermal shields are mounted inside the pressure vessel. These shields reduce thermal stresses in the vessel wall during reactor operation by absorbing gamma radiation emanating from the core. A portion of the primary coolant flows past the thermal shields and pressure vessel inner wall to remove the gamma heat generated. A 3-in.-thick SS wool insulation around the pressure vessel reduces the heat transfer to the neutron shield tank.

The reactor pressure vessel is mounted in a fixed position. Thermal expansion of the primary coolant system is accomodated by the 24-in.-o.d. SS primary piping or in the sliding boiler supports.

The vessel is designed in accordance with the ASME Boiler and Pressure Vessel Code, Section I.

The design pressure and temperature are 1800 psia and 650°F, respectively. All stainless steel welds will be dye penetrant inspected. Upon completion of fabrication, the vessel will be stress-relieved, radiographed, and subjected to hydrostatic testing. The vessel is being manufactured by The Babcock & Wilcox Co.

Fuel Handling and Storage System

Refueling is accomplished by the remote handling of fuel elements and control rods through a pair of pool systems connected by a transfer tube. The reactor pool is a stainless steel lined concrete structure and the transfer tube is of stainless steel, to maintain purity of the contained water and to prevent contamination of the shielding concrete. The system is designed to permit a normal refueling operation to be performed in approximately five days from the time the reactor control rods are positioned for shutdown to the pre-start-up testing of the freshly fueled core.

The arrangement of the pool systems and transfer tube, showing their location with respect to the containment vessel, reactor, and fuel handling building, is shown in Figures 4 and 5.

The reactor pool system is inside the containment vessel and adjacent to the reactor. A rotating handling platform, with a removable gantry monorail to which hoists and various handling tools are attached, serves as a major refueling device. The platform together with its supporting structure is designed to provide a vapor barrier over the pool opening. A negative pressure differential insures that any air leakage will be into the pool from above, while the depth of water maintained over parts being handled provides a radiation shield. By rotating the handling platform, which has a slot for passage of handling tools, any point of the reactor may be serviced. A crane is provided to move fuel between the transfer tube and the reactor.

Provisions are also afforded for the removal, inspection, maintenance, storage, and replacement of reactor closure and internal components. A 40-ton capacity rotating crane services this area.

The storage pool system is totally inside the fuel handling building. All operations upon the fuel elements, with the exception of installation in and removal from the reactor, are accomplished in this building. A monorail crane system provides storage for spent and fresh fuel core loadings in separate compartments in this pool system.

The spent fuel is cooled by natural circulation of the water. The pool water is circulated through a filter and heat exchanger where the water is processed and the decay heat is transferred to an intermediate cooling system.

The monorail crane system moves fuel to and from the transfer tube and services the element assembly and disassembly areas of the building. Space is provided in the pool system where shipping casks are loaded with spent fuel bundles. Provisions are made for the storage and handling of control rods and control rod followers.

The pool systems described above are connected by a transfer tube of stainless steel slightly over 2 ft i.d. Fuel elements, both fresh and spent, are transported in this tube between the reactor pool systems and the storage pool system. Control rods and control rod followers, both new and used, are also handled through this tube.

The fresh fuel is placed into the transfer tube carriage at the storage pool and is drawn up the tube by a cable powered by a winch. At the reactor pool the fuel is removed from the carriage and transported to the reactor for loading into the core. For removing spent fuel the reverse procedure is followed.

OPERATING FEATURES

The reactor will be regulated to provide constant steam pressure in the boiler regardless of the load on the turbogenerator. This avoids the use of a main line pressure reducing valve which would otherwise be necessary if the reactor were controlled for constant reactor temperature. The reactor will also be designed so that load may be increased from 15% to 100% load over the period of ½ hr and so that the load may be taken off the unit at the same rate. Operation below 15% of full load is not contemplated because of reactor limitations. If the turbogenerator trips out or is taken out of service for minor reasons and the expectation is that the unit will be restored in a few hours, the reactor will be kept in operating condition and loaded to 15% of capacity by means of a steam bypass around the main turbogenerator. By means of a pressure reducing valve and desuperheater in the bypass, steam will be passed directly to the condenser and the heat rejected to the river.

Survey of Th-U^{233} Technology

A. Ottenberg
Atomic Energy Division, American-Standard Corporation, Mountain View, California

This report is based on Report ASAE-S-4, prepared for the AEC by the Atomic Energy Division of American-Standard, and contains a summary of the information obtained through interviews with persons closely associated with the technology of thorium and U^{233} and through an examination of the classified and unclassified literature.

It was found that a substantial effort has gone into the development of specific phases of the total Th-U^{233} fuel cycle, but only on an uncoordinated basis and not within a total fuel cycle context.

In examining the status of the technology, it seems most desirable to think of the problem in terms of two parts: 1) physics data and the problems of reactor design operation and control, and 2) fuel cycle, which includes processing and fabrication.

The consensus of opinion among people interested in using the physics data for design work is that the available microscopic data are good, but a great deal more data must be gathered. It is assumed that the Th-U^{233} cycle can give breeding in all ranges of neutron energies. However, these assumptions are based only on incomplete data on cross sections and η – this is especially true in the epithermal region.

Work is in progress at several sites on the gathering of the necessary microscopic physics data such as cross sections, η, fission yields for U^{233}, cross sections of the fission products, etc. The latest data published by Los Alamos on the fraction of delayed neutrons for U^{233}, U^{235}, and Pu^{239} are of considerable importance to the future development of both the U^{233} and Pu^{239} programs. These values are given below, together with the previously accepted values.

Fraction of Delayed Neutrons

	U^{235}	U^{233}	Pu^{239}
1948 Values	0.0073	0.0024	0.0036
1957 Values	0.0064	0.0026	0.0021

The latest values for Pu^{239} and U^{233} are very similar and are considerably lower than the values for U^{235}. In addition, the value for Pu^{239} is much lower than had been previously assumed; therefore, the hazards problems associated with the plutonium loading of the MTR have had to be re-examined. Presumably, if plutonium loading of the MTR is deemed safe, there should be no objection to U^{233} fueling.

The entire question of the control and safety of reactors fueled with material having very small fractions of delayed neutrons must be given serious consideration. Since the Th-U^{233} cycle can presumably give breeding in a homogeneous thermal reactor, it seems to have an advantage over the uranium-plutonium cycle in this case. In such a reactor, the large and almost instantaneous negative power coefficient tends to minimize the hazards inherent in the use of material with a very small fraction of delayed neutrons.

The major deficiency in physics data for the Th-U^{233} cycle is in the field of macroscopic data or critical experiments. As of the time our report was being prepared, there had been no critical facilities using U^{233} except for the fast critical experiment at Los Alamos. Critical experiments should be performed in conjunction with the various reactor concepts to obtain information about critical mass, resonance escape probabilities, breeding gain, effective fraction of delayed neutrons, and reactivity change as a function of flux and time.

The amount of U^{233} needed to carry through this program is a problem of some importance because of the rather limited supply available. In the preparation of the report on the status of the U^{233} program, two forecasts were made of the amount of U^{233} needed for a critical evaluation of the Th-U^{233} power program. One forecast was based on the apparent requirements for the minimum program that could yield the necessary information (Figure 1), i.e., further basic physics work and critical experiments planned for the near future. The

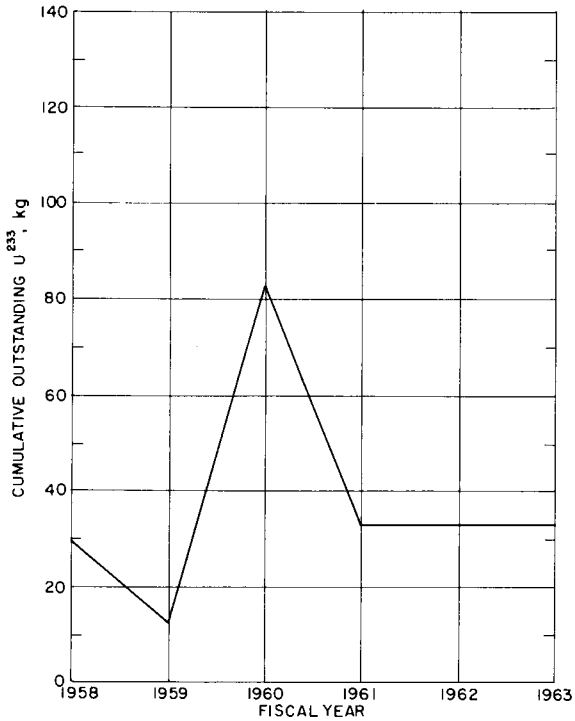


Figure 1. Forecast of U^{233} demand to support the minimum reactor development program.

second forecast (Figure 2) contains the minimum requirements and also the requirements for the critical facilities and reactor loadings that various groups plan to pursue as the U^{233} becomes available. Only those plans were considered that would shed information directly on a Th-U^{233} power program. Thus, although U^{233} would be expected to give higher flux-to-power ratios than U^{235} for a research reactor, this application was not considered. It should be noted that both forecasts contain the requirements for a loading of the MTR with U^{233}, which is expected to provide a great deal of information not only in the realm of reactor physics but also in the field of fuel cycles. Neither forecast contains a requirement for U^{233} for experiments in chemical processing, fabrication, or any other phases of the fuel cycle. At present the Thorex process is in operation and can provide some U^{233}.

When the fuel cycle is considered, the first question that arises is the availability of thorium. No authoritative survey of our available reserves exists, and many of the estimates are quite contradictory. Nevertheless, there appear to be sufficient reserves available to the U.S. to support a full-scale power program based on thorium. For example, E.D. Arnold of ORNL has estimated that, if by the year 2000 about 37% of all reactor fuel requirements were made up through the use of thorium, there would be a total demand of 60,000 tons of thorium to that time. Considering the facts that Davison Chemical Company of Erwin, Tennessee, feels that it can guarantee to supply 100,000 tons of thorium over the next 20 years from native American sources, and that the Blind River, Canada, uranium mine has estimated thorium reserves of from 40,000 to 100,000 tons, thorium reserves do not seem to be a major stumbling block. Certainly in some countries such as India and Brazil the availability of thorium is one of the main attractions at present for basing a power system on the Th-U^{233} cycle.

The information available indicates that thorium as the metal or oxide is quite stable to radiation. Thorium metal slugs have been irradiated over a two-year period with no radiation damage problems or slug failures. These thorium slugs were bonded to aluminum cans by the hot pressing method, and then aluminum caps were welded

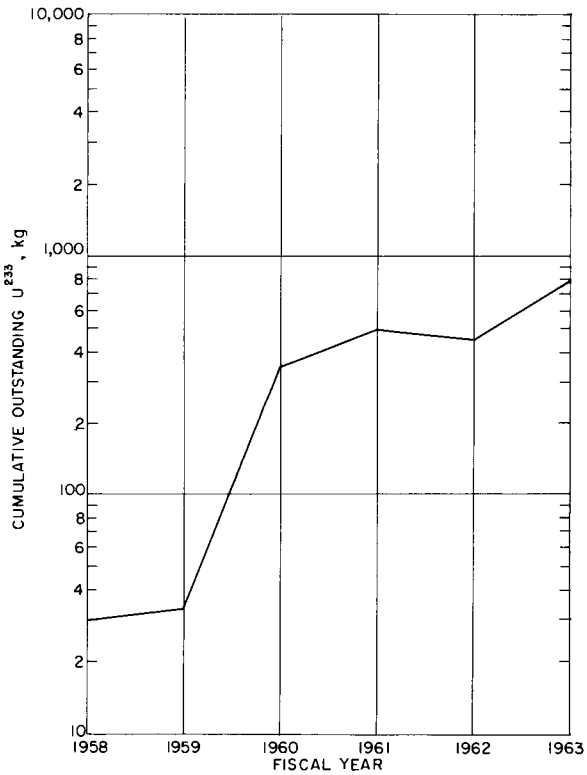
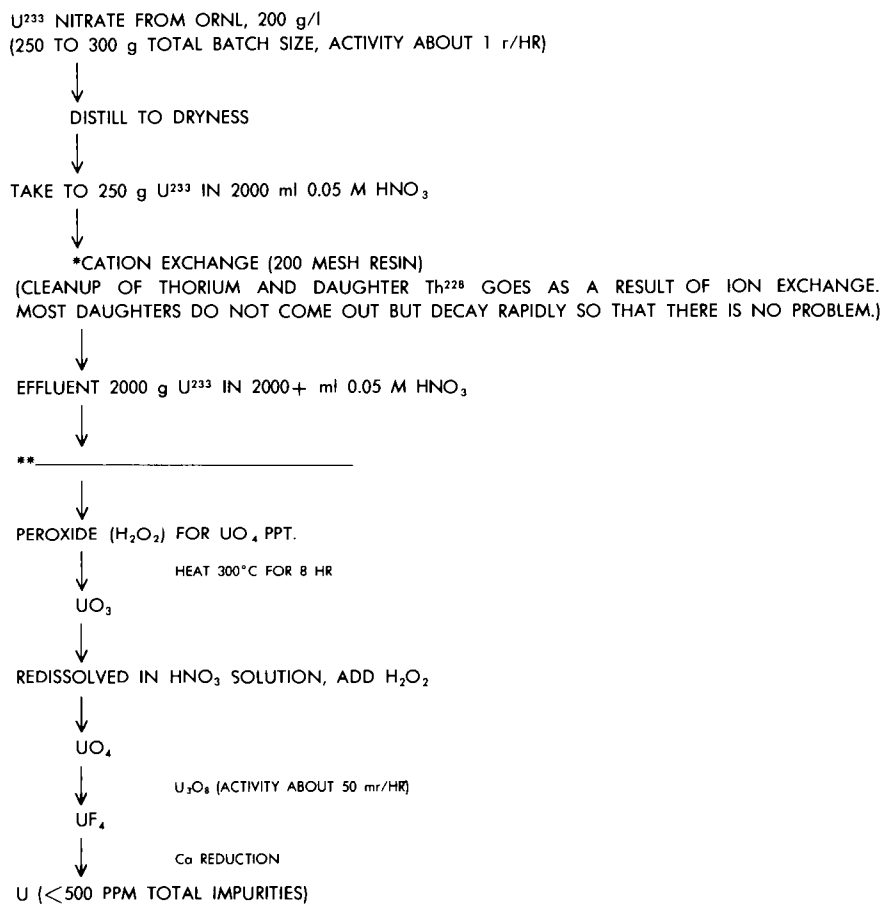


Figure 2. Total foreseeable U^{233} demand to support the reactor development program.

on. The exposures were generally carried out to <3000 g/T. At the MTR thorium slugs have been irradiated to a level of 7000 g/T with no radiation damage observed. A slug which had been irradiated to 4000 g/T at the MTR was found to have only a 0.2% change in diameter, and thorium metal has been reported to be very resistant to dimensional changes under irradiation exposures $>10^{21}$ nvt. Thorium alloyed with uranium appears to have excellent radiation damage resistance and engineering properties, as do thorium-plutonium alloys. Considerable work remains to be done in the field of thorium alloys, however.

The chief experience with thorium oxide as a potential reactor fuel is currently being accumulated at Argonne's Borax IV reactor which employs $\approx$6.5% UO_2-ThO_2 cold pressed and sintered pellets clad in a 1% nickel aluminum alloy. Slurries of thorium oxide have proven to be excellent for use as fertile blanket material. There is no transformation of thorium oxide at elevated temperatures. Thorium oxide slurries show no crystal growth and they pump easily. They are readily dispersible, although they have a tendency to cake in the presence of certain impurities.

It appears that an extensive program of irradiation experimentation on both the metal and the oxide will be necessary before maximum permissible exposures can be estimated for given power reactor conditions. This is of great importance since it will help to determine the type of reactor used and the life of the reactor. Most of the avail-



*ABOUT 50 g U233 ARE TIED UP IN RESIN, THEREFORE THE RESIN MUST BE TREATED BY ELUTION WITH HCl AND RECYCLED TO ION EXCHANGER.

**SHIELDED EQUIPMENT USED BEFORE THIS POINT; UNSHIELDED EQUIPMENT USED AFTER THIS POINT.

Figure 3. Los Alamos U^{233} processing flowsheet.

able experience has been obtained through the U^{233} production program where fuel burn-up is very small and temperatures are low. Much more information is needed on the behavior of thorium under power reactor conditions.

The fabrication of thorium recovered following U^{233} removal is complicated by its activity; the problems arising from the activity will be taken up after the discussion of processing.

There has been relatively little experience in the fabrication of fertile elements from thorium. Indications are that, provided material of adequate purity has been produced, thorium can be fabricated by most conventional methods. Because of the experimental nature of the work to date, no reliable cost estimates are available. A number of areas appear to require research for the full engineering potential of thorium to be realized:

1) It is well known that certain impurities or minor constituents can markedly affect the mechanical behavior of thorium. The effects of these trace elements on fabricability must be studied as a function of concentration.

2) Melting and casting operations must be investigated in order to develop methods which minimize impurity pickup, as well as internal and surface defects such as laps, seams, shrinkage cavities, and hot tears.

3) A correlation of the effects of various alloys on the mechanical working properties of thorium is very much needed.

Oxide pellets for fuel element fabrication have been produced at ANL and at Davison Chemical Company. The technology appears to be in a relatively advanced state (ORNL has produced ThO_2 to nearly 100% of theoretical density by use of a calcium oxide binder). Cost estimation probably can be done satisfactorily for the oxide elements.

In the case of U^{233}, it is possible to say that the fabrication technology, radiation and thermal stability, etc., are in exactly the same state of development as in the case of conventional uranium

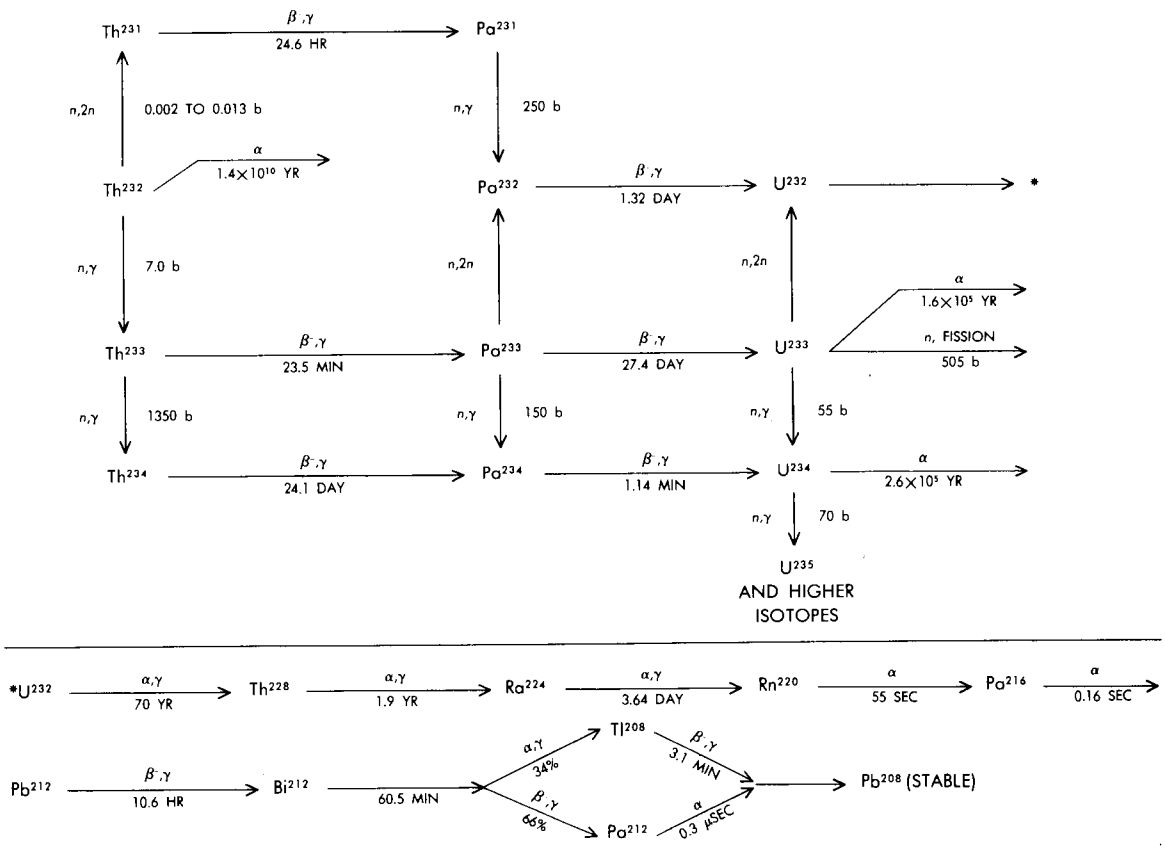


Figure 4. Nuclear reactions occurring in the neutron irradiation of thorium.

technology, except for the problems of activity. Thus, if the activity hazards are neglected, the engineering characteristics of U^{233} may be considered to be the same as those of the more familiar isotopes U^{235} and U^{238}, and it is possible to apply the large amount of information on uranium available in the literature to the engineering problems associated with U^{233}. (See Figure 3).

Immediately following the removal of irradiated thorium from the reactor, the major radiation hazard is due to Pa^{233} and fission products. This activity in the case of 3000-g/T thorium is roughly equivalent to 600-g/T uranium. The problems associated with this activity are typical: heavy shielding is required, extended cooling times are necessary if a wet chemical scheme is to be used in order to permit the level of activity to drop sufficiently to prevent severe damage to the solvent, etc.

However, the major problem associated with the Th-U^{233} cycle is the activity arising from the formation of U^{232}, which decays through the chain shown in Figure 4. The activity resulting from the high energy gamma emitters in this chain presents a severe shielding problem.

Because of the mode of decay and half-lives involved, the problems arising from the formation and decay of U^{232} are entirely different from those ordinarily associated with processing uranium-plutonium mixtures, since any U^{232} present will be processed along with the U^{233} fraction while the Th^{228} resulting from U^{232} decay will be processed along with the thorium fraction. Unless certain very stringent time limitations are met, both the U^{233} and the thorium products will be so highly active as a result of U^{232} daughter activity or Th^{228} daughter activity, respectively, that they will require remote fabrication regardless of the separation scheme used.

The time limitations necessary may be approximated as follows: Assuming a g/T level of about 3000 to 4000 and a flux level near 10^{14}, to avoid the necessity for remote fabrication of the reprocessed thorium, the irradiated thorium slugs must be put through a separation process within 30 to 60 days after irradiation. In the case of the U^{233} product, the holdup time before processing has essentially no effect upon the activity arising from the U^{232} content; but after processing, the U^{233} must be fabricated within two weeks to prevent the necessity of remote fabrication. If this time limit is exceeded appreciably, the U^{232} daughters may be removed by a relatively simple purification step and nonremote fabrication may again be done within a two-week limit.

It should be pointed out that under any circumstances the U^{233} would have to be handled in a contained facility of the plutonium type because of the health hazards from the U^{233} alpha activity.

The problems associated with the U^{233} formed in a thorium blanket will be present to an even greater extent in U^{233} fuel elements which must be processed, because the latter will contain not only the U^{232} present when they were fabricated, but also an appreciable amount formed by the $n,2n$ reaction on the U^{233} fuel elements. No consideration of this problem was uncovered during the survey, but it is believed to be quite severe.

One other activity problem in this cycle is that arising from the n,γ reaction on the Th^{233} to give Th^{234} with the decay scheme

$$Th^{234} \xrightarrow{\beta,\gamma} Pa^{234} \xrightarrow{\beta,\gamma} U^{234}.$$

This chain, however, dies out very rapidly, and its major effect is to require a cooling period for the thorium product of about 8 months to a year after processing; it also complicates control of the separation process.

Figure 5 indicates the problems associated with the activity in the products. The long cool scheme is designed to permit all the Pa^{233} to decay to U^{233}. This simplifies the processing and reduces the damage to the chemicals used for the extraction process; however, it yields a thorium product which must be remotely fabricated, and requires a large U^{233} inventory. The short cool scheme is designed to give a low activity thorium product which will permit nonremote or semiremote fabrication. It can also yield some isotopically pure U^{233}.

Table 1, which is taken directly from the work of E.D. Arnold, gives some idea of the effect of the g/T level and cooling time on the activity in the thorium product due to the Th^{228} daughters. It should be mentioned that the lower the flux level in the reactor, the less chance there is of reducing the activity in the thorium product by control of the cooling time prior to processing.

Various methods are available for processing the irradiated thorium to give thorium and U^{233}. However, it must be remembered that they are all limited by the activity considerations discussed above.

The Thorex process (Figure 6) is the separation scheme which has been most extensively studied

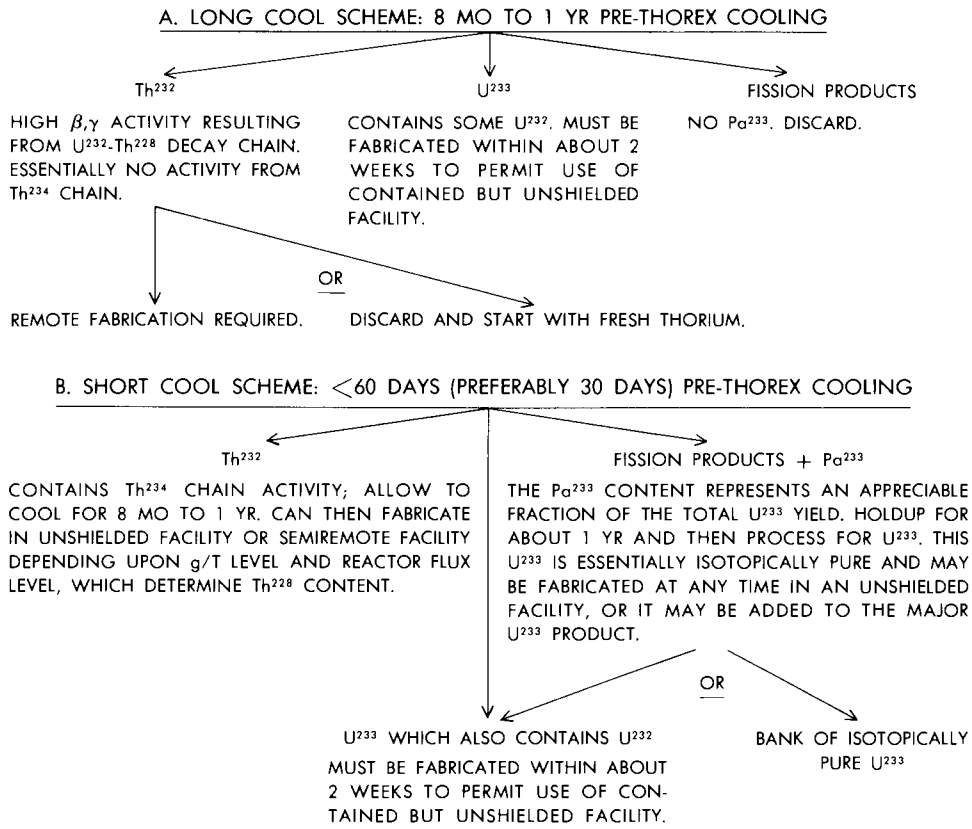


Figure 5. Alternative Thorex routes.

Table 1

Calculated Activity of Thorium Slugs as a Function of g/T Level and Cooling Period (1680 g Th; 1 cycle)

g/T Level (g U^{233} per ton Th)	Slug surface activity from U^{232} daughters (r/hr) — Pre-Thorex cooling (days) 60	130	200	300
1000	0.017	0.041	0.043	0.059
2000	0.083	0.135	0.181	0.244
3000	0.228	0.343	0.443	0.590
4000	0.475	0.676	0.846	1.088

for the purpose of separating U^{233} from irradiated thorium. It is a solvent extraction process using tributyl phosphate in an organic diluent. This process appears to give the desired separations, but there is still some question as to whether the chemicals are sufficiently radiation stable for a short cool process to be economical. If a short cool process is used with Thorex, the added cost over that of the long cool process is about 25%; but this is offset by advantages such as low activity thorium metal and smaller U^{233} inventories.

There is essentially no production-scale cost information available on processing of thorium blanket material to yield U^{233}. The Thorex process

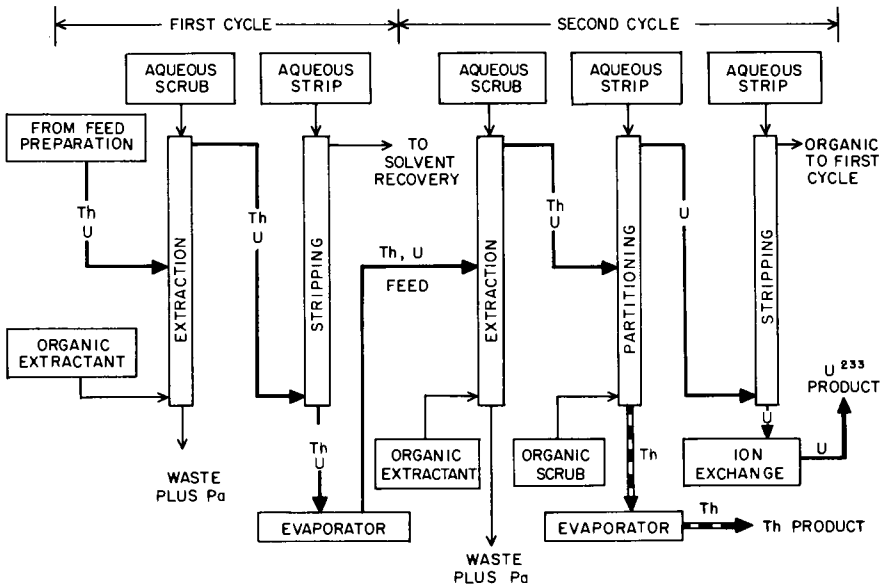


Figure 6. Thorex co-decontamination flowsheet.

has been estimated to cost about \$8/g U^{233} when processing 2000-g/T thorium. The cost for 4000-g/T material is expected to be about \$4/g U^{233}. Not too much significance can be attached to these figures since they are based only on pilot plant production.

Besides wet chemical processes such as the Thorex process, pyroprocessing schemes may be used. In general, the latter do not give decontamination factors approaching those obtained by the former, and it is assumed that the products will be fabricated remotely. Holdup times in such schemes would not be dictated by radiation stability of the solvent, but rather by the path taken by the protactinium.

In any cost comparison between pyroprocessing and wet chemical processing it must be taken into account that the former requires remote fabrication, which is expensive. However, if the assumption that wet chemical processing can permit nonremote fabrication is not true, possibly because of inability to fabricate U^{233} rapidly enough after processing or inability of the Thorex system to handle a short cool material, then the pyroprocessing scheme becomes much more competitive. Processing and associated fabrication methods represent an area in which further research and development are clearly justified.

A few more details can be provided relating to the radiation hazards associated with refabricating thorium and U^{233}. Table 2, which is taken directly from the work of E.D. Arnold, gives an idea of the activity problems or radiation hazards encountered in the fabrication of thorium metal that has been reprocessed. These are calculated values and are based on different values of cooling time and g/T (infinite recycle would increase these values by a factor of 2 to 3). It seems possible, if a short cool process can be utilized, to fabricate infinite recycle thorium in a nonremote or semiremote facility depending on the g/T level and the flux of the reactor.

The U^{232} content of U^{233} under normal irradiation conditions usually is of the order of 20 to 40 ppm. The radiation resulting from the U^{232} daughter chain builds up until it reaches a maximum after ten years. The hazards can be indicated by considering the activity at the surface of a sphere of U^{233} of ≈ 3 cm radius. After one year the activity at the surface of the sphere is 90 r/hr; after two years, 150; after five years, 240; and after ten years, 270. As mentioned earlier, even if the U^{233} can be processed within the very short time limit of about two weeks, it is still necessary to fabricate the material in a contained facility of the plutonium type.

At present a major problem in implementing the U^{233} research and development program is the availability of facilities capable of processing U^{233} nitrate from the Thorex process at ORNL through

Table 2

Calculated Activity of Thorium Slugs at Distances of 5 cm and 1 ft as a Function of g/T Level and Cooling Period (1680 g Th; 1 cycle)

g/T Level ($g\ U^{233}$ per ton Th)	Slug activity from U^{232} daughters (mr/hr) at 5 cm, Pre-Thorex cooling (days) 60	130	200	300	at 1 ft, Pre-Thorex cooling (days) 60	130	200	300
1000	2.4	4.4	6.0	8.2	0.12	0.22	0.31	0.42
2000	11.5	19.1	25.5	34.4	0.58	0.93	1.3	1.75
3000	32	48.3	62.0	83	1.62	2.4	3.1	4.1
4000	67	95	118	152	3.3	4.8	6.0	7.7

the various forms required. Chemical compounds such as sulfate, fluoride, and oxide, as well as the metal, will be necessary. In addition, the oxide and metal must be fabricated to desired forms. Oxide will be required as pellets or as highfired powders for dispersions, and the metal will be required as foil, or as metal for alloying purposes. If an expanded program is to be followed, it would seem most desirable to establish a new facility for the purpose of metal reduction and fabrication, and also for oxide production, or to modify an existing plutonium facility such as the #350 facility at ANL.

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Session II

BASIC PHYSICS

The Thorium Resonance Integral

D. J. HUGHES
Brookhaven National Laboratory, Upton, New York

This paper includes a few of the items of most interest at the present time to the Compilation Group at Brookhaven. This group is concerned with cross sections for monoenergetic neutrons, and not with measurements involving neutrons whose energies cover a wide range; nevertheless, the Th resonance integral will be discussed because of the great interest in it.

First, some thermal cross sections in thorium are presented. Actually, there is very little new, and at present the values are very much as they stand in the *Supplement to BNL 325*, i.e., the "world's best values" are

$$\sigma_{act}=7.34\pm0.15 \text{ b},$$

which is the same as in the *Supplement*, and

$$\sigma_{abs}=7.52\pm0.16 \text{ b},$$

which is slightly different from the value in the *Supplement.*

The evidence for these values is reviewed in an article[1] by Harvey and Schwartz, which also deals with the cross sections of other heavy elements. Since the *Supplement* came out, there has been a report of a Soviet measurement[2] of σ_{act}, resulting in

$$\sigma_{act}=7.31\pm0.1 \text{ b}.$$

The measurement was a very careful one and agrees extremely well with the values quoted above. The Soviet paper appeared in the *Journal of Nuclear Energy* in 1957, and must have appeared in the *Soviet Journal of Atomic Energy* about six months before; nevertheless, it is newer than anything in the *Supplement.*

To sum up, there are really no changes to report in the thermal cross sections of thorium.*

*In response to a question, it was stated that there is probably no real difference between σ_{abs} and σ_{act}, unless there is some odd additional reaction going on. In this connection, note that the errors cause the values to overlap.

Concerning the resonance integral (RI) in thorium, it has become apparent that the disagreements have been very large. Macklin and Pomerance[3] measured the RI as 67 ± 5 b. It is interesting that they computed the RI from the values of resonance parameters measured at BNL. Performing the computation for the first seven resonances, they obtained about 62 b, and, naturally thinking that the higher resonances would increase this slightly, they concluded that the value of 67 b was in good agreement. Since then, a Soviet measurement has been reported[2] of 96 ± 6 b. (Actually, the value was 88 b relative to a value of the resonance integral in gold of about 1300 b, but, if this is corrected by normalizing it to the resonance integral in gold of 1513 b that Macklin and Pomerance used, the value 96 ± 6 b is obtained.) Neither the USSR nor the Macklin and Pomerance result includes the $1/v$ tail in the thermal cross section. Thus there is a definite disagreement here well outside the limits of error.

Since the USSR measurement, improved values of the resonance parameters have been obtained, and the surprising thing is that the calculated value of the RI goes up. According to Harvey and Schwartz,[1] the breakdown is as follows:

- 67 b from calculations based on the resonance parameters reported in BNL 325, including the first seven resonances only,
- 25 b from calculations based on Dresner's formula, for the levels higher than the first seven,
- 3 b from the $1/v$ tail.

The total, 95 b, is the value quoted by Harvey and Schwartz. Subtraction of the $1/v$ component gives 92 b, which is to be compared with the measured values. It agrees extremely well with the measured Soviet value, but as previously noted, not with the Macklin and Pomerance value.

The large contribution of the higher levels to the RI is surprising, and one is tempted to suspect the Dresner formula, except that a calculation by Sampson and Chernick[4] of the RI including con-

tributions from the first eighteen levels gave 79 b, and, if the 13 b which Schwartz calculated from the higher levels (applying Dresner's formula) is added to this, the result, again 92 b, is in agreement with the previous calculation, which supports the view that there is indeed a large contribution from the higher levels.

As far as the thermal cross sections in U^{233} are concerned, there is not much new information, but there has been a substantiation of the values already listed in BNL 325 and the *Supplement*. The latter gave as the "world's best values"

$$\sigma_F = 532 \pm 6 \text{ b},$$

$$\sigma_{abs} = 588 \pm 7 \text{ b}.$$

Subsequently there have been two developments which will affect these values a little:

1) The British values included in the "best value" of σ_{abs} were not the latest ones available at the time, it turned out. The latest results available were actually slightly lower than those used, and consequently in the next edition the "world's best value" of σ_{abs} for U^{233} will be lower by at most one or two barns.

2) Since publication of the *Supplement* the results of measurements at Chalk River have been reported (at the Columbia Neutron Physics Conference in September 1957). The U^{233} fission cross section was measured, and also the fission cross sections of U^{235} and Pu, relative to $\sigma_F(233)$. The measurements were made not with monoenergetic neutrons but in a Maxwell distribution. The distribution was carefully controlled – i.e., it was felt that thermal equilibrium had really been attained – since the experiment was performed not at the center of a reactor but inside a large volume of D_2O.* The result of this very careful measurement was

$$\sigma_F(233) = 524 \pm 4 \text{ b},$$

which is lower than the published "world's best value," but not by a great deal, so that the effect on the latter will be slight.

The results obtained at Chalk River for σ_F of U^{235} are also very interesting in light of some doubts that have arisen in the past two years about the "world's best value" for this isotope, which was given as about 580 b. Recent measurements by Bollinger[5] and by Leonard[6] gave about 603 and 550 b, respectively. The Chalk River experiments resulted in a value somewhere between 570 and 580 b, say 575 b, which is very encouraging, since it agrees well with the "world's best value."*

There is not much new to report about the resonance parameters in U^{233}. Since the *Supplement* was issued there have been some new measurements at KAPL of fission and total resonance parameters, and measurements of the fission cross section at the MTR. These measurements of fission and total cross sections and of η have been made in the region 0.01 to say 10, 20, or 30 ev, and all with more or less similar equipment. There have been many measurements, but there is little to report because it is very difficult to extract from the measurements information on more than a few levels in addition to previously known ones. This difficulty in extracting the resonance parameters from the data is much greater for U^{233} than for almost any other isotope. For thorium, for instance, the situation is much better: the agreement between laboratories is good, predictions of resonance integrals agree well with the data, radiation widths agree well from level to level, etc. The reason for the difference in the two situations is the presence of fission in U^{233}. There even seems to be some fission cross section present between the normal levels, and no one knows how to handle this extra fission in analyzing measurements to get resonance parameters. The result is that there are good parameters for only five or six levels in U^{233}, and these are not useful for computations.

Another difficulty with U^{233} is that the fission widths are extremely large. The average fission width in U^{235} is about 80 mv, but those in U^{233} are many hundreds of millivolts. In the most recent analysis at the MTR, in which an attempt was made to fit the MTR experimental fission data with some sort of theoretical curve, it was necessary to assume that one level had a fission width over 600 mv and another of over a volt. Furthermore it was necessary to assume that these levels did not interfere with the others, but that the other levels did interfere with each other. Thus, rather extreme assumptions must be made in order to fit the data with curves; and it will be some time before really good sets of parameters for

*In response to a question, it was emphasized that an isotropic flux, not a beam, was involved.

*In response to a question, it was stated that the errors listed in the previous discussion are the most probable errors.

U^{233} are available because of these great difficulties in the analysis.

An encouraging development in the resonance region is the behavior of $\eta(233)$ as it has recently been measured at the MTR and at KAPL. Improved techniques are being used, and η can now be measured fairly well. Comparison of the MTR curves with older BNL and Harwell results shows good agreement. The value of $\eta(233)$ is very nearly constant from 0.01 ev to 1 ev, then begins to oscillate as resonances appear. Similar η measurements at KAPL agree well with this MTR work. The $\eta(233)$ results therefore seem rather consistent, but attempts to analyze them to get information about the individual resonances encounter the trouble mentioned before: the analysis is very difficult. The total cross section of U^{233} has also been measured at KAPL up to several hundred volts with very good resolution.

In my opinion the general conclusion about the situation in U^{233} is that the theory cannot yet be used to predict results of value. That is, for some materials the theory is good enough to help interpolate or extrapolate the experimental values, but in this case, where the theory is so difficult to develop, the situation is that for a long time to come the experimental results will be used to develop the theory, rather than the reverse. The very difficult questions such as interference or noninterference in fission, the number of open channels in fission, etc., are really still not decided.

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DISCUSSION

The general conclusion of the discussion which followed was that the apparent differences in behavior of $\eta(233)$ and $\eta(235)$ or $\eta(Pu)$ – e.g., the constancy in the region 0.01 to 1.0 ev – are real effects, arising from the differences in nuclear structure (as for example from the comparatively great fission widths in U^{233} and possibly from the presence of levels very much broader than normal levels) rather than merely from experimental difficulties which might arise in U^{233} but not in U^{235} or Pu. It was pointed out, by way of support for these conclusions, that if the differences were due, for instance, to a failure to resolve the individual resonances in U^{233}, the sharp dip in $\eta(233)$ beyond 1 ev would not be observed.

In response to a question, Dr. Hughes said that the Brookhaven group preferred to obtain the resonance integral from the resonance parameters themselves, rather than by direct graphical integration of the experimental data, since in this way tricky effects such as different sample thicknesses, etc., are avoided. The area under the curves is treated as the experimental quantity.

General Comments on Reactor Design Involving U^{233} and Thorium

B.I. Spinrad
Argonne National Laboratory, Lemont, Illinois

The design of thermal lattices using Th as fertile material must be conditioned on the physical facts that Th metal is more than 50% more absorptive than U^{233} metal, and ThO_2 more than twice as absorptive on a volume basis. This means that the reactive equivalent of natural U is about 1.2% U^{233} in Th, and about 1.5% in ThO_2. Higher rod blackness implies smaller rod size and more "homogeneous" lattices.

The need for separate enrichment of Th, with U^{233} originally, and the realization that high flux (power density) systems need an inventory of fissionable material tied up as Pa^{233}, both emphasize the essential importance of achieving high burn-up to be attractive economically. In addition, the material advantages of Th and ThO_2 are only truly realized under long burn-up. The best way of doing this is to achieve a high internal conversion ratio (ICR).

It is therefore disappointing to observe that such prototypes as Borax IV and the American Machine & Foundry and Babcock & Wilcox designs are all low ICR systems in which ThO_2 is considered basically as a diluent rather than as a fertile material. They are all relatively "loose" lattices. The experience would indicate some pessimism as to the nuclear compatibility of H_2O and Th; H_2O lattices require a somewhat restrictive range of coolant channel dimensions to be operationally stable as power producers, and it is a tricky procedure to reconcile this range with a high ICR. More hope would appear justified in moderators with less absorption (D_2O and C).

Experience with conceptual designs involving Th indicates that optimized designs show a sharper optimized peak for Th than for U systems. Hence, although the basic nuclear data are in good shape compared with those for U^{235}, U^{238}, and Pu, still higher precision is necessary, particularly in resonance integrals and age effects. At the moment it is still not possible to predict with assurance that Th systems are more promising economically than U systems.

Neutron Yields for U^{233}

R. J. Beeley
Atomics International, A Division of North American Aviation, Inc., Canoga Park, California

The work on the Advanced Thorium Reactor, utilizing an epithermal spectrum, has just begun. Our first concern was to obtain the best available information on the neutron properties of U^{233} in the intermediate energy range. In particular we wished to obtain values of η as a function of energy.

Good cross section information exists in the low energy range. Values of the capture and fission cross sections have been obtained with good accuracy and are reported in BNL 325 and its *Supplement No. 1.* Values of η obtained from the curves give reasonable agreement with direct measurements published in NRDC-85,[1] which cover the energy range from about 0.01 to 1.0 ev. The Russian data[2] would indicate that η is essentially constant, when arranged over the energy intervals used in their experiments, up to about 130 ev.

We have attempted to use the curves and the resonance parameter data of the *Supplement* to obtain η for U^{233}. Our efforts to use the resonance parameter data to obtain the capture cross section failed, as other similar efforts have failed. We therefore turned to direct integration of the cross section curves to obtain average values of η over eight energy groups.

The results obtained are indicated in Table 1. A constant scattering cross section of 10 barns was assumed in obtaining the absorption cross section from the total cross section curve of the *Supplement*, and a constant ν of 2.47 was used.

Table 1

Group	Energy	$\bar{\sigma}_f$	$\bar{\sigma}_c$	η
1	1 – 2.8	327	91.3	1.96
2	2.8 – 5.5	99.6	0.4	2.50
3	5.5 – 8.2	132	51.6	1.81
4	8.2 – 14.5	126	4.3	2.43
5	14.5 – 20	102	12.1	2.24
6	20 – 46	69.7	0	2.51
7	46 – 100	31.6	9.0	1.96
8	100 – 300	21.7	12.1	1.61

Errors in σ_c due to the assumption of a constant scattering cross section are probably quite important, and make suspect the η values obtained.

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Effective Resonance Integral of Thorium

LAWRENCE DRESNER
Oak Ridge National Laboratory, Oak Ridge, Tennessee

In the last year three separate measurements have been reported of the effective resonance integral of thorium rods (see Table 1). These measurements do not agree with one another at all well, and on the basis of the experiments alone it is not possible to distinguish which, if any, of the experiments is correct. This distinction may be made, however, on a theoretical basis as follows:

According to the theory of resonance absorption in lumps, the dependence of the resonance contribution to the effective resonance integral, I, on surface-to-mass ratio, S/M, can be expressed as[1]

$$I=A\left[1+\frac{m}{8\sigma_p}C(Nl\sigma_p)\frac{S}{M}\right], \qquad (1a)$$

$$C(Nl\sigma_p)=\frac{2}{1+\sqrt{1+(Nl\sigma_p)^{-1}}} \qquad (1b)$$

where m is the mass per absorbing atom, σ_p is the potential scattering per absorbing atom, N is the density of absorbing atoms, and l is the average chord length of the lump, defined as 4 times the volume-to-surface ratio. A is a constant independent of S/M. It is of great importance to note that Equations (1) predict a geometric dependence of the effective resonance integral quite independent of the resonance parameters. A point that is not mentioned in Equation 1 is that this law ought to hold only for $S/M \gtrsim 0.2$ cm^2/g and to improve in accuracy with increasing S/M.

It can also be shown that from a curve of I vs S/M for an absorber, U^{238} for example, a curve of I vs S/M can be obtained for chemical compounds of the absorber, $U^{238}O_2$, say. This is done by scaling the abscissa and ordinates of the first curve according to the law

$$I \propto \sqrt{\sigma_p}; \quad S/M \propto \sigma_p/m\,. \qquad (2)$$

Conditions on S/M similar to those for Equations 1 hold for Equation 2.

That these laws actually are upheld by experiment can be seen by comparison with the very careful experiments of Hellstrand[2] on U and UO_2 noted in Table 1. For $S/M \geqslant 0.7$ cm^2/g, A for U is perfectly constant within less than 0.1%; for $S/M=0.5$ cm^2/g it is 0.5% less than its asymptotic value; for $S/M=0.3$ cm^2/g it is 2% less; and for $S/M=0.2$ cm^2/g it is 5% less. Agreement is even better for UO_2. This is very good confirmation of Equations 1. The scaling law predicts values for the resonance integral of UO_2 from those for U which are between 2% and 3% less than the directly measured ones, the larger error occurring at the lowest $S/M(=0.2$ cm^2/g). This confirms Equation 2.

Let us now consider the measurements of Davis[3] given in Table 1. Since the measurements are for rather low S/M we shall not apply the theory but rather first make a comparison of the uranium experiment with Hellstrand's. Davis' experiment gives in its range of applicability results which are higher than Hellstrand's by a fixed factor of $1.294 \pm 1.6\%$. The geometric dependence thus is correct, but the correct normalization appears to be in doubt. Since Davis' thorium experiment was done by the same method as his uranium experiment, we may provisionally assume that its geometric dependence is correct.

Let us now consider Sher's measurements,[4] given in Table 1. If we normalize A for the U experiment to its value at $S/M=1.1$ cm^2/g, then it is down by 11% at $S/M=0.7$ cm^2/g, 17% at $S/M=0.5$ cm^2/g, and 24% at $S/M=0.3$ cm^2/g. The difficulties with Sher's measurements seem to be at the higher values of S/M (0.3 cm^2/g $\leqslant S/M \leqslant 1.1$ cm^2/g), for in the range 0.1 cm^2/g $\leqslant S/M \leqslant 0.3$ cm^2/g, they are related to Hellstrand's by a fixed factor of $0.997 \pm 1.3\%$. The factor then seems to increase by about 7% for every increment of 0.2 cm^2/g in S/M. If we normalize A for the Th experiment to its value at 1.1 cm^2/g, we find it is down by 8% at $S/M=0.7$ cm^2/g, 15% at $S/M=0.5$ cm^2/g, and 24% at $S/M=0.3$ cm^2/g. In the range of 0.1 cm^2/g $\leqslant S/M \leqslant 0.3$ cm^2/g it is lower than Davis' data by a factor which equals 1.376 at

Table 1

Summary of Measurements*

Material	Effective resonance integral (barns)	Reference
U^{238}	$2.81+24.7\sqrt{S/M}$	Hellstrand[2]
	$0.07 \leqslant S/M \leqslant 0.53$	
$U^{238}O_2$	$4.15+26.6\sqrt{S/M}$	
	$0.08 \leqslant S/M \leqslant 0.70$	
U^{238}	$6.0\{1+15.6(S/M)[1-2.18(S/M)+2.19(S/M)^2]\}$	Davis[3]
	$0.1 \leqslant S/M \leqslant 0.3$	
Th^{232}	$6.11\{1+5.0(S/M)[1-0.87(S/M)]\}$	
	$0.1 \leqslant S/M \leqslant 0.3$	
U^{238}	$9.10\left(1+\frac{3.33}{(M/S)+0.112}\right)$	Sher[4] Includes $1/v$ part
Th^{232}	$7.5\left(1+\frac{3.4}{(M/S)+0.34}\right)$	
Th^{232}	$-0.6+24.1\sqrt{S/M}$	Dayton and Pettus[5]
	$0.1 \leqslant S/M \leqslant 1.3$	
$Th^{232}O_2$	$-3.6+35.2\sqrt{S/M_{Th}}$	
	$0.2 \leqslant S/M_{Th} \leqslant 1.3$	

*$1/v$ part has been substracted except as noted.

$S/M=0.1$ cm²/g and falls to 1.177 at $S/M=0.3$ cm²/g. In the U case Sher's and Davis' data agree in shape in this range with each other and with Hellstrand's data. Moreover, Sher's data agree with Hellstrand's in normalization in this range too. In the Th case, however, Sher's and Davis' data do not agree even in shape; since both authors used the same technique for the Th measurements as for the U, the source of this discrepancy is obscure.

Finally, let us consider the data of Dayton and Pettus,[5] given in Table 1. Normalizing A as before, we find it is down by 3%, 7%, and 14%, respectively, for Th, and 5%, 10%, and 19%, respectively, for ThO_2, for $S/M=0.7$, 0.5, and 0.3 cm²/g. Moreover, the scaling law predicts values for the resonance integral for ThO_2 from those for Th which are between 10% and 20% less than the directly measured ones in the range 0.3 cm²/g $\leqslant S/M \leqslant 1.1$ cm²/g. The larger error occurs at the highest $S/M(=1.1$ cm²/g). Thus it appears that there is some systematic error in the work of Dayton and Pettus.

In conclusion it appears that there is no reliable absolute measurement of the effective resonance integral for Th. The situation is somewhat better in U, where the experiments seem consistent with respect to shape in the range of S/M from 0.1 to 0.3 cm²/g, and where at least one of them agrees with theory for larger values of S/M.

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Effective Resonance Integral in Thorium

R. SHER
Brookhaven National Laboratory, Upton, New York

We have made measurements of resonance escape probability in lattices fueled by 0.387-in.-diameter rods of 2% U^{235} - 98% Th metal. These experiments actually measured the Cd ratio of the Th^{233} production in a rod. The lattices differed from one another by having different water-to-metal volume ratios ranging from 1:1 to 4:1. (There was only one value of S/M.)

We write

$$p=\exp\left[-\frac{N_{\mathrm{Th}}V_{\mathrm{Th}}}{\xi\Sigma_{\mathrm{SM}}V_{\mathrm{M}}}\times\mathrm{R.I.}\right]$$

where the subscripts Th and M stand for Th and water respectively.

We originally used the Untermyer form of the effective absorption integral:

$$\mathrm{R.I.}=A-\frac{1}{v}+\frac{AB\delta}{(M/S)+C}$$

where $1/v$ stands for the $1/v$ absorption (3.2 barns), and δ is the Dancoff correction for the shielding by neighboring rods. For each lattice δ was calculated by the methods of Dancoff and Ginsburg given in CP-2157. The $1/v$ term is written in this fashion because $1/v$ absorptions have been subtracted from p in the measurements.

We can then write for each lattice (labeled by subscripts i)

$$\frac{\ln p_i}{\mathrm{const.}_i}\pm 3.2=A+\frac{AB\delta_i}{(M/S)+C}$$

where everything except A, B, and C is known. Alternatively we could use the form $A+AB\sqrt{S/M}$ on the right-hand side. It will be noted that the values of A, B, and C obtained by solving this set of equations give the effective resonance integral *including* the $1/v$ absorption.

The results, based on measurements in 4 lattice spacings, were as follows.

Untermyer form: $A=7.5$, $B=3.4$, $C=0.34$.

$A(1+B\sqrt{S/M})$: $A=5.6$ $B\pm 4.05$.

Measurements of the Effective Resonance Integral of Thorium and Thorium Oxide

WILLIAM G. PETTUS
Atomic Energy Division, The Babcock & Wilcox Company, Lynchburg, Virginia

The complicated energy and space dependence of neutron resonance absorption in lumps and the scarcity of accurate information on resonance parameters has so far prevented the reliable prediction from first principles of effective thorium resonance integrals for heterogeneous systems. This state of affairs has led to several attempted direct measurements, and we seek in this discussion an appraisal of the results of these measurements.

The three direct measurements of resonance integrals of lumped thorium reported to date are those of Untermyer and Eggler[1] at Argonne, Davis[2,3] at Hanford, and Dayton and Pettus[4] of Babcock & Wilcox. Untermyer and Eggler studied the absorption in thorium cylinders by the danger coefficient technique, and in addition they made activation measurements on stacked thorium foils. In the former set of measurements uranium cylinders were used as standards, and in the latter measurements the data were normalized to the infinite dilution value obtained by Hughes and Eggler.[5] The results obtained were as follows:

Danger Coefficient:

Diameter, cm	Length, cm	Resonance integral
0.9	38.5	16.0±20%
1.9	23	13.4±20%
3.2	15.2	12.6±20%

Activation:

$$R=13\left(1+\frac{0.42}{(M/S)+0.08}\right)\pm 30\%. \qquad (1)$$

It should be noted that these results include the $1/v$ contribution. It should also be noted that the results are standardized with respect to rather early uranium data, and some renormalization may therefore be justified.

The recently published results of Davis for thorium and thorium oxide were obtained by reactivity measurements at the Hanford Test Pile. The thorium measurements were made on cylinders having surface-to-mass ratios in the range 0.113 to 0.285 cm^2/g, and the data are found to be consistent with the following relation:

$$R=6.11\left[1+5.0\frac{S}{M}\left(1-0.87\frac{S}{M}\right)\right]+ (1/v \text{ contribution}). \qquad (2)$$

U^{238} is used as the standard in these measurements, and the experimental uncertainty appears to be of the order of 5 to 10%. In reference 3, effective resonance integrals for 3.46-cm-diameter thorium and thorium oxide cylinders are given as 12.5±0.3 and 15.4±0.8 respectively, including the $1/v$ contribution. The density of the thorium oxide used in these measurements is given as 9.64 g/cm^3.

The results of Dayton and Pettus were obtained from reactivity measurements at the Pennsylvania State University research reactor. Measurements were made on thorium rods and plates and on thorium oxide rods of two different densities. The principal results are given in Tables 1 to 4. Calibration for these experiments was obtained through the use of boron samples. In addition, the reduction of the surface components of the resonance absorption resulting from shielding by neighboring pins (Dancoff effect) was investigated. This effect was found to conform, within the limits of experimental uncertainty, to the theoretical description given by Dancoff and Ginsburg.[6]

It is difficult to decide from an inspection of the data what is the most satisfactory representation of the experimental results. The large uncertainties in the data of Untermyer and Eggler render it of little value in resolving this question. For the more precise results of Davis, a linear relation in S/M was found to be inadequate, and as suitable alternate descriptions the quadratic function in Equation 2 and the relation

Table 1

Effective Resonance Integral of Th^{232} Metal Rods
(Rods 6 in. long, average density 11.7)

Diameter, in.	S/M_{Th}, cm^2/g	$\langle\sigma_a\rangle_{eff}$, barns
0.158	0.860	26.0±9.4
0.279	.496	20.5±2.6
0.397	.352	18.7±1.1
0.530	.270	16.1±0.5
0.655	.219	13.9±0.3
0.780	.185	13.1±0.2
0.905	.160	12.5±0.2
1.155	.128	11.4±0.1
1.405	.104	10.7±0.1

Table 2

Effective Resonance Integral of Th^{232} Metal Plates
(Plates 6 in. long, 1.016 in. wide)

Thickness, in.	S/M_{Th}, cm^2/g	$\langle\sigma_a\rangle_{eff}$, barns
0.056	1.303	27.5±2.1
.223	0.402	18.6±0.5
.390	0.256	14.9±0.3
.557	0.201	13.6±0.2
.724	0.175	12.9±0.2
.891	0.159	12.7±0.1

$$R=6.3+18.2\sqrt{S/M}$$

have been proposed. A linear relation in $\sqrt{S/M}$ may also be shown to fit the data of Dayton and Pettus better than a linear relation in S/M, both for the metal and for the oxide. Least-squares adjustments yield the following results:

$$R=\ \ 2.9+24.1\sqrt{S/M}\quad \text{for metal,}$$

$$R=-0.1+35.2\sqrt{S/M}\quad \text{for oxide.}$$

These data are also represented quite well by linear relations in CS/M where C is the Wigner non-collision correction[7,8] given by

$$C=\frac{2}{1+\sqrt{1+(1/\Sigma_p l)}}\,.$$

In this representation least-squares adjustments yield

$$R=6.9+43.4\ CS/M\quad \text{for metal,}$$

$$R=7.8+48.0\ CS/M\quad \text{for oxide.}$$

Table 3

Effective Resonance Integral of ThO_2 Rods
(Rods 6 in. long, average density 7.1)

Diameter, in.	S/M_{Th}, cm^2/g	$\langle\sigma_a\rangle_{eff}$, barns
0.291	0.977	40.4±5.1
0.405	.653	37.2±2.1
0.535	.505	26.6±1.0
0.653	.399	22.5±0.7
0.808	.338	21.6±0.4
0.936	.293	19.1±0.3
1.155	.236	17.1±0.2
1.398	.197	15.5±0.1

Table 4

Effective Resonance Integral of ThO_2 Rods
(Rods 6 in. long, average density 2.6)

Diameter, in.	S/M_{Th}, cm^2/g	$\langle\sigma_a\rangle_{eff}$, barns
0.555	1.281	41.7±2.4
0.680	1.083	34.3±1.7
0.805	0.939	35.3±1.2
0.930	0.797	31.1±0.9
1.180	0.627	26.6±0.5
1.430	0.557	25.7±0.4

This representation is preferable from the standpoint of the theory as long as the average lump thickness is sufficiently large so that neutrons having energies corresponding to resonance peaks have only a small probability of traversing the lump without a collision.

There is a significant discrepancy between the slope in the $\sqrt{S/M}$ relation of Davis and that of Dayton and Pettus. Otherwise the three experiments appear to be in general agreement within the experimental uncertainties and the uncertainties involved in the calibration procedure.

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Age Determination From CETR Critical Assembly Data

CLIFFORD J. HEINDL
Atomic Energy Division, The Babcock & Wilcox Company, Lynchburg, Virginia

An assembly consisting of 14.5% by volume thorium metal, 8.5% polyethylene tape containing U^{235} oxide fuel, 24% aluminum, and 53% light water was brought to criticality at a series of seven different water heights by changing its radius. At the highest water level used, greater than 10 cm dry core material remained above the water to provide constant axial reflector savings. At each critical height, small perturbations were made in water level in both increasing and decreasing directions, and resultant periods measured. The average rate of change of reactivity with water height obtained at each level is listed in Table 1.

The experimental results can be interpreted[1] as follows:

$$k_{\text{eff}}=\frac{k_\infty}{1+M^2B^2}=1\ ,$$

$$B^2=\left(\frac{2.405}{R+\lambda_R}\right)^2+\left(\frac{\pi}{h+\lambda_H}\right)^2$$

where λ_R and λ_H are total radial and axial reflector savings, respectively.

Utilizing the usual definition of reactivity, and the fact that λ_H is constant with water height,

$$\rho=\frac{k_{\text{eff}}-1}{k_{\text{eff}}}=\frac{k_\infty-1-M^2B_g^2}{k_\infty}\ ,$$

$$\frac{\partial\rho}{\partial h}=\frac{2\pi^2M^2}{k_\infty}\ \frac{1}{(h+\lambda_H)^3}\ ,$$

$$\left(\frac{\partial\rho}{\partial h}\right)^{1/3}=\frac{1}{(h+\lambda_H)}\left(\frac{2\pi^2M^2}{k_\infty}\right)^{1/3}\ ,$$

$$h=\left(\frac{2\pi^2M^2}{k_\infty}\right)^{1/3}\left(\frac{\partial\rho}{\partial h}\right)^{-1/3}-\lambda_H\ .$$

Thus a graph of h, the core height, as a function of $(\partial\rho/\partial h)^{-1/3}$ should give a straight line of slope $(2\pi^2M^2/k_\infty)^{1/3}$ and intercept $-\lambda_H$. The data of Table 1 have been plotted in this manner in Figure 1.

A least-squares fit was used to find slope and intercept. After correction for units and calibration of the manometer used in height measurement, the values found were:

Table 1

Water height	$d\rho/dh$, cents/cm
74.0	14.18
86.4	10.57
98.5	6.64
114.7	4.71
133.8	3.55
151.6	2.22
168.6	1.67

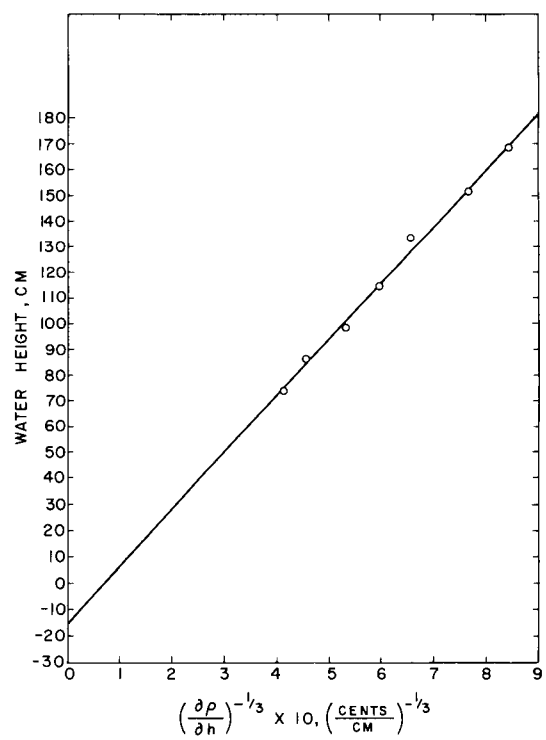

Figure 1.

$$M^2/k_\infty = 39.1 \text{ cm}^2, \quad \lambda_H = 15.2 \text{ cm}.$$

The value of k_∞ obtained from measured critical buckling is 1.15, and L^2 has been calculated to be about 2 cm^2. This leads to $\tau = M^2 - L^2 = 43$ cm^2.

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Age and Resonance Escape Probability for the THUD Critical

W.C. Redman
Argonne National Laboratory, Lemont, Illinois

The term THUD designates a system of thoria-urania fuel elements and heavy water currently under investigation in both exponential and critical experiments at Argonne. The critical experiment has been in progress since July 1957. Certain data related to the determination of neutron age and resonance escape probability in this system will be reviewed here, following a statement of the reasons for the THUD program and a brief description of the critical facility.

MOTIVATION

The investigation of the nuclear properties of the thoria-urania-D_2O system was undertaken for several reasons. Oxide fuels, especially thorium oxide, offer the prospect of achieving high burn-up and are quite compatible with high temperature water. Interest in the thorium cycle is based on the desirability of tapping the nuclear energy available in the more abundant fertile material. Good neutron economy is achievable with D_2O, and a D_2O system is attractive for a forced circulation reactor. Favorable operating characteristics have been observed for a thoria-urania-light water system currently under test at Argonne (BORAX-IV). Even greater stability is anticipated for a ceramic fuel–heavy water system in that two factors contributing to stability, namely long neutron lifetime and small excess reactivity in steam, are more favorable in a heavy water system. The specific objective of the THUD program at its outset was to develop the information required for the design of a heavy water–oxide fuel loading for the EBWR.

DESCRIPTION OF THE ZPR-VII FACILITY

The ZPR-VII is a water critical facility of conventional design. It has been described in detail in ANL-5715.[1] Of particular interest are the provision for precision adjustment of the water level through a variable level overflow, electrical heating of the water to its atmospheric boiling point, and the use of pulleys and cables to keep the top of the system relatively uncluttered. The core tank and some of the internal structure are shown in Figure 1. The core is located very deep in the core tank in order to minimize loss of heavy water and its contamination by light water in the atmosphere when the cover plate is removed for loading changes. The core structure duplicates that existing in the EBWR. The pattern of nine 10-in.-span cross rods and 4-in.^{2} fuel elements is maintained.

The detailed structure of the element cluster and fuel rods is shown in Figure 2. Element clusters consisting of perforated material with 5/16-in. holes on a 3/8-in. triangular spacing held by hollow corner tubes provide a means for conveniently assembling a variety of fuel rod lattices. The fuel rods consist of 0.234-in.-diameter by 0.60-in.-high pellets having a thorium-U^{235} atom ratio of 25 or 50 placed inside a 5/16-in.-o.d. aluminum tube to a height of 60 in. The geometrical density of these pellets is 8.6 g/cm^3. Voids are introduced into this assembly in the form of empty aluminum tubes having the same o.d. but a thinner wall (0.014 in.).

PERTINENT DATA

Measurements in the related exponential system have involved a range of fuel to moderator ratios for both concentrations of U^{235}, but critical experimentation has been concentrated on a 3/4-in. triangular lattice, mainly with fuel of the higher U^{235} content. A preliminary evaluation of certain of the experimental results was presented[2,3] at the October 1957 American Nuclear Society meeting. Those discussions were limited to measurements of clean criticals, differential core worth, integral rod worth, and integral void coefficient of reactivity in the ZPR-VII facility, and bucklings and temperature and void coefficients in the exponential.

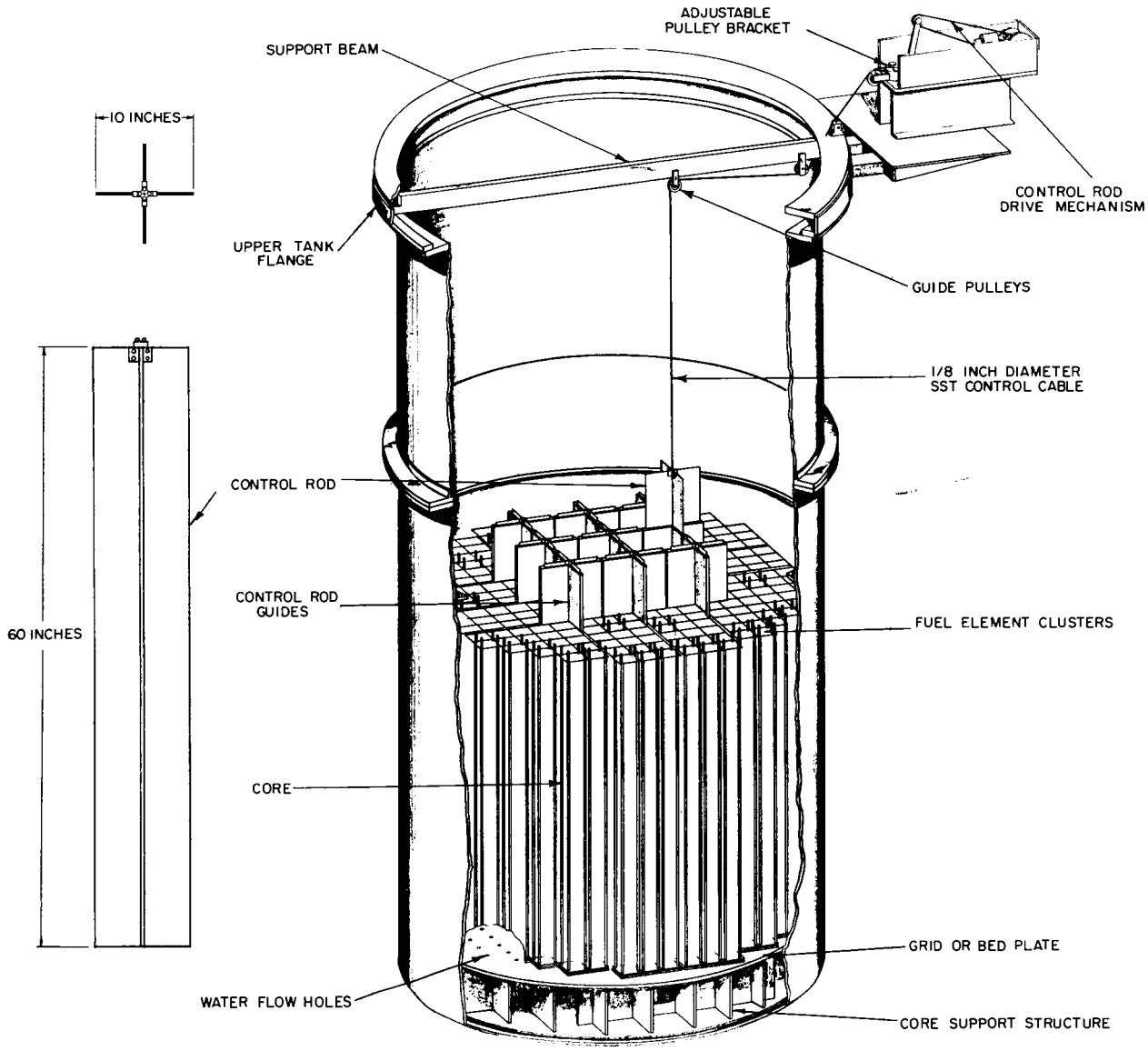

Figure 1. Cutaway view of tank showing core and control mechanism.

Here attention will be directed primarily to results from several methods used to determine the neutron age and resonance escape probability. Certain ancillary data required for interpretation of these measurements, such as reflector savings, buckling, disadvantage factor, and the inhour equation, will also be mentioned. The main body of data to be analyzed involves a series of fuel substitution experiments.

Fuel Substitution Experiments

Lattices containing various ratios of thorium to U^{235} have been constructed with the two available types of thoria-urania fuel rods, i.e., having thorium to U^{235} atom ratios of 50:1 and 25:1. In the original cylindrical core having a lattice consisting of 836 25:1 fuel rods in a ¾-in. triangular spacing, 50:1 fuel rods have been substituted in increments up to a total of 208.

For each loading the critical D_2O level and the differential D_2O level worth have been measured. The critical D_2O level and U^{235} content of the lattices studied are listed in Table 1. Certain additional data are required for the interpretation of the results of loadings 63 to 71.

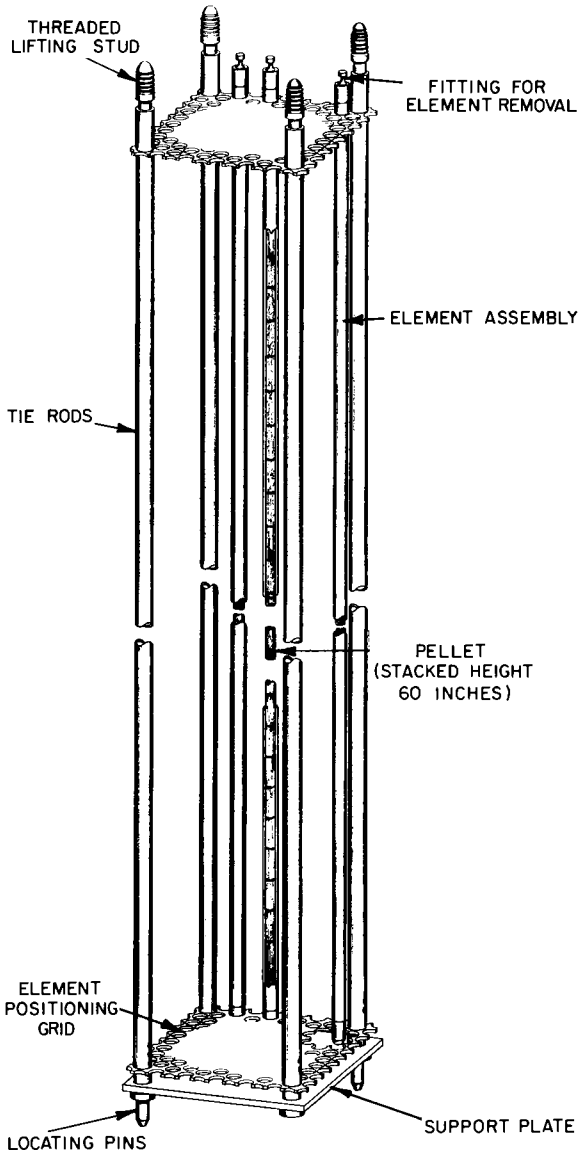

Figure 2. Fuel cluster.

B_g^2 From Clean Criticals

The geometrical buckling for a ¾-in. triangular lattice of 25:1 thorium to U^{235} fuel rods was determined from a sequence of seven clean criticals. All the systems had cylindrical geometry and were completely reflected except at the top. The reflector was always of constant outer diameter, fixed by the 6¾-ft internal diameter of the core tank. The bottom reflector consisted of 12 in. of a mixture of aluminum and heavy water containing a trace of stainless steel and void.

The term "clean" as applied to these criticals requires some qualification. The loading pattern used in a standard cluster is shown in Figure 3. Each contains 28 fuel rods, but no void tubes. Also shown are representative boundaries as defined by the peripheral rods in specific critical assemblies. Note that the water channels associated with the control rod pattern contribute a certain structure deviating from an ideal lattice and making a smooth periphery difficult to achieve at times. Repetition of the standard 3⅞-in.^{2} cluster on a 4-in. center contributes to a lesser extent to the inhomogeneity.

In Table 2 are summarized the critical dimensions for the seven assemblies constructed in this sequence of experiments. The number of rods for each loading is given and the computed area per rod. For an ideal ¾-in. triangular pattern, the cell area is 0.49 in.^{2}. If one assumes a unit cell composed of nine clusters and one half of each of the bounding water channels, a figure of 0.645 in.^{2}/rod results. This agrees favorably with the actual values shown in Table 2.

The defining equation for the geometrical buckling of a cylindrical system and its partial derivatives with respect to the height and radius can be combined to yield the following relation:

$$H_c = \frac{\pi}{B_g}\sqrt{1+\left(\frac{2.405}{\pi}\frac{\delta H}{\delta R}\right)^{2/3}} - (\lambda_{H_1}+\lambda_{H_2}).$$

This is the equation for a straight line of π/B_g slope and $(\lambda_{H_1}+\lambda_{H_2})$ intercept.

In the initial treatment of the clean critical data this equation was used to determine the geometrical buckling and axial reflector savings. Values of $\bar{H}_c$ and

$$\sqrt{1+(2.405\Delta H_c/\pi\Delta R_c)^{2/3}}$$

from successive pairs of observations were plotted and are shown in Figure 4. The straight line drawn through these points yields a value of 1.89×10^{-3} cm^{-2} for B_g^2 and 9.0 in. for $\lambda_{H_1}+\lambda_{H_2}$. The scatter in the points is due primarily to difficulty in establishing the actual core radii. Implicit in this treatment of the clean critical data is an assumption that the reflector savings are independent of core dimensions.

Reflector Savings

Actually the graphical determination of the geometrical buckling was assisted by supplemental knowledge of the axial reflector savings.

Table 1

Critical Data for Fuel Substitution Experiments

Loading	Critical height, in.	No. of 50:1 fuel rods	Mass U^{235}, kg	
			50:1	25:1
63	45.07	30	0.1795	9.618
64	46.87	64	0.3833	9.211
65	48.73	96	0.5747	8.828
66	50.36	120	0.7183	8.541
67	55.15	176	1.0536	7.873
68	58.29	208	1.2450	7.512
69	46.58	60	0.3535	9.313
70	45.15	32	0.1916	9.639
71	43.71	0	0	10.027

Total No. of fuel rods=836
Core radius=12.70 in.

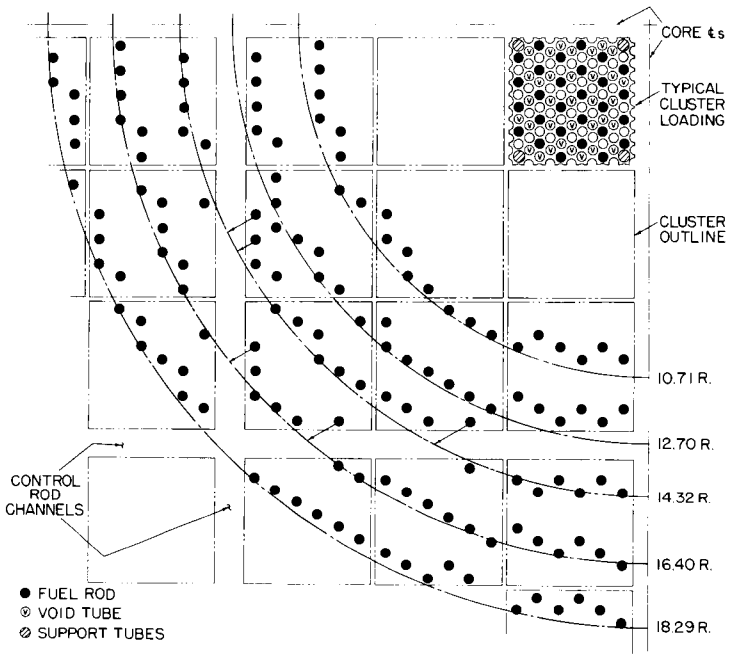

Figure 3. Outline of representative cores and typical cluster loading.

The scatter of the points in Figure 4 would not permit a unique determination of the reflector savings, and so the results of seven axial flux plots were analyzed to yield a knowledge of the axial reflector savings. A cosine function was fitted to the bare minus cadmium-covered response of a U^{235} fission counter moved along a line parallel to the core axis by processing of these data on the AVIDAC. Figure 5 illustrates the fitting of one such set of data. The treatment of seven such sets of data yielded a value of 9.0±1.0 in. for the axial reflector savings for a core having only a bottom reflector. This information was used as a starting point for the straight line drawn in Figure 4. The corresponding radial reflector savings is 13.2 in.

Relation Between Period and Reactivity

The inhour curve applicable to cores of the THUD type has been calculated from the absolute

Table 2

Summary of Clean Criticals

Loading No.	No. of fuel rods	Radius, in.	Height, in.	Area/rod, in.^{2}
6	568	10.71	60.00	0.635
10	629	11.17	54.00	.624
12	688	11.65	49.67	.620
13	748	12.09	46.73	.614
14	836	12.70	43.11	.605
15	924	13.60	40.00	.630
16	1012	14.38	37.51	.642

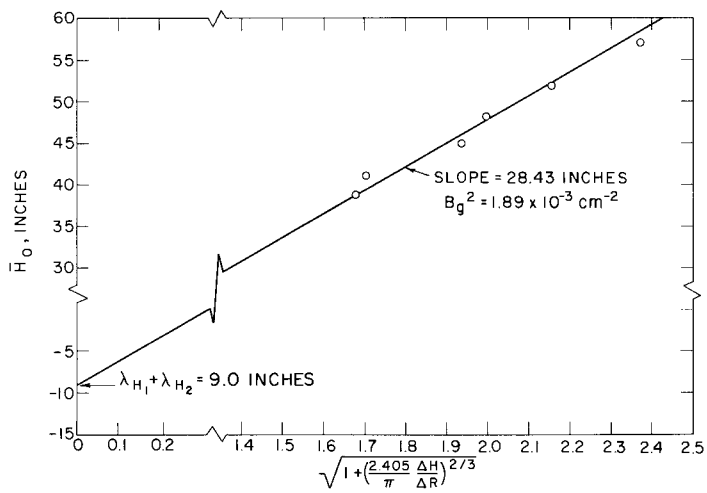

Figure 4. Graphical determination of B_g^2 and λ_H.

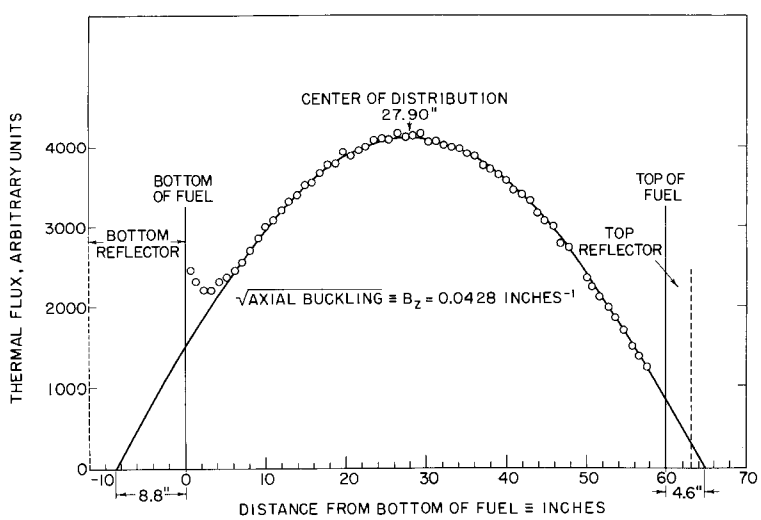

Figure 5. Determination of reflector savings from flux distribution.

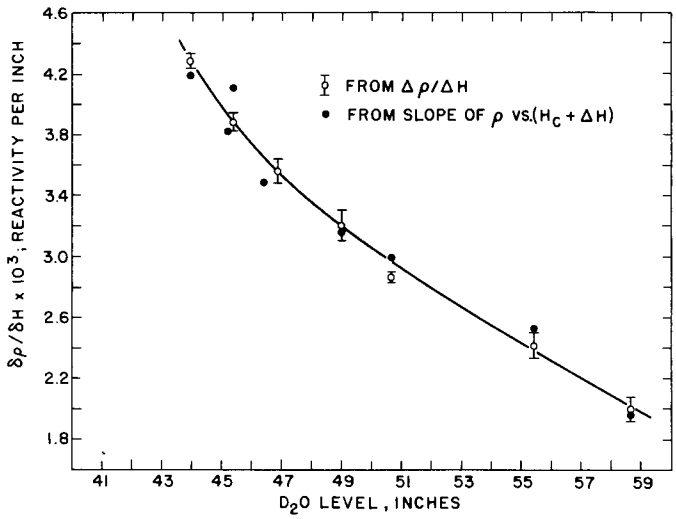

Figure 6. Differential water level worth in fuel substitution experiments.

yields and half-lives of delayed neutrons from thermal fission in U^{235} reported by Keepin et al.,[4] the relative yields and half-lives of photoneutrons from fission products in heavy water reported by Bernstein et al.,[5] and the ratio of 0.100 between total photoneutrons and total delayed neutrons found by fitting the observed neutron intensity after the shutdown of the THUD reactor by insertion of a control rod. This method provides a convenient means to account for the absorption of the photoneutrons: production of gamma-rays by the fuel. (For infinite dilution of U^{235} in D_2O, $\beta_{\gamma-n}/\beta_{\text{delayed}} = 0.159$.) The absolute yields of the delayed neutrons are also corrected by a factor of 1.09 to account for the lower probability of epithermal leakage of delayed neutrons as compared to prompt for the THUD core.

Values for f and L^2

The thermal utilization and thermal diffusion area have been calculated for the various fuel mixtures existing in loadings 63 to 71. These calculations are based on a preliminary experimental value of 1.19 for the moderator to fuel thermal flux ratio, a theoretical flux peaking of 1.3 in the control rod channels, and an assumed flux ratio of unity between the 50:1 and 25:1 fuel rods.

NEUTRON AGE FROM FISSION TO THERMAL ENERGIES

Two independent methods have been employed to establish experimentally the neutron age for the THUD system. One involves the measurement of the differential worth of the core near criticality and the other results from an analysis of the fuel substitution criticals. The results are in pronounced disagreement, but the latter value agrees well with the calculated age.

τ From $\Delta\rho/\Delta H$

The reactivity worth of an increment of core at criticality was measured for each of the criticals listed in Table 1. After criticality was established, the positive period associated with a small increase in water height was observed and converted to reactivity through an inhour equation based on the yields and periods of delayed neutrons and photoneutrons. These results are summarized in Figure 6. Each value of $\Delta\rho/\Delta H$ is based on at least two determinations, as determined in one of two ways. For each critical, $\Delta\rho/\Delta H$ was determined both from the average of the separate observations and from the slope of a plot of the reactivity as a function of the control height plus the increment in water level. Both methods appear to have comparable precision, but together they yield a more accurate determination of variation in differential reactivity with water height.

The treatment of these data to yield information on the migration area, and hence the age, was based on an equation derived in the following manner:

$$\frac{\delta\rho}{\delta H} = \frac{\delta k}{\delta B^2} \cdot \frac{\delta B^2}{\delta H} \cdot \frac{\delta\rho}{\delta k}.$$

Table 3

Age Determination by Differential Water Worth

Loading	$\bar{H}$, in.	$(\bar{H}+\lambda_H)^3$, in.$^3\times10^{-5}$	$\Delta\rho/\Delta H$, in.$^{-1}\times10^3$	M'^2, in.^{2}	L^2, in.^{2}	$L^2/(1+L^2B^2)$, in.^{2}	τ, in.^{2}
65	48.98	1.949	3.20	31.59	4.350	4.14	27.45
66	50.66	2.123	2.99	32.16	4.401	4.19	27.97
67	55.43	2.674	2.41	32.65	4.524	4.31	28.34
68	58.65	3.096	2.00	31.37	4.586	4.37	27.00
69	46.87	1.744	3.56	31.45	4.256	4.05	27.40
70	45.37	1.607	3.88	31.59	4.202	4.00	27.59
71	43.96	1.485	4.29	32.27	4.138	3.94	28.33

From the two-group age-diffusion theory relation for criticality,

$$k=\frac{k_\infty e^{-B^2\tau}}{1+B^2L^2}, \quad \frac{\delta k}{\delta B^2}=-k\left(\tau+\frac{L^2}{1+B^2L^2}\right).$$

From the geometrical buckling for a cylindrical critical assembly,

$$B^2=-(\pi/H)^2+(2.405/R)^2, \quad \delta B^2/\delta H=-2\pi^2/H^3.$$

The definition of reactivity

$$\rho=(k-1)/k$$

yields

$$\delta\rho/\delta k=1/k^2.$$

Substitution of the expressions for these three derivatives in the first equation gives

$$\frac{\delta\rho}{\delta H}=\frac{2\pi^2}{H^3k}\left(\tau+\frac{L^2}{1+B^2L^2}\right)$$

or

$$M'^2=\tau+\frac{L^2}{1+L^2B^2}=\frac{k(H+\lambda_H)^3}{2\pi^2}\,\frac{\delta\rho}{\delta H}.$$

Here $k=1$. The evaluation of τ is shown in Table 3. An average value of $\tau=27.7\pm0.3$ in.^{2} results.

τ From Fuel Substitution

The age has also been determined from the critical heights observed in the fuel substitution experiments, combined with the calculated values of the thermal utilization and the thermal diffusion area.

The age-diffusion equation

$$\eta f p=e^{\tau B^2}(1+L^2B^2)$$

may be written in the form

$$\ln[f/(1+L^2B^2)]=\tau B^2-\ln(\eta p\varepsilon).$$

If $\ln[f/(1+L^2B^2)]$ is plotted as a function of B^2, the slope will give the neutron age. Note also, for subsequent use, that the intercept, $\ln(\eta p\varepsilon)$, involves the resonance escape probability.

The determination of the age (and resonance escape probability) in this manner is indicated in Table 4 and Figure 7. A value of $\tau=22.96$ in.^{2} results.

Comparison with Theory

The values 179 and 148 cm^2 for the neutron age, as obtained from the water level reactivity and fuel substitution methods respectively, differ by far more than can be explained on the basis of experimental errors. Consequently it is of interest to compare these values with the calculated age for the THUD system.

The volume percentages of the various constituents of the THUD core are 83.8% D_2O, 6.7% fuel (mainly ThO_2), 9.0% Al, and 0.5% void.

Table 4

Determination of Age and Resonance Escape Probability

Loading	B^2, in.$^{-2}$	f	$-\log[f/(1+L^2B^2)]$
63	0.012132	0.76418	0.13843
64	.011918	.76038	.14060
65	.011717	.75669	.14267
66	.011557	.75385	.14426
67	.011154	.74696	.14805
68	.010935	.74296	.15029
69	.011951	.76108	.14013
70	.012121	.76408	.13843
71	.012308	.76755	.13643

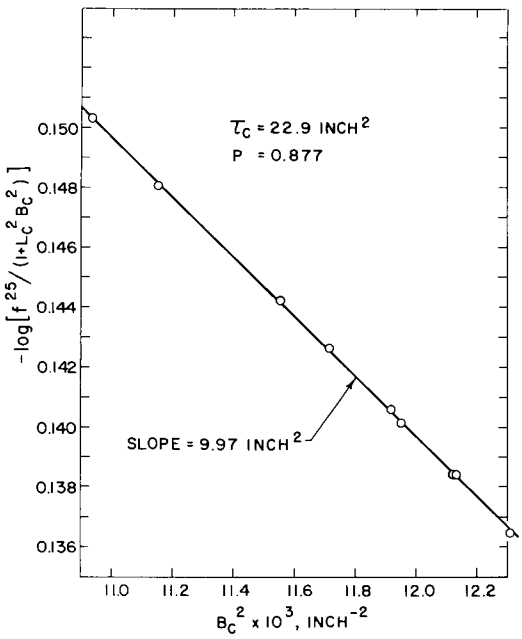

Figure 7. Graphical determination of core age and resonance escape.

The age for aluminum-heavy water mixtures has been calculated by the Weinberg modification of the Fermi method.

For aluminum to D_2O volume ratios up to 0.9, the results are well fitted by an expression of the form $\tau = 125.0 + 191 V_{Al}/V_{D_2O}$.

Tobias[6] has made similar calculations for mixtures of ThO_2 and D_2O.

If it is assumed that the small portion of uranium oxide behaves as thorium oxide, a value of $\tau = 128$ cm^2 is obtained for the THUD ratio of fuel to D_2O from the latter calculation. The effect of the 0.5% void is to increase this to 129.5 cm^2. Use of the value 0.107 for the aluminum-heavy water ratio in the expression given above increases this value to 151 cm^2. This is in good agreement with the value determined from the fuel substitution experiment.

Rather drastic assumptions are required to achieve a theoretical age comparable with that obtained from the water level reactivity data. For example, if it is assumed that both the fuel and the aluminum act as voids, the age would be 178 cm^2.

RESONANCE ESCAPE PROBABILITY

Values of the resonance escape probability for the ¾-in. triangular lattice have been obtained by foil activation and analysis of the fuel substitution experiments. Good agreement results between the directly measured value and that derived from the graphical analysis of the substitution experiments. However, as will be seen in the next section, there is an inconsistency between these values and those based on various measurements of the effective resonance integral of Th and ThO_2.

p By Foil Activation

The resonance escape probability has been measured directly by activation of bare and cadmium-covered thorium foils within the fuel rods. One-mil-thick, 0.230-in.-diameter foils wrapped in ½-mil aluminum have been inserted between fuel pellets for a direct measurement of the thermal plus epithermal absorption of neutrons by thorium. A sleeve and discs of 0.011-in. cadmium surrounded the foil and two adjacent fuel pellets for the determination of epicadmium capture. The capture rates have been determined by measuring the activity of the Th^{233} produced. Two bare and two cadmium-covered foils were irradiated simultaneously in symmetric positions in each of several determinations.

The 100-kev x-ray peak associated with Th^{233} decay has been observed with a single-channel scintillation detector. The activity of these foils was followed over a minimum of three half-lives, and the background correction was derived from an unactivated foil. Originally chemical separation of the thorium from its daughter and descendant activities was done prior to irradiation, but rapid build-up of this activity made the use of a higher nvt the preferable procedure. Typical net counting rates at the end of the activation are 26,100 counts/min for the bare foil and 12,370 for the cadmium-covered. The resonance escape probability is calculated directly from the following equation:

$$p = \left[1 + \frac{\Sigma_a^{(Th)}/\Sigma_{a\ \text{thermal}}^{(\text{total})}}{\text{C.R.} - 1} \cdot \frac{\exp(-B^2\tau_R)}{1 + L^2B^2}\right].$$

For the THUD system the fraction of thermal captures by thorium is 0.20, and the combined subresonance and thermal nonleakage factor is 0.91. Substitution of these values and the activities given above yields a value of 0.859 for p. This is the average obtained from the foil measurements to date.

Table 5

Calculation of Resonance Escape Probability

Loading	H, in.	λ_H, in.	B^2, in.$^{-2}$	τ, in.^{2}	L^2, in.^{2}	k_∞	ηf	p
63	45.07	9.0	0.012132	27.7	4.216	1.471	1.584	0.928
64	46.87	9.0	.011918	27.7	4.284	1.462	1.576	.928
65	48.73	9.0	.011717	27.7	4.350	1.454	1.568	.927
66	50.36	9.0	.011557	27.7	4.041	1.447	1.562	.926
67	55.15	9.0	.011154	27.7	4.524	1.430	1.548	.924
68	58.29	9.0	.010935	27.7	4.586	1.421	1.539	.923
69	46.58	9.0	.011951	27.7	4.256	1.463	1.578	.927
70	45.15	9.0	.012121	27.7	4.202	1.470	1.584	.928
71	43.71	9.0	.012308	27.7	4.138	1.478	1.591	.929

Radial buckling$=B_R^2=0.0087557$ in.$^{-2}$

p From Fuel Substitution Experiments

From the average value of the core age determined by the differential D_2O level worths, and the theoretical values for f, η, and L^2, the resonance escape probability has been calculated from the age-diffusion criticality equation for each lattice studied. This determination, indicated in Table 5, yields a mean value of 0.927.

In addition to this analysis, a resonance escape probability of 0.877 was obtained from the intercept of the curve in Figure 7 at zero buckling, with a value of 2.073 for η and 1.00 for ε.

Comparison of Values for p

For convenience in comparison, the various determinations of the resonance escape probability are summarized below:

Foil Activation	
Direct	0.859
Corrected for epicadmium $1/v$	0.885
Fuel substitution experiments	
With τ from water worth data	0.927
Graphical analysis	0.877

The value of resonance escape probability determined from Figure 7 is in good agreement with that obtained from the thorium foil activation measurements when a correction is made for the $1/v$ component of resonance capture in thorium. The value of p determined by use of the age found from water level worth is about 6% higher than that from the foil activation measurement. Recall, however, that the age from the water worth experiments was appreciably higher than the theoretical and other experimental values.

It should be mentioned that the age determinations in the fuel substitution experiment are dependent on the axial reflector savings, but independent of the radial reflector savings. The resonance escape probability, however, is dependent on both these values. With an assumed uncertainty in the radial reflector savings of ± 1 in., the uncertainty in p would be about ± 0.020 in the water worth method and ± 0.016 in the graphical determination.

EFFECTIVE RESONANCE INTEGRAL

Several experimental determinations have been made of the effective resonance integral for thorium and thorium oxide with which the values inferred by the measurements discussed in the preceding section may be compared. These include results from an evaluation of measurements prior to 1955,[7] from foil activation in lattice cells,[8] from reactivity coefficient measurements on a variety of samples,[9] and from measurements in progress within the THUD system.

Current Measurements

The effective resonance integral for ThO_2 is being measured by pile oscillator techniques in the THUD critical. Six samples of thorium oxide, having a range of surface to mass ratio from 0.43 to 1.74, have been oscillated in a 0.63-in.-i.d. aluminum tube wrapped with 11 mils of cadmium in a 56-in.-high core. This tube displaced one fuel rod in the ¾-in. triangular lattice, near the axis of the critical assembly.

A stroke of 33 in. moved the sample in continuous linear motion from the center of the reac-

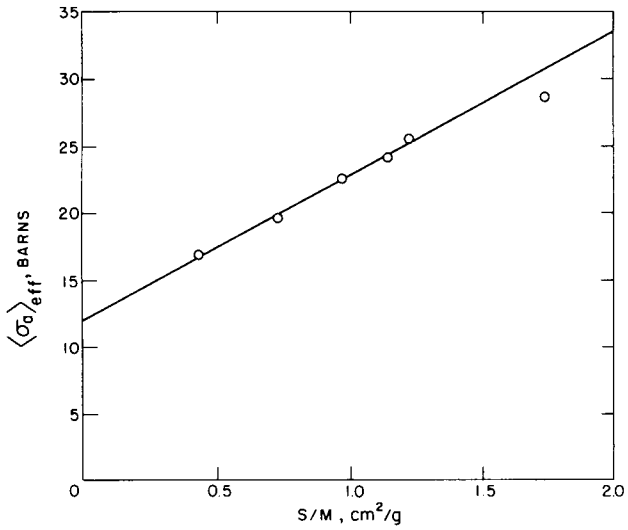

Figure 8. Effective resonance integral of ThO_2 as a function of surface to mass ratio ($1/v$ contribution included).

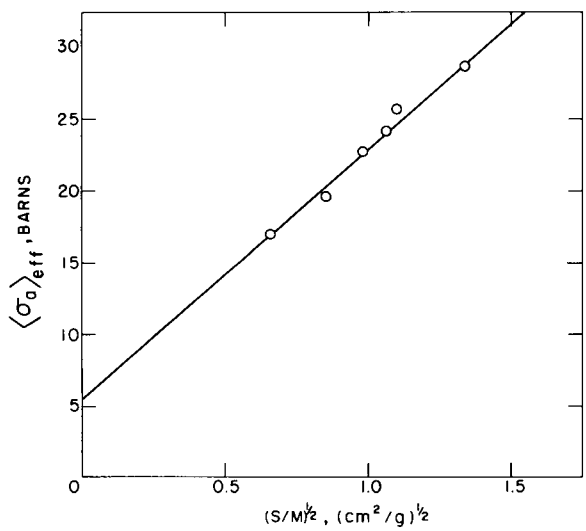

Figure 9. Effective resonance integral of ThO_2 as a function of square root of surface to mass ratio ($1/v$ contribution included).

tor to a position slightly above the top, and back, at a rate of one cycle each 20 sec, for a minimum of 50 cycles. Four B^{10} coated ion chambers provided a signal to a vibrating-reed electrometer as a measure of the fluctuating flux level in the reactor. A bucking voltage of the order of 1 v was used to achieve a highly amplified strip-chart recording of the fluctuation in the pile power. Five samples of varying thicknesses of boron on an aluminum backing and an aluminum blank were also oscillated to provide a standardization. Two samples of indium-aluminum alloy were also oscillated.

The resulting fluctuations in flux level were analyzed on an IBM-650 to determine the amplitude of the reactivity swing associated with each sample. The results for the boron samples have been extrapolated to the effect of a sample of zero thickness for normalization. Preliminary results for the ThO_2 samples plotted as a function of surface to mass ratio and its square root are shown in Figures 8 and 9 respectively.

These results should be considered provisional for several reasons. The boron samples are currently being analyzed both chemically and mass-spectrometrically to establish the actual B^{10} content. A check on the normalization with the indium results has not yet been made. The experimental conditions resulted in a sample shielding by adjacent fuel rods characteristic of the THUD system, but the data have not yet been corrected for this or for the effect of reduction in shielding of the adjacent elements by removal of the sample.

Other Determinations of RI_{eff}

A form

$$RI_{eff} = A\left[1 + \frac{B}{\frac{M}{S}\cdot\frac{1}{1-c} + D}\right]$$

is commonly used to fit the experimental measurements. In Table 6 are summarized several sets of reported values for these constants. The values determined for thorium metal have been modified to account for the additional scattering due to the presence of O_2 and U in the THUD fuel. However, the resonance capture in $U^{238}O_2$ was neglected. The Dancoff correction factor for the ¾-in. THUD lattice is $(1-c)=0.843$.

Comparison

The various values of resonance escape probability determined in the THUD critical experiments have been converted to resonance capture integrals, assuming unity resonance disadvantage factor, with the following results:

Method	RI_{eff}
Foil activation	
Direct	17.64
Corrected for epicadmium $1/v$	13.94
Fuel substitution experiments	
With τ from water worth data	8.80
Graphical analysis	15.23

Table 6

Constants in $RI_{eff} = A\left[1 + \frac{B}{\frac{M}{S}\cdot\frac{1}{1-c} + D}\right]$

	Macklin and Pomerance[7]		Sher[8]		Dayton and Pettus[9]	
	Th	THUD Fuel	Th	THUD Fuel	ThO_2	
A	8.37	10.27	7.5	9.619	10.4*	−0.1**
B	0.55	0.5114	3.4	3.304	2.64*	352 **
D	0.08	0.0885	0.34	0.4332	0 *	0 **

*$RI_{eff} = A\,[1 + B\,(S/M_{Th})(1-c)]$.

**$RI_{eff} = A\,[1 + B\sqrt{S/M_{Th}}\,(1-c)]$.

The $1/v$ contribution of 3.7 barns, applied to the foil activation value, is based on a thorium thermal cross section of 7.4 barns and a cut-off energy of 0.40 ev for 11-mil cadmium.

For comparison, a calculation of the effective resonance integral predicted by the various direct measurements was made for a ThO_2 mass to surface ratio of 1.28 g/cm^2 and a shielding factor of 0.843. The results were:

Source	RI_{eff}
Macklin and Pomerance[7]	13.5
Current THUD, S/M	16.7
Sher[8]	25.9
Dayton and Pettus,[9] S/M_{Th}	28.3
Dayton and Pettus, $\sqrt{S/M_{Th}}$	25.0

All values exclude the $1/v$ contribution. It is not known whether Sher's values for A, B, and D are derived from data corrected for shielding by adjacent fuel, but it has been so assumed in the above evaluation.

The various values for the effective resonance integral for the THUD fuel lattice may be divided into two groups, the values in one being approximately twice as large as those in the other. The values derived from the THUD criticals, namely 13.9 from foil activation, 15.2 from fuel substitution experiments, and the provisional value of 16.7 from oscillator measurements, are in reasonable agreement among themselves and with the Macklin and Pomerance evaluation. However, the agreement between the recent Brookhaven[8] and Babcock & Wilcox[9] measurements, at the higher values, leaves the present knowledge of the effective resonance integral for thorium fuels in a very confused state.

CONCLUSION

The material presented here should be considered as a status report on certain phases of a current program. Only the raw experimental data reported here should be considered as final results, and these might be supplemented by the results of further experimentation. Values derived from these data should be viewed as tentative. The data analysis presented here has been introduced primarily to reveal the extent to which the experimental values are consistent, internally and with other existing data.

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Criticality Data on Metal U^{233} Spherical Systems

E.A. Plassman and D.P. Wood
Los Alamos Scientific Laboratory, Los Alamos, New Mexico

Table 1

Criticality Data

I.	2.41-kg ball:	U^{233}(98.2%); ρ(total)=18.45 g/cm^3; radius=1.239 in.
	1) reflector :	1.887-in. Oy(93.8%) at $\rho = 18.8_0$ g/cm^3
II.	10.0-kg ball:	U^{233}(98.25%); $\rho = 18.63$ g/cm^3; radius=1.986 in.
	1) reflector :	0.458-in. Oy(93.8%) at $\rho = 18.8_0$ g/cm^3
	2) " :	0.799-in. Be at $\rho = 1.83$ g/cm^3
	3) " :	0.885-in. U at $\rho = 18.92$ g/cm^3
	4) " :	0.942-in. W alloy(91.3 wt %) at $\rho = 17.21$ g/cm^3

Table 2

Predicted vs Observed Critical Dimensions

			Observed radius, cm		Predicted radius, cm	
			Core	Total	Core	Total
I.	2.41-kg ball	1) Oy reflector	3.15	7.94	3.13	7.91
II.	10.0-kg ball	1) Oy reflector	5.04	6.21	5.05	6.21
		2) U reflector	5.04	7.29	5.01	7.24

Table 3

Six-Group Cross Sections for U^{233} in Barns

	Group					
	1	2	3	4	5	6
E_n range (Mev)	0–0.1	0.1–0.4	0.4–0.9	0.9–1.4	1.4–3.0	3.0–∞
χ (fission spectrum)	0.014	0.090	0.180	0.168	0.344	0.204
ν	2.51	2.53	2.57	2.61	2.70	2.96
σ_f	3.23	2.24	1.94	1.89	1.83	1.75
σ_c	0.60	0.23	0.15	0.11	0.08	0.05
σ_{tr}	12.0	8.4	5.7	4.8	4.5	4.25
$\sigma_{i\to i}$	8.17	5.88	3.27	1.99	1.51	1.18
$\sigma_{i\to i+1}$	—	0.05	0.29	0.45	0.18	0.20
$\sigma_{i\to i+2}$	—	—	0.05	0.30	0.50	0.27
$\sigma_{i\to i+3}$	—	—	—	0.06	0.35	0.45
$\sigma_{i\to i+4}$	—	—	—	—	0.05	0.31
$\sigma_{i\to i+5}$	—	—	—	—	—	0.04

Data consisting of critical reflector thicknesses for 2.41-kg and 10.0-kg U^{233} metal spheres are summarized in Table 1.

Qualitatively, critical masses of U^{233} and δ-phase Pu are similar for similar reflectors. The unreflected critical mass of U^{233} (which should be close to

15 kg) is definitely less than that for δ-phase Pu (16.45 kg). For thick U reflectors the critical mass of U^{233} should be essentially the same as that of δ-phase Pu, namely 5.8 kg.

Six-group S_4 predictions are compared with observed results for the Oy* and U reflected cases in Table 2.

The multigroup parameters (still provisional) are consistent with current cross section data and are listed in Table 3. Although multigroup parameters for U^{235} and U^{238} were also involved in the predictions, it is sufficient to say that these parameters are also consistent with present cross section data and, in addition, properly predict critical dimensions of the LASL fast U^{235} – U^{238} mixed critical assemblies. The average $\nu(23)$ values predicted from Table 3 for the Topsy and Jezebel spectra are $\approx$2½% lower than those given by the reactivity coefficient data.

*Oralloy-enriched uranium.

Reactivity Coefficient Data on U^{233} in Fast Critical Assemblies

G.E. Hansen
Los Alamos Scientific Laboratory, Los Alamos, New Mexico

Table 1

Reduction to ν Values

	Topsy	Godiva	Jezebel
$(\nu-1-\alpha)\sigma_f(49)/(\nu-1-\alpha)\sigma_f(25)$	1.94±0.02	1.92±0.02	1.96±0.02
$(\nu-1-\alpha)\sigma_f(23)/(\nu-1-\alpha)\sigma_f(25)$	1.73±0.02	—	1.70±0.02
$(\nu-1-\alpha)(49)/(\nu-1-\alpha)(25)$	1.39	1.36	1.36
$(\nu-1-\alpha)(23)(\nu-1-\alpha)(25)$	1.12	—	1.11
$(\nu-\alpha)(25)$	≡2.45	≡2.47	≡2.49
$(\nu-\alpha)(49)$	3.02	3.00	3.03
$(\nu-\alpha)(23)$	2.63	—	2.66
$\nu(25)$	2.56	2.58	2.59
$\nu(49)$	3.08±0.02	3.05±0.02	3.08±0.02
$\nu(23)$	2.70±0.02	—	2.72±0.02

The data presented here are reactivity coefficient ratios obtained at the centers of Topsy (U reflected Oy), Godiva (bare Oy), and Jezebel (bare Pu). Although noncentral reactivity coefficient data have been collected, they give negligible additional information on the spectrum-averaged production cross sections $(\nu-1-\alpha)\sigma_f$. The coefficients listed below have been corrected for sample size (this correction is relatively small and the correction procedure has been checked experimentally).

Reactivity coefficient ratio	Topsy	Godiva	Jezebel
$\Delta K(49)/\Delta K(25)$	$1.93\pm0.01_5$	$1.91\pm0.01_5$	$1.98\pm0.01_5$
$\Delta K(23)/\Delta K(25)$	$1.72\pm0.01_5$	–	$1.71\pm0.01_5$

These data may be reduced with little loss of accuracy to yield production cross section ratios (by computing out "inelastic" contributions), with further loss of accuracy to yield $(\nu-1-\alpha)$ ratios (through computed fission cross section ratios). Thence, using an absolute value of $(\nu-1-\alpha)$ for U^{235} obtained via Godiva critical mass and current fission and scattering cross sections, one may obtain $(\nu-1-\alpha)$ values for U^{233} and Pu^{239}. In the case of Pu^{239}, a consistency check is available through the critical mass of Jezebel. Since $\alpha(Pu^{239})$ is known to be small in the fast spectra here involved, and $\alpha(U^{233})$ may be presumed similarly small, one finally obtains average ν values. This series of reductions is given in Table 1, the listed uncertainties corresponding only to that propagated by the initial uncertainties in production cross section ratios.

The flux-weighted average neutron energies in the centers of Topsy, Godiva, and Jezebel are computed to be 1.40, 1.47, and 1.67 Mev, respectively. If it is assumed that fission cross section data are good to 3% when used in ratios, then an additional ±0.06 is added to the above $\nu(49)$ and $\nu(23)$ values. Nearly seven years ago, on the bases of the Topsy reactivity measurements and $[\sigma_f(23)/\sigma_f(25)]$ Topsy measurements by L.L. Lowry, it was concluded that $(\nu-\alpha)(23)=2.60$ with the assumption $(\nu-\alpha)_{Oy}=2.46$. In the present work it seemed advisable to use computed fission ratios, since fission ratio data for the various ele-

ments in the fast critical assemblies exhibit spreads somewhat greater than the uncertainties in the basic fission cross section data. The $\nu(49)$ values listed above are consistent with the Jezebel critical mass, but the $\nu(23)$ values are $\approx 2\frac{1}{2}\%$ higher than that suggested by the metal U^{233} criticality data.

Physics Design of the AMF-CCBR

OTTO A. SCHULZE
American Machine & Foundry Company, Greenwich, Connecticut

INTRODUCTION

The American Machine and Foundry Company has designed a 58-Mw (heat) natural circulation, boiling water reactor to operate at 900 psi. This paper will be concerned with some of the physics design aspects of the core and their influence on the thermal design and on the economics of the plant. Figure 1 is a cutaway view of the core and pressure vessel.

FUEL

The fuel consists of a mixture of thoria and urania in the form of pellets in zirconium tubes. The nominal composition is 25% UO_2 and 75% ThO_2 by weight with an average U^{235} content of 9% of the uranium. Nominal dimensions of the pellets are 0.445-in. diameter by 0.445-in. height in a Zircaloy tube 0.500 in. o.d. and 0.450 in. i.d. The volume between pellets and tube is occupied by helium. Figure 2 shows the fuel element assembly.

SELECTION OF FUEL AND STRUCTURAL MATERIAL

The selection of the fuel material was governed to a large extent by the fuel operating economics. Thorium is converted to fissionable U^{233} by the thermal and resonance capture of neutrons. If a large percentage of the neutrons available from fission can be captured in thorium, a significant amount of free fuel can be obtained for sustaining the reactor operation over a longer period of time without refueling. To this end, it is desirable to achieve as high a conversion ratio as possible within the over-all design limits. Calculated conversion ratios obtainable for various fuel and cladding materials for cores meeting the thermal design objectives are given in Table 1. The urania content of the fuel was selected as 25 wt % so that the export limit of 20% on U^{235} enrichment would not be exceeded.

In addition to consideration of neutron economy, the fuel mixture was chosen on the basis of metallurgical properties. The UO_2-ThO_2 ceramic fuel mixture is dimensionally stable under irradiation and inert to chemical attack by degassed water and steam. Moreover, it is completely isotropic with respect to processing and fabricating history and undergoes no allotropic phase change up to the melting point. This is true over the full range of composition of the ThO_2-UO_2 system.

Another factor in the basic stability of the ThO_2-UO_2 fuel material is its complete resistance to oxidation in air at temperatures up to 3270°F. Sintering of the oxide mixture during manufacture forms solid solutions which effectively eliminate the further oxidation of UO_2, whereas in a straight UO_2 nuclear fuel the UO_2 will convert to higher oxides in the presence of air at temperatures above 260°F. This oxidation is accompanied by rather large volume changes and is rate-dependent on the temperature and the amount of oxygen available. In terms of a nuclear reactor, this means that a cladding failure may be progressive in the case of UO_2 but not in the case of UO_2-ThO_2.

The maximum steady-state fuel center temperature was set at 4100°F or 70% of the melting point temperature. This value was selected as a safe operating maximum in view of standard refractory practice in many metallurgical processes where homologous temperature of ceramic components as high as 85 to 90% of the melting temperature is commonly used. It is further felt that the 1000° differential between the maximum steady-state temperature and the original sintering temperature of the fuel will not result in sufficient additional shrinkage of the high density fuel to affect heat transfer functions adversely. Thus, the fuel will be worked to a reasonable degree of its maximum capability while an adequate margin of safety is maintained for transient conditions and

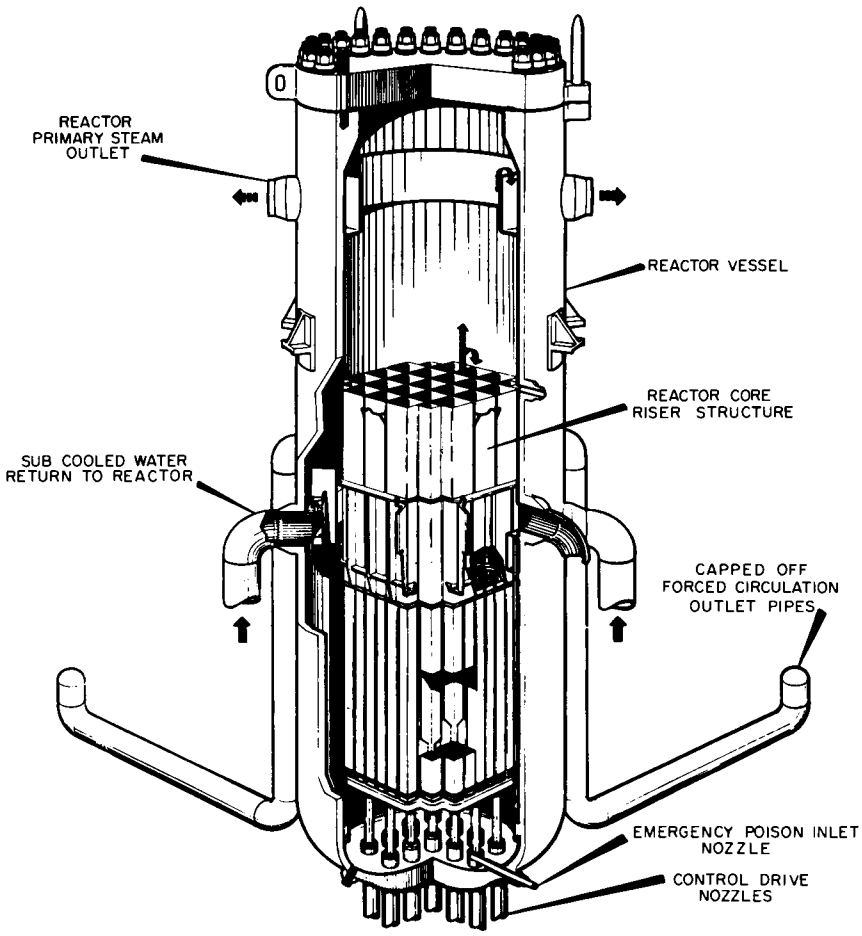

Figure 1. Closed cycle boiling water reactor: reactor vessel and core structure.

allowable manufacturing variations. Melting temperatures of various UO_2-ThO_2 mixtures are given in Table 2.

The reference density for the fuel components has been set at 93% of theoretical, since this value is a practical balance between the cost of manufacture on one hand and optimum performance characteristics, i.e., increased fission gas retention and decreased water absorption, on the other.

The selection of Zircaloy cladding material for the core design was based upon improved neutron economy. The stainless steel core requires a higher critical mass and wastes neutrons because of the high absorption cross section of stainless steel. As shown in Table 1, the conversion ratio may be improved if Zircaloy is used in comparison with stainless steel.

The material and fabrication costs for the stainless steel core would probably be lower than for the Zircaloy core at this time. However, improved production and fabrication techniques within the next few years should considerably reduce the cost of the Zircaloy core, whereas stainless steel costs will probably rise or, at best, remain constant.

CORE DESIGN

The reference core is a cylinder $\approx$5 ft in diameter and 5.5 ft high. It consists of a uniform distribution of 49- and 36-fuel-rod assemblies, 40 of each type of assembly. The square assemblies are 5.3 in. on a side. Control rod channels on 11.66-in. centers divide the core into clusters of four fuel assemblies as shown in Figure 3. The core contains 12 borated stainless steel cruciform rods of 10¼-in. span and ¼-in. thickness and four central hafnium cruciform rods of 10¼-in. span and ⅛-in. thickness. The core is capable of containing a total of

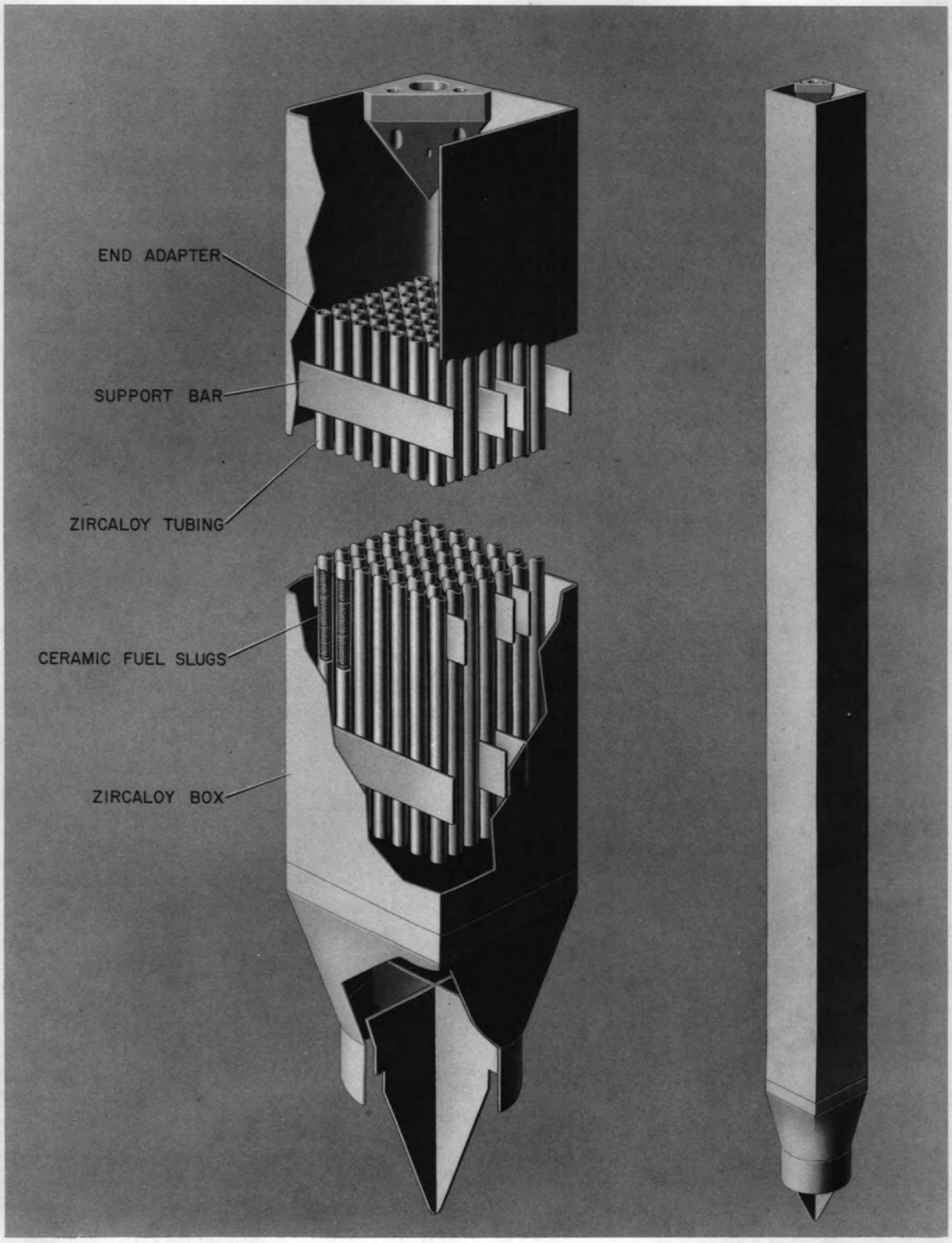

Figure 2. Rod type fuel element assembly.

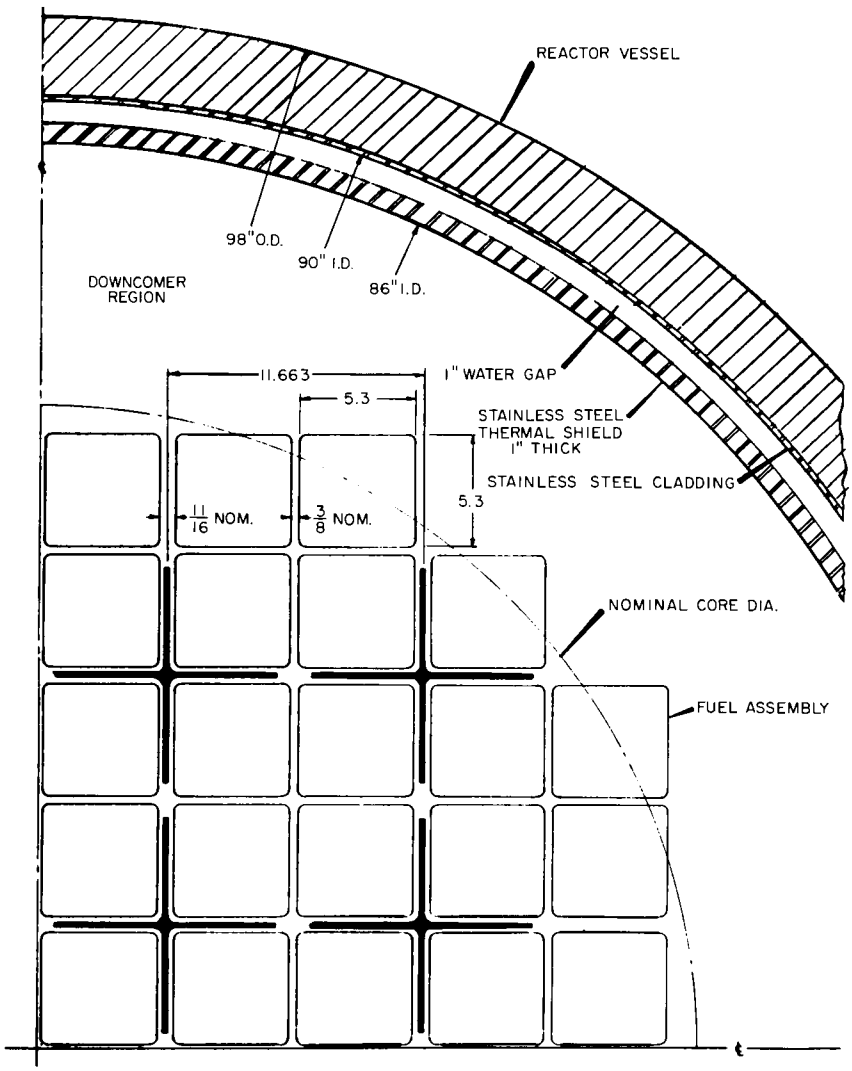

Figure 3. Reactor core cross section.

88 assemblies with sufficient downcomer area so that downcomer velocities are tolerable. The core is contained within a 7½-ft-i.d. pressure vessel 3¾ in. thick, clad on the inside with ¼-in. stainless steel. The total fuel rod complement in the core is 3400 rods, with fuel pellet diameters of 0.445 in. The core-averaged volume fractions of fuel, Zircaloy, and moderator are 0.2023, 0.0946, and 0.7031, respectively, with 11.2% of the moderator volume occupied by steam. Table 3 is a tabulation of the design data.

FLEXIBILITY

Because of the scarcity or inconsistency of nuclear data for this type of fuel, certain errors are expected in the critical mass and void coefficient calculations. If, for lack of money or time, no critical experiments are performed on a prototype, reasonable flexibility must be provided so that alterations in loading and void coefficient may be ef-

Table 1

Initial Conversion Ratio
(Water to fuel ratio=3.14)

Fuel material, wt %	Structure and cladding	ICR
25 UO_2 – 75 ThO_2	Zr	0.657
100 UO_2	Zr	0.568
100 UO_2	SS	0.412

Table 2

Melting Temperature of Fuel Mixtures

Fuel material, wt %	Melting temperature, °F
100 Urania	5210
75 Urania – 25 Thoria	5320
50 Urania – 50 Thoria	5630
25 Urania – 75 Thoria	5850
100 Thoria	5975

Table 4

Void Coefficients for Various Fuel Assembly Distributions

Core loading	Void coefficient, % $\Delta K/K$ per % void
40 "wet" inside + 40 "dry" outside	−0.068
40 "wet" + 40 "dry" uniformly dispersed	−0.090
40 "dry" inside + 40 "wet" outside	−0.148

Table 3

Design Data Tabulation

(1)	Volume Fractions of Core Materials:	
	Fuel	0.2023 (ThO_2 0.1475, UO_2 0.0426, CaO 0.0122)
	Zr	0.0946
	H_2O plus steam	0.7031
(2)	Fertile and Fissionable Material Content, kg:	
	U^{235}	104.8
	UO_2	1322
	ThO_2	4040
(3)	Fuel Properties:	
	Density of UO_2-ThO_2 mixture (25-75 wt %), g/cc	9.42
	Density of UO_2 (maximum theoretical), g/cc	10.96
	Density of ThO_2 (maximum theoretical), g/cc	9.68
	Fuel pellet diameter, in.	0.445
(4)	Moderator Properties:	
	Vapor fraction (averaged over fuel boxes and channels)	0.112
	Density of steam, lb/ft^3	2.04
	Density of H_2O, lb/ft^3	47.2
	Effective volume fraction of full density H_2O	0.4767
(5)	Core Size:	
	Average core radius (80 assemblies), cm	73.3
	Core height, cm	167.6
	Core volume, cm^3	2.83×10^6

fected without major redesign. Flexibility was achieved by choosing an arrangement of "wet" assemblies (36 fuel rods, water/fuel = 3.56) and "dry" assemblies (49 fuel rods, water/fuel = 2.25) with a nominal loading of 40 of each type uniformly dispersed in the core. In addition, two enrichments would be provided for each type of assembly so that the loading of fissionable material may be adjusted.

VOID COEFFICIENT

The void coefficient (% $\Delta K/K$ per % void in moderator) for the reference core (40 "wet" and 40 "dry" assemblies uniformly dispersed) was selected such that it was essentially zero in the cold, clean condition. At operating conditions, the coefficient is −0.09. Thus, with 11.2% average steam voids, the reactivity in steam will be about 1% $\Delta K/K$. Table 4 indicates the range in void coefficient obtainable with various loadings.

POWER DISTRIBUTION AND HOT SPOTS

The power distribution per fuel rod was investigated for various arrangements of the "wet" and "dry" assemblies. Although the "wet" assembly contains less fissionable material than the "dry"

Table 5

Maximum/Average Power Generation Factors
(Control rods all out)

	Flexibility	No flexibility
Radial (average void)	2.13*	1.77
Axial (average void)	1.43	1.43
Radial (nonuniform void correction)	0.90	0.90
Axial (nonuniform void correction)	1.03	1.03
Water channel (1-in. effective gap)	1.56	1.56
Enrichment	1.05**	1.00
Calculational model uncertainty	1.10	1.10
Mechanical tolerances	1.08	1.08
Total	5.5	4.35

*In "wet."
**Estimated.

because of flux peaking, it produces approximately the same power as a "dry" in an equivalent location in the core. Hence, the power production per rod is high in the "wet" assemblies with a maximum to average hot spot factor of 5.5 occurring in a "wet" assembly located in the core center. By placing 40 "dry" assemblies in the center, the maximum/average factor can be reduced to 3.9. However, this may be incompatible with the void coefficient requirements. A core with no flexibility and 49 rods of somewhat smaller diameter per assembly would have a calculated maximum/average power generation of 4.35. Table 5 lists the individual factors in the hot spot factor.

FUEL TEMPERATURE

The fuel temperature distributions were based on a thermal conductivity of the fuel mixture of 1.1 Btu/hr-ft-°F. This value was determined experimentally by using irradiated specimens of UO_2 in high thermal flux experiments. Experimental data on unirradiated samples of the 25 wt % UO_2 – 75 wt % ThO_2 fuel mixture have been made very recently. Preliminary analysis of the data indicates that the thermal conductivity will probably be greater than 1.1 Btu/hr-ft-°F for this fuel mixture at the operating temperature. Figure 4 indicates the maximum fuel rod center temperature as a function of the hot spot factor. The possible range obtainable in the flexible core is from 3540° to 4800°F, corresponding to hot spot factors of 3.78 to 5.5. The maximum temperature in the nonflexible core would be 3450°F with a hot spot factor of 4.35. The maximum temperature for a fuel rod consisting of two regions of equal area, but with the outer region having four times the heat generation of the center, was calculated. A significant reduction in center temperature was obtained as can be seen from Figure 4.

LONG-TERM REACTIVITY

The long-term reactivity study was based on a uniform exposure of the fuel throughout the reactor cycle. This assumption is justified if the fuel were to be circulated at various points during the cycle. Equations describing the $Th^{232} \rightarrow Pa^{233} \rightarrow U^{233} \rightarrow U^{234}$ chain, the $U^{235} \rightarrow U^{236}$ chain, and the $U^{238} \rightarrow U^{239} \rightarrow Np^{239} \rightarrow Pu^{239} \rightarrow Pu^{240} \rightarrow Pu^{241}$ chain, including fissions, were set up for computation on the AMF Datatron Computer. These equations were solved, with the average power

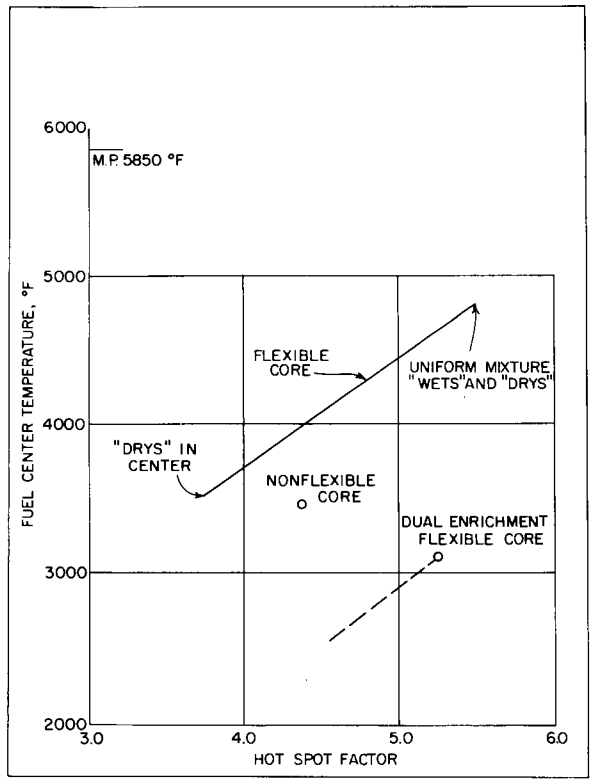

Figure 4. Maximum fuel temperature vs hot spot factor. $K_f = 1.1$ Btu/hr-ft-°F.

Table 6

Fuel Loading Scheme Employed in Long-Term Reactivity Studies

Cycle	Fuel section in core	Partially spent fuel section stored outside core	Spent fuel sections for reprocessing
1	ABCDE	—	—
2	aBCDE	A	—
3	abCDE	AB	—
4	abcAB	—	CDE
5	abcdA	—	BCDE
6	abcde	—	ABCDE
7	bcdef	—	aABCDE
8	cdefg	—	abABCDE

kept constant (the average thermal flux varies because of the variation of Σ_{fiss} with exposure), at exposure intervals of one month, to give a numerical description of the fuel constituents and the reactivity. The program yields, for each solution of the equations, the concentration (in atoms/cm^3) of Th^{232}, Pa^{233}, U^{233}, U^{234}, U^{235}, U^{236}, U^{238}, Pu^{239}, Pu^{240}, and Pu^{241}, and the reactivity available.

The cross sections used in the study were taken at the neutron energy (including spectrum hardening effects) at operating temperature, namely, 0.0592 ev. The nonsaturating fission product poisons were assumed to have an average cross section of 80 barns/fission.

The loading scheme used is given in Table 6. The capital letters indicate original core elements with an average enrichment of 9%, and the lower case letters indicate "spiked" elements of ≈12% enrichment.

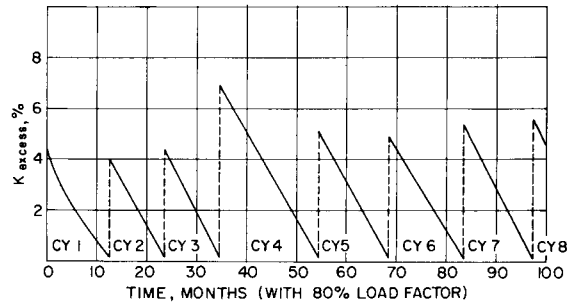

Figure 5. Long-term reactivity; 25-75 UO_2-ThO_2, Zr cladding; K_{excess} vs time for successive fuel cycles.

Figure 5 is a plot of K_{excess} versus time for the cycle studied. Note that the K_{excess} of cycle 4 is particularly high because (from Table 6) the core loading consists of elements which have received relatively little exposure. Note also that cycles 6, 7, and 8 are nearly the same, since a repetitive pattern is being established at this point.

The results of this study are summarized in Table 7, which shows the cycle duration in months at an 80% load factor, and the amounts of fissionable material added or removed at each cycle interval. The average repetitive cycle was taken as the average of cycles 6, 7, and 8 in which 28.2 kg U^{235} were added to each, about 17.3 kg U^{235} were burned during each cycle, and about 10.1, 7.1, and 1.1 kg U^{235}, U^{233}, and $Pu^{239+241}$ were recovered. The cycle times average about 1¼ years each.

Table 7

CCBR Material Balance
Long-Term Reactivity of 25% UO_2 – 75% ThO_2 Fuel Mixture

Cycle No.	Approx. cycle length @ 80% load factor, months	U^{235} added, kg	U^{235} burned, kg	Material removed, kg		
				U^{235}	U^{233}	$Pu^{239+241}$
1	12½	104.4	18.6	—	—	—
2	11	28.2	15.2	—	—	—
3	11	28.2	14.5	36.8	12.6	2.4
4	20	28.2	25.5	10.9	5.0	0.9
5	14	28.2	16.7	10.7	5.2	1.0
6	15	28.2	17.8	10.2	7.0	1.1
7	14	28.2	16.5	10.0	7.1	1.1
8	15	28.2	17.7	10.1	7.1	1.1

SESSION III

THORIUM CRUDES
TO
FUEL GRADE THORIUM

The Production of Thorium Metal

O. R. Magoteaux
National Lead Company, Mount Healthy Station, Cincinnati, Ohio

In this paper the processes used for the production of reactor grade thorium metal fuel elements from thorium nitrate are reviewed.[1,2] The quality of raw materials and the quality of the metal product are briefly described. Important operating techniques are emphasized.

INTRODUCTION

Reactor grade thorium metal fuel elements were produced in a semiworks plant at the National Lead Company of Ohio during the period April 1954 through December 1955 and subsequently evaluated at the Savannah River Operations. During the period of production, the development of improved methods of production was accomplished. At present there is no production of thorium metal at the National Lead Company. This report describes the production methods used.

DESCRIPTION OF PROCESS

The production process includes chemical and metallurgical steps. The chemical process (Figure 1) consists of the preparation of thorium oxalate from thorium nitrate, the conversion of the thorium oxalate to thorium oxide, and the hydrofluorination of thorium oxide to thorium tetrafluoride. The metallurgical process (Figure 2) consists of the reduction of the thorium tetrafluoride to a massive thorium-zinc alloy, the distillation of the zinc from the alloy to form sponge thorium metal, arc melting of the sponge into ingots, and the fabrication of ingots into rods and fuel elements. The processing steps are described below.

Chemical Process

Preparation of Thorium Oxalate from Thorium Nitrate – A thorium oxalate [$Th(H_2C_2O_4)_2$] slurry is prepared from a warm (130°F) solution of slightly acidic (0.5 $\mathcal{N}$) thorium nitrate [$Th(NO_3)_4$] received from the Lindsay Chemical Company. The slurry is filtered and the cake washed with water. During the filtration step, the acid soluble oxalates of uranium and iron, particularly, are removed. The filtrate produced contains about 50% water. The thorium oxalate process has been found to be the best production method to remove impurities and prepare a product which can be calcined to thorium oxide.

Conversion of Thorium Oxalate to Thorium Oxide – In the conversion of thorium oxalate to thorium oxide, the first step is predrying to about 5% moisture in a Holo-Flite twin screw dryer at 270°F. The dried oxalate is then calcined in a Bartlett-Snow gas-fired rotary calciner which utilizes a counter-current air flow to remove the moisture and to oxidize the carbon in the oxalate. An exit gas temperature of 1400°F is attained. The thorium oxide product contains $\approx$0.5% moisture and $<$0.5% carbon.

Conversion of Thorium Oxide to Thorium Tetrafluoride – The thorium oxide is converted to thorium tetrafluoride in a hydrofluorination unit, which consists of four screw-type reactors identical to the type used to convert uranium oxide to uranium tetrafluoride. In the first chamber of the unit, the thorium oxide is again calcined (1200°F) to reduce the carbon content to $<$0.1%. It is then passed through the other three chambers, which are heated to 500°, 700°, and 1050°F, respectively, and in which anhydrous hydrofluoric acid is passed counter-current to the flow of the oxide. The thorium tetrafluoride passes from the hydrofluorination unit and is packaged for use in the metallurgical process.

In the chemical process no major refining step is used; therefore, product purity is determined by purity of the thorium nitrate, with the exception of corrosion elements. Sulfur content in the thorium nitrate has caused severe corrosion problems in the hydrofluorination equipment. It has been determined that the sulfur content of the

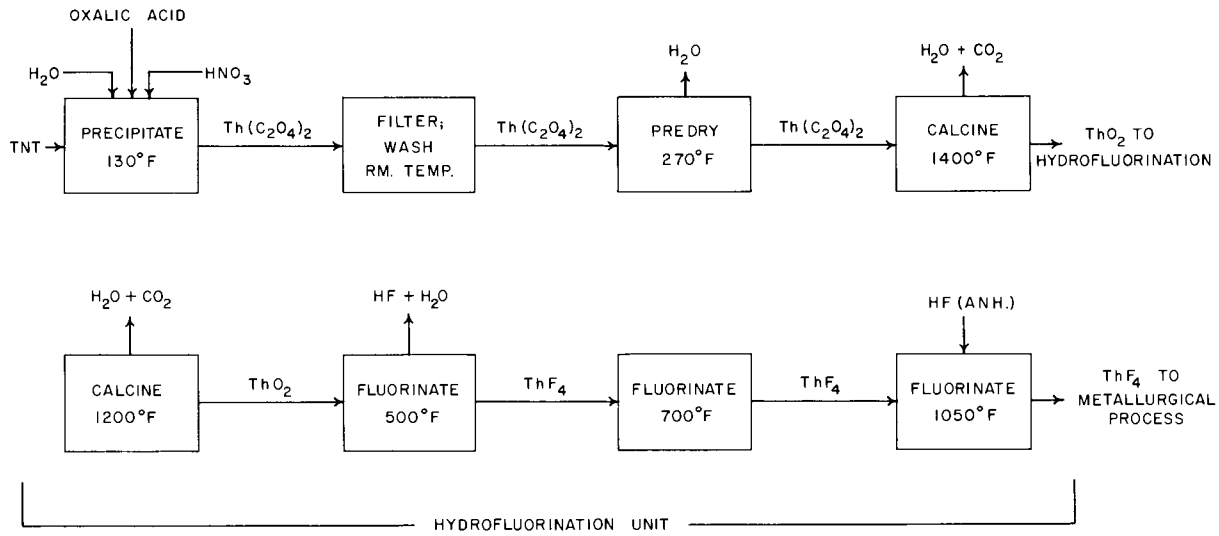

Figure 1. Thorium chemical process

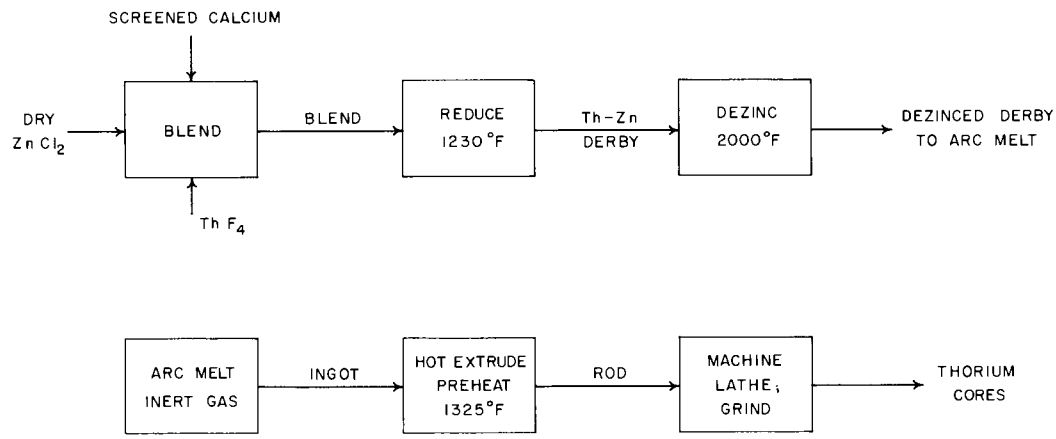

Figure 2. Thorium metallurgical process.

thorium nitrate should be maintained at <100 ppm.

Metallurgical Process

Reduction of Thorium Tetrafluoride to a Thorium-Zinc Alloy – In the first step of the metallurgical process, the thorium tetrafluoride is reduced to a massive thorium-zinc alloy by the reduction of both the tetrafluoride and the zinc chloride with calcium metal. The alloy is produced by blending the tetrafluoride, zinc chloride, and calcium metal, followed by charging the blend into a flanged steel vessel, called a furnace pot, which is lined with dolomite. The charged furnace pot is placed in a Rockwell furnace preheated to 1230°F. A reduction reaction takes place and produces a thorium-zinc alloy which conforms to the shape of the dolomite liner. The furnace pot is cooled to room temperature and the alloy removed. A typical alloy product, called a derby because of its shape, weighs ≈108 lb and contains ≈93.5% thorium and 5.4% zinc.

All reductions are performed remotely behind protective walls, since occasional blowouts occur.

Close attention must be given to the moisture content of the thorium tetrafluoride and the zinc chloride and to the particle size of the calcium metal, to reduce the probability of a premature reaction during the blending operation. The zinc chloride, therefore, is dried in a vacuum, and the

calcium metal is screened to remove the fines. For safe operation a maximum moisture content of 0.1% in the thorium tetrafluoride and 0.5% in the zinc chloride is recommended. The calcium metal should not contain any <50-mesh particles. Redistilled calcium should be used for minimum impurity content.

Distillation of the Alloy to Thorium Sponge – Four of the alloy derbies are heated under vacuum in a steel retort for 6 hr at 2000°F to remove the zinc and other volatiles. A vacuum of 200 μ is required to reduce the zinc content to <500 ppm. After distillation, the retorts are purged with helium and cooled to room temperature. The product from the distillation step is $\approx$10 in. in diameter and 4 to 5 in. thick, and resembles a spongy mass.

Primary Ingot Preparation – Two arc-melting steps are required to refine the thorium sponge into high purity ingots because of the impurities which remain in the sponge after the distillation step.

Electrodes for the preparation of a primary ingot are fabricated by sawing the sponge into strips (2¼ × 2¼ × 10 in.) and then butt-welding these strips together and onto a threaded "stub." Welding of the electrodes is done in a steel tank which is evacuated and backfilled to atmospheric pressure with argon. A thoriated tungsten electrode is used to carry a current of 200 amp at 20 to 25 v. Each electrode weighs 30 to 35 lb.

Primary ingots are prepared by arc-melting seven electrodes, one on top of the other, in a water-cooled copper crucible. The furnace used to arc-melt is evacuated to <500 μ and backfilled to 25 in. with argon. The ingot is melted with 2000 to 3000 amp of current at 25 to 30 v.

Secondary Ingot Preparation – The electrode for the arc-melting of the secondary ingot is formed by butt-welding several primary ingots inside a tank which is evacuated and backfilled with argon to a slightly negative pressure. Welding is done with a thoriated tungsten electrode with a current of 400 amp at 20 to 30 v. A "stub" is also welded to one end of the electrode for attachment to the electrical connector of the furnace.

Final ingots (7⅜-in. diameter) are arc-melted in a manner similar to that used for melting and casting the primary ingot. The furnace is evacuated and then backfilled to 25 in. absolute pressure. Melting of the ingot is done with a current of 6500 amp at 25 to 30 v. The cast ingot, which weighs $\approx$275 lb, is cropped at the top and bottom and scalped to remove the major impurities and condition it for hot extrusion.

The composition of arc-melted virgin ingots is given in Table 1.

All arc-melting operations are carried out behind protective walls by remotely operated equipment because of the possibility of an explosion which can be caused by the thorium metal reacting with water to form hydrogen.

Fabrication of Ingots into Fuel Elements – The conditioned arc-melted ingots, which weigh $\approx$250 lb each after conditioning, are hot extruded into rods and machined into fuel elements. Conditioned billets are heated for 1 hr at 1365°F, and the dies, dummy blocks, cones, and a liner are heated to 650°F. A 2450-ton-capacity horizontal press at Bridgeport Brass Company, Adrian, Michigan, is used to extrude the billet to rods. The metal prepared by hot extrusion is 100% recrystallized.

The thorium rods are machined by a sequence of rough turning, cut-off, centerless grinding, and facing. Rough turning operations are carried out with a hollow mill tool at spindle speeds of 400

Table 1

Analysis of Arc-Melted Virgin Ingots*

	Average	95% Confidence level (upper)
Chemical		
ThO_2, %	2.50	4.40
N, ppm	192	390
C, ppm	219	380
Spectrochemical, ppm		
Al	11.2	15.2
B	0.6	1.0
Ca	<75	400
Cd	<0.2	<0.2
Cr	40	80
Cu	55	115
Fe	448	670
Mg	5.3	8
Mn	6.8	12
Ni	192	450
SiO_2	32.5	55
U	6.6	13.0
Zn	130	260
Physical		
B.H.N. (500 kg)	59.4	71.0
Density, g/cc	11.54	11.66

*Data from over 500 ingots.

rpm and 0.050 in. Centerless grinding is accomplished at 1250 rpm. A rest blade of the carbide-insert type ground to a 30° angle can be used for grinding. Water soluble coolant in the ratio of 1:16 was found to be satisfactory. Fuel elements fabricated in this manner were acceptable.

SUMMARY

High grade thorium metal fuel elements were produced at National Lead Company of Ohio. Although the process described was used for production, a need remains for further development work to improve yields in certain steps. Improved methods for electrode fabrication and for recycling arc-melted scrap are required. A hydrofluorination reactor should be constructed specifically for thorium to reduce the high degree of contamination by chromium, iron, and nickel in the hydrofluorination step.

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Thorium Ores and Extraction of Thorium from Ores

HOWARD E. KREMERS
Lindsay Chemical Company, West Chicago, Illinois

SUMMARY

Thorium Ores

Three kinds of ores are of commercial interest, monazite, thorite-type materials, and uranium mining by-product thorium. Monazite is the classical thorium ore, most sources giving concentrates containing from 3 to 9% ThO_2. It is found in many parts of the world, notably in Brazil, India, Union of South Africa, Australia, Ceylon, Korea, and in several of our United States. Present production is from both placer and vein monazite deposits.

Thorite-type materials occur in this country predominantly in Colorado, Idaho, Montana, Wisconsin, and in some other localities. No large production of thorite has yet been made, but it is expected that these thorite deposits will add significantly to our usable thorium reserves.

By-product thorium from uranium mining may become of some importance, particularly in the Algoma district in Canada. These sources are currently under development.

Present comsumption of thorium ores in this country is on the order of 10,000 tons of monazite (6% ThO_2) annually.

Extraction

All principal extraction processes involve an initial leach or cooking of the ore with acids or sodium hydroxide, followed by appropriate wet chemistry to remove rare earths which always accompany thorium. The crude thorium products so obtained are further purified by classical wet chemical methods or by liquid-liquid extraction to produce commercial thorium products such as the nitrate, oxide, fluoride, etc. Commercial thorium materials contain 5 to 100 ppm rare earths as impurities.

Present commercial productive capacity for thorium materials is on the order of about 1,250,000 lb thorium oxide annually.

Chief nonenergy uses for thorium are in magnesium-thorium alloys, incandescent gas mantles, and refractories.

The production of thorium materials is tied very closely to the production of rare earths, since both are generally obtained from the same ore.

THORIUM ORES

Two kinds of ore minerals are of present commercial interest, monazite and thorite-type materials. A third source of thorium is potential by-product production from uranium mining and milling.

Monazite

Monazite is the classical thorium ore. It is essentially a phosphate of the rare earths and thorium. Commercial monazites may contain from a few tenths to as much as 20% gangue materials. The purity of commercial monazite concentrates is related to the ore deposit and to the amenability of the ore to upgrading.

Monazite occurs in primary form in some feldspathic granites, in many alkalic rocks, in some pegmatites, and in some hydrothermal vein deposits. Commercial production has come largely from stream, beach, and dune placers derived from host rocks containing up to a few tenths of a percent monazite. Such placers are found in many parts of the world. The most important beach placers are in Travancore, India; the states of Espirito Santo, Bahia, and Rio de Janeiro in Brazil; Ceylon; and Australia. Stream placers are notable in Idaho, North and South Carolina, Malay States, Dutch East Indies, Belgian Congo, Korea, Egypt, and many other places. Ancient litholized stream placers are found in the Big Horn Mountains in Wyoming. The Florida monazite deposits are typical dune placers.

In placer deposits, monazite concentrates with other resistant heavy minerals; ilmenite, garnet,

zircon, staurolite, kyanite, gold, cassiterite, etc. are commonly associated with monazite. Placer deposits are usually mined by dredging. Following screening to remove pebbles and boulders, the sands are concentrated by gravity separation methods such as jigging, tabling, etc., to yield a heavy mineral concentrate. The dried heavy mineral concentrate is separated into its component minerals by high tension and electromagnetic methods.

Vein deposits of monazite are rare, and at present only one is of importance. This is a hydrothermal deposit in the Van Rhynsdorp district of the Union of South Africa. There are several deposits in this area, but only one is being actively exploited. Production and shipment of monazite concentrates from this deposit began in 1953, and since then this monazite has supplied most of the requirements of England and the United States.

The Van Rhynsdorp monazite occurs as a high grade deposit containing chiefly monazite and apatite with smaller amounts of iron and copper minerals, pyrite, zircon, and quartz. It is beneficiated by tabling and flotation.

The ratio of rare earths to thorium in monazite varies from about 20 to 1 to about 7 to 1. Typical values for monazite from various sources are given in Table 1 together with similar data for thorite concentrates.

The composition of the rare earth mixture in commercial monazites from most parts of the world is reasonably constant. The rare earths in monazite are chiefly the lighter ones. Typical compositions for the rare earth mixture in monazite, thorogummite, and some other rare earth minerals are given in Table 2.

Thorite-type Ores

Thorite-type ores are related to the zirconium minerals zircon and cyrtolite. Thorite, $ThSiO_4$, is the analog of zircon, and thorogummite, $Th(SiO_4)_{1-x}(OH)_{4x}$ is analogous to cyrtolite. Thorite is a primary high temperature mineral, and thorogummite is a secondary low temperature hydrothermal mineral. Both are commonly altered to hydrothorite, a hydrated silicate of indefinite composition.

Thorite-type minerals occur most frequently in hydrothermal vein deposits formed in fault breccia zones. In this country there are at least four general areas each containing perhaps several hundred of these deposits. Major occurrences are in Colorado in the Wet Mountain and St. Peters Dome areas, in Wisconsin, in the Bitterroot Mountains in Montana, and in several places in Idaho.

Most thorite deposits are small, and only a few will probably be able to be mined economically at today's price structure. However, many of the small deposits will probably be worked to supply odd lots of ore for custom milling if there is a central mill nearby.

Aside from pilot plant quantities, there has been no real production of thorite materials to date. Provided that costs of the ore are reasonable, thorite materials are attractive sources of thorium because they do not contain an overwhelming amount of rare earths. The production of thorium materials from monazite is preferable provided there is a balanced sale of both thorium and rare earths, but such a balance cannot be expected to exist if demand for thorium becomes appreciable.

Uranium By-product Production

A potentially important source of thorium is by-product production from the uranium milling operations in the Algoma district in Canada. Thorium occurs with uranium principally in the mineral brannerite in the proportion of 2 to 3 parts U to 1 part Th. Uranium is recovered by an acid leach of the ore, and thorium can potentially be recovered from the dilute spent uranium liquors. Estimates of potential thorium recovery range from 3 to 9 million pounds ThO_2 annually. Serious consideration is at present being given to this recovery.

Economics of Thorium Ores

Costs for thorium ores have varied considerably in the last 15 years. From the early 1920's until the end of World War II, the price of monazite sand containing about 6 to 8% ThO_2 never exceeded about $50 a short ton delivered from India or Brazil. Rising costs, together with exaggerated ideas about the atomic energy value of thorium, resulted in a sharp increase in the price of monazite from Brazil and India between 1945 and 1950 until the delivered price reached about $400 per ton. Freight costs remained nominal, about $20 to $25 per ton.

India embargoed the export of thorium ores in 1947, and Brazil in 1951. U.S. users of monazite, therefore, were forced to obtain ore from other sources. Fortunately, marginal deposits in this country became economically profitable to oper-

Table 1

Thorium and Rare Earth Contents of Various Commercial Minerals
(Approximate)

	% Rare earth oxide	% ThO_2	Ratio ThO_2:Rare earth oxide
Monazite concentrates			
India	59.5	8.5	1:7
Brazil	62	6	1:10.5
Florida	51	4.5	1:11.3
North and South Carolina	61 to 62	5 to 6	1:11.2
Idaho, Big Creek Placer	63	3	1:21
Idaho, Bear Valley Placer	61	5.5	1:9
South Africa, massive monazite	45	6	1:7.5
Thorite concentrates			
Colorado, Idaho and Montana	1 to 5	10 to 25	1:0.1 to 0.5
Wisconsin	10 to 25	10 to 25	1:0.4 to 1

Table 2

Percent Composition of Total Rare Earth Oxides in Various Minerals
(Based on "as ignited" oxides, not including thorium)

	Monazite	Thorogummite	Gadolinite	Bastnasite
La_2O_3	24	P	1	38
CeO_2	48	P	2	48.5
Pr_6O_{11}	6	P	2	3.6
Nd_2O_3	19	0.5	5	8.8
Sm_2O_3	2		5	0.5
Eu_2O_3	0.002	P	Trace	0.6
Gd_2O_3	0.4	3	5	"
Tb_4O_7	0.002	P	0.5	"
Dy_2O_3	0.1	9	6	"
Ho_2O_3	0.03	2	1	"
Er_2O_3	0.05	6	4	0.6
Tm_2O_3	0.005	0.5	0.6	"
Yb_2O_3	0.01	2	4	"
Lu_2O_3	0.001	P	0.6	"
Y_2O_3	0.4	77	60	"
	100%	100%	100%	100%

P=Present in low concentrations.

ate when the monazite price reached the range of $300 to $400 per ton, with the result that by 1951 adequate supplies of monazite were being produced in Idaho and Florida, augmented by bastnasite production from California for rare earth production.

Prospecting and development work by industry and the Bureau of Mines since 1946 has resulted in the production of monazite from Florida, Idaho, and South Carolina, and the finding of several useful deposits.

Since 1953, the production and sale of monazite concentrates from the Union of South Africa at delivered prices in the range of $250 to $285 a ton has stabilized the price structure of monazite ores at about $25 to $40 per %-ton of contained thorium

oxide; the actual value is generally subject to negotiation and is related also to the composition of the monazite concentrate.

These costs for monazite do not reflect a direct cost for thorium, since monazite is used also as a source of rare earths. The recovery and sale of rare earths from monazite tends to lower the contained thorium cost. Until about 1920, monazite was of value solely for its thorium content. Today, the value is based generally on the total content of both thorium and rare earths, since both are valuable commercially.

With thorite-type ores, the situation is quite different. Sufficiently large deposits of thorite were not found in this country until uranium prospecting was at its peak in the late 1940's and early 1950's. Most deposits show less than 0.5% ThO_2 in the ground, and a few show up to 1% ThO_2 or higher. For chemical treatment of thorite ores to obtain salable thorium chemicals, it is the general feeling that at least 10% ThO_2 material must be used as plant feed. This means that upgrading must be done on the raw ore. It is problematical whether or not a mechanically made thorite concentrate can be produced for less than about $1 per lb contained thorium oxide; in many cases, costs may be higher than this by a factor of 1.5 to 2 or more.

Since the rare earth content of thorite materials is much smaller than in monazite, the rare earths cannot contribute greatly, if at all, to reducing the cost of the thorium content.

Except for pilot production, there has been no real production of thorite ores. Because of increasing demands for thorium, however, some thorite production is expected to be started within the next year or two.

Present known free world monazite production is probably on the order of about 12,000 to 14,000 tons annually containing 5 to 6% ThO_2. Most of this comes from the Union of South Africa, and the rest from South Carolina, Idaho, Florida, Ceylon, and Australia. This rate of production is the highest so far experienced in the industry, and is about three times the average production for the last 10 to 20 years.

The present use of thorium ores in this country amounts to about 11,000 tons of monazite containing 6% ThO_2 annually. This roughly approximates the present productive capacity of about 1.25 million pounds of thorium oxide equivalent made per year.

Commercial thorium materials of greatest importance are the metal, and salts such as thorium nitrate, thorium oxide, thorium chloride, thorium fluoride, and thorium sulfate. Thorium nitrate is the principal thorium salt of commerce.

There are two major uses for thorium. The classical and oldest use is in incandescent gas mantles. The gas mantle consists of a web-like structure of thorium oxide containing about 1% ceric oxide formed by burning a loosely knitted rayon sock impregnated with thorium and cerium nitrates. Until the middle of 1957, this was the principal use of thorium. World consumption of thorium nitrate for this use is about 150,000 lb annually.

The largest use for thorium today is in magnesium-thorium alloys. These alloys contain about 3% thorium, and have excellent mechanical strength at temperatures beyond those generally useful for the less exotic magnesium alloys. These alloys are used largely in jet engine castings and air frame structures.

EXTRACTION OF THORIUM FROM MONAZITE

Two general processes are commonly used to extract thorium from monazite. The classical process is the sulfuric acid method with its many variations. In recent years the caustic soda process has received considerable attention.

In the conventional sulfuric acid process, the monazite sand or ground monazite ore is mixed with about 1.5 to 2 times its weight of 98% sulfuric acid, and the mixture is stirred and heated in cast iron pots until the metathesis reaction between the phosphates and the acid is complete. The product is a putty-like mass of anhydrous rare earth and thorium sulfates in a slurry of phosphoric and sulfuric acids. This is treated with water to solubilize the rare earths and thorium, and the gangue material is removed by filtration.

The processes used to recover thorium from such solutions are usually considered as carefully guarded arts. However, a few methods can be mentioned. A common method of recovering thorium from the monazite rare earth + thorium solution is to precipitate thorium pyrophosphate by carefully adding alkali pyrophosphate solutions. Sometimes the careful selective precipitation of thorium fluoride with hydrofluoric acid can be used to produce a primary thorium product. Careful neutralization of the monazite-sulfate solution re-

sults in preferential precipitation of thorium phosphate. Generally these processes yield a crude thorium material containing 60 to 90% ThO_2 in the total ThO_2+rare earth oxide.

The caustic soda process involves heating the finely ground monazite ore with about 60 to 70% sodium hydroxide solution in excess to convert the phosphates to hydroxides. On lixivation in water, the phosphates are removed as trisodium phosphate, and the insoluble hydroxides are filtered and washed.

Separation of the rare earths from thorium is accomplished by treating the hydroxide slurry with dilute mineral acids, preferably HCl, to *p*H about 3 to 4 to dissolve the rare earths selectively. The resulting insoluble sludge is filtered and washed to give a product containing 60 to 80% ThO_2 in the total ThO_2+rare earth oxide. "Brazil thorium sludge" is typical of such a material.

Refining to Commercial Thorium Materials

Subsequent purification steps start with any of the crude thorium products prepared by either the acid or the basic process.

The classical chemical methods of purification also involve closely guarded arts. However, they all involve the selective precipitation of insoluble thorium or rare earth materials, and conclude with the crystallization of thorium nitrate. The individual processes are covered in the literature and involve, for example, precipitation of thorium sulfate, thorium pyrophosphate, or thorium fluoride, and precipitation of rare earth carbonates or oxalates with simultaneous formation of soluble tho-

Table 3

Typical Analyses of Commercial Thorium Nitrates
(All values in ppm unless otherwise stated)

	Code 100	Code 101	Code 102	Code 103	Code 103.5	Code 104
ThO_2	47%	46%	47%	46%	46%	46%
Rare earth oxide	50	50	40	20	10	2 max
Sulfate, SO_3	6000**	200	200	100	200	50
Chloride, Cl		20	20	10 max		10 max
Fluoride, F		20	20	10 max		10 max
Phosphate, P_2O_5	50	50	50	50 max	10	1
Iron, Fe	50 max	15	5	1	10	1
Fe+Cr+Ni				50 max		10
Lead, Pb				10 max		
Calcium oxide, CaO	500	1000	500	10	10 max	10 max
Magnesium oxide, MgO	500	500	500	400 max	200	5
Ca+Mg+Ba				500 max	500 max	500 max
Alkalis, Na+K+Li				500 max	500 max	500 max
Alkali salts*	2000	2000	2000			
Aluminum, Al*	pass test	pass test	pass test	pass test	pass test	pass test
Heavy metals*			pass test	pass test	pass test	pass test
Titanium*	pass test	pass test	pass test	pass test	pass test	pass test
Water solubility*	pass test	pass test	pass test	pass test	pass test	pass test
Silica, SiO_2	100	100	100	50 max	100	50
Uranium, U	1–50	1–50	1–50			10 max
Boron, B	1	1	1	0.5	0.5	0.5
Rare earths						
Ce	5	5	3	1	0.5–2	ND
Sm	5	5	4	0.5–1	0.5	ND
Eu	0.5	0.5	0.4	0.1	0.01 max	0.01 max
Gd	5	5	4	0.5	0.2	0.01 max
Dy	0.5	0.5	0.4	0.5 max	0.2 max	0.01 max

*J. Rosin, *Reagent Chemicals and Standards*, 2nd Ed., pp. 455-6, Van Nostrand, New York, 1956.
**Intentionally added for mantle manufacture.

Table 4

Typical Analyses of Commercial Thorium Oxides
(All values in ppm unless otherwise stated)

	Code 111	Code 112	Code 112 Heavy	Code 113	Code 113.5	Code 114	Code 115***
Purity designation	99.5%	99.9%	99.9%	98%	99.9%	99.9+%	99.9%
ThO_2*	99% min	99% min	99% min	98% min	99% min	99% min	99% min
Rare earth oxide	100	50 max	50 max	100	10–20	5 max	50 max
Sulfate, SO_3	100	50		5000	50	50 max	50
Phosphate, P_2O_5	50	10	30	300	10	1	10
Fe+Cr+Ni		25 max			25	10	25 max
Fe	50	2	5	500	2		2
CaO	100	10	50	2000	5	5	10
MgO	200	10	50	5000	5	5	10
Na+K+Li	2000	100	1000	5000	200	25 max	100
Silica, SiO_2	1000	50	500	2000	50	50	50
Boron, B		0.1			0.1	0.1	0.1
Uranium, U		10 max			10 max	10 max	10 max
Cu+Mn+Zn		10				5 max	10
Loss on ignition*	5000	5000	5000	5000	5000	5000	5000
Rare earths							
Sm	10	1–2	1–2	10	1	ND	1–2
Eu	1	0.2 max	0.2 max	1	0.02 max	0.02 max	0.2 max
Gd	10	1	1	10	0.4	0.02 max	1
Dy	5	1 max	1 max	5	0.4 max	0.02 max	1 max
Bulk value (g/cc)	2.8–3.1	2.8–3.1	4–5	4–5	2.8–3.1	2.8–3.1	2–2.4
Average particle size**	1–4	1–4		1–4	1–4	1–4	0.6

*Normal ThO_2 contents are 99% except for code 113 (98%), since thorium absorbs up to about 2% moisture and carbon dioxide when allowed to stand in air.

**Values in microns, determined by Fisher sub-sieve sizer.

***Prepared from thorium oxalate by low temperature ignition (see A.S. Kites and R.N. Lyon, *Proc. Intern. Conf. on Peaceful Uses of Atomic Energy*, UN, New York, 1956, Paper 933).

rium oxalate or carbonate alkali complex compounds.

Although much untidy batch chemistry is involved in the classical methods of thorium purification, the results are surprisingly good. Commercial thorium materials as a rule contain from about 20 to 100 ppm total rare earths in the contained thorium oxide, and it is not too difficult to make thorium materials containing less than a few ppm total rare earths.

Some typical examples of commercial thorium material compositions are given in Tables 3 and 4.

Solvent extraction methods for purifying thorium are also useful, but no details on these procedures will be given here, since they are covered in other papers in this symposium.

Thorium Refining from Brazilian Sludge Concentrate by Solvent Extraction

S. Cseplo and J.O. Davis
National Lead Company, Mount Healthy Station, Cincinnati, Ohio

INTRODUCTION

A solvent extraction refining process for recovery of thorium from Brazilian sludge concentrate was developed and demonstrated on a pilot plant scale.

A preliminary report, *Solvent Extraction of Thorium from Brazilian Sludge*, FMPC 435, presented the development and initial demonstration test of a process for purification of thorium from Brazilian sludge* by tributyl phosphate solvent extraction.

Further tributyl phosphate solvent extraction studies were made in 1954 to furnish design data for a production plant and to test process improvements. The purified thorium nitrate product was needed for the FMPC thorium metal production plant operated by National Lead Company of Ohio. Since the supply of "mantle-grade" thorium nitrate purchased from vendors was not sufficient to fulfill the needs of the thorium metal fabrication plant as estimated at that time, a thorium refinery was needed to supply the balance of the thorium feed material from unrefined thorium concentrates such as Brazilian sludge, and from thorium scrap produced in thorium metal production steps. The minor uranium content of the sludge was also to be recovered in the form of a concentrate suitable for feed to a uranium refinery. A contract for installation and operation of a thorium refinery was awarded to Monsanto Chemical Company at Mound Laboratory in November 1954. Even though several points of the refining process needed further investigation, both on a laboratory and pilot plant scale, further work by National Lead pertaining to the thorium refinery was curtailed. The status of the thorium refining pilot plant studies at the time of curtailment is described below.

*Brazilian sludge analysis, %

ThO_2	45	ZrO_2	1.4
Re_2O_3	15	P_2O_5	5.3
SiO_2	4.5	U_3O_8	1
TiO_2	7	Cl	2.6
Fe_2O_3	4.3	Loss on ignition	14

SUMMARY OF TEST RESULTS

A series of four pilot plant solvent extraction tests was conducted in a 6-in.-diameter column system in order to test the process for thorium recovery from the Brazilian sludge concentrate, and to determine the degree of removal of rare earths, uranium, and other impurities. In addition data were obtained on equipment corrosion, column capacities, waste disposal methods, choice of solvent diluent, and method of treatment of solvent.

Approximately 99% recovery of the thorium values in the Brazilian sludge was demonstrated by digestion of the sludge in HNO_3 at 180°F for 2 hr, followed by room-temperature solvent extraction with 30% tributyl phosphate at 70 to 78% of theoretical organic extraction saturation.

Product purification in a one-cycle extraction process was indicated to be adequate with respect to rare earths and other impurities, except that complete uranium decontamination was not demonstrated in these tests, with limited column height.

Uranium removal of 95 to 98% was attained with a single extraction cycle which represents a reduction from 20,000 ppm U based on thorium in the feed to about 500 ppm in the product solution (OK liquor).

Organic-phase-continuous operation of the extraction column was found necessary to eliminate the solids carryover with the organic which was noted with aqueous-phase-continuous operation.

Rated extraction column capacities at 450 GSFH throughput should be used for design basis for plant scale-up, based on preliminary results.

The material of construction of digestion equipment should be chloride resistant (probably glass-lined) to eliminate corrosion during acid digestion

because of the chloride content of the sludge (about 2.6%).

Lime-slurry solvent treatment in a countercurrent, jet-mixer column resulted in better uranium removal from the spent solvent than treatment with sodium carbonate. Good solids removal was also realized with lime treatment, which lessened the emulsion tendencies in the strip column.

Although satisfactory extraction results were obtained with the aromatic diluent Solvesso-100 in the short duration tests made, it was considered essential to substitute an all-paraffinic diluent if at all possible. An aromatic diluent is seriously attacked by the nitric acid solution employed, and it also affords much lower column throughputs because its density is much higher, about 0.87 compared to 0.74 for paraffinic. This means about half the density difference, organic-aqueous. A range of solvent extraction conditions was therefore determined within which an all-paraffinic diluent could be used, and satisfactory performance was demonstrated under these conditions.

Metallic Reduction of Thorium Halides

F.E. Block
Bureau of Mines, Albany, New York

Thorium tetrachloride is prepared by chlorinating calcined thorium oxalate or nitrate with carbon tetrachloride, and is purified of residual oxygen compounds by double vacuum distillation at 800°C. The purified tetrachloride is reacted with sodium at 800°C followed by high vacuum distillation at 900°C to remove by-product salt and excess reductant. The product of the reduction is a sponge metal which is consolidated by vacuum arc-melting to ingot form.

CHLORINATION

Thorium nitrate or oxalate is decomposed by heating at 450° to 550°C under vacuum to form a porous bed of highly active thorium oxide. Chlorine gas and carbon tetrachloride are slowly passed through the bed at 500° to 600°C to yield a crude thorium chloride containing 5 to 20% thorium oxide. This crude product is transferred to a nickel crucible and heated to 800°C in the lower part of an 8-in.-diameter by 60-in. retort. Because some oxide entrainment occurs, this operation is sometimes repeated. The doubly distilled chloride is transferred under argon to an inert atmosphere box where it is placed in a titanium or type 430 SS crucible together with a 60% excess of sodium metal.

METALLIC REDUCTION

Reduction is carried out in an 8-in.-diameter vertical retort under a positive pressure of 10 to 12 lb helium with up to 10 kg thorium chloride per reduction batch. The reaction is initiated by heating to 500° to 550°C, at which point a temperature rise of 100° to 250°C occurs. This initial step is complete in about 1 hr, but the reaction becomes slower and is not complete until 8 to 12 hr heating at 800°C.

The excess sodium and by-product NaCl are removed from the thorium sponge by heating the evacuated retort to 900°C for 16 hr. The terminal vacuum at the end of the distillation cycle is $\approx 0.1\ \mu$.

The sponge metal is fairly dense and rather soft. Reduction yields average 85 to 90% of the theoretical, the remainder of the thorium values being found in the distilled by-product salt. The sponge is removed from the crucible, pressed into 1×1-in. bars, and consolidated by standard cold-mold arc-melting techniques. Double melting is usually necessary to eliminate porosity.

The arc-melted ingot shows a Brinell hardness of 25 to 45 (500-kg load). Fabrication is carried out by upset forging in a press at room temperature to about 70 to 80% reduction, annealing the billet under inert atmosphere at 700° to 800°C for 1 hr, and cold-rolling to sheet. Rolling may be carried out to about 90 to 95% reduction before excessive work-hardening occurs.

Anhydrous Thorium Tetrachloride Production

C.C. Fogel and J.O. Davis
National Lead Company, Mount Healthy Station, Cincinnati, Ohio

Anhydrous thorium tetrachloride was prepared by packing thorium oxalate (in the form of round pellets) in a 6-in.-diameter graphite reactor, heating to 1100° to 1200°F by means of an electrically heated tube furnace, and reacting with gaseous chlorine and carbon tetrachloride. Conversion averaged 90% under the preferred operating conditions.

Tonnage quantities of anhydrous $ThCl_4$ were needed for conversion to thorium metal at ORNL in the Metallex pilot plant. A specification of 90% minimum methyl-alcohol-soluble was the principal criterion of quality. This work was conducted in the NLO pilot plant during March 1955 to September 1956.

A thorium oxalate pellet was produced with sufficient dry strength to withstand handling. Dry thorium oxalate was fed into a rotating horizontal stainless steel drum. A fine mist of deionized water was directed into the rotating drum to cause the oxalate to agglomerate as round pellets. The pellets were screened, the −4 mesh, +10 mesh being retained, and dried to a moisture content of <1% at temperatures below 300°F.

Fifty pounds of thorium oxalate pellets were charged into the 6-in.-i.d., 72-in. graphite reactor tube. Before the chlorine and carbon tetrachloride were introduced, the bed temperature was brought up to 400° to 500°F during a 3-hr heating period while helium was passed through the bed. Then helium was shut off and the chlorine and carbon tetrachloride streams were introduced. Variations in the temperatures at which chlorine and carbon tetrachloride were introduced (starting temperatures) caused no discernible change.

The reaction started rapidly, and the maximum bed temperatures were held under 1200°F with difficulty by regulating the rates of chlorine and carbon tetrachloride addition. Bed temperatures higher than 1200°F invariably produced a fused material. The best control temperature was 1100°F.

Bed shrinkage was about 50%. About 30 lb of additional pellets were added after reaction started. After about 2 hr of reaction, the bed temperatures started dropping, and additional external heat had to be supplied. The rates at which the reactants were added were also increased, and bed temperatures were maintained at about 800°F during the remainder of the run.

Several runs gave low-quality product which was later charged back into the reactor and rechlorinated, yielding good product. It was found that a good thorium chloride product (90% $ThCl_4$ or better) could be made from low-grade thorium chloride only if the material had not been previously fused or sintered. The best ratio of moles chlorine per mole thorium was 8.5, and of moles carbon tetrachloride per mole thorium, 2.5. Reaction time was 17 to 24 hr.

The bed was allowed to cool to 200° to 300°F under a helium atmosphere, and the hygroscopic thorium tetrachloride was discharged with a minimum of exposure to the atmosphere. Specifications on impurities (maximum levels) were as follows: Fe, 100 ppm; Ni, 50 ppm; Cr, 50 ppm; Cu, 50 ppm; Mn, 25 ppm; SiO_2, 100 ppm; and "methyl-alcohol-insoluble," 10%.

An average cycle time of 28 hr was experienced: 3 hr heat-up, 20 hr reaction, 4 hr cooling, and 1 hr loading and unloading. With this cycle, the productivity was ≈65 lb $ThCl_4$ per 24-hr day, or 35 lb Th content. This rate would produce about 1100 lb $ThCl_4$ per month, allowing for downtime.

Development of a continuous process for thorium tetrachloride production was tried, but was terminated because of operational difficulties and because the required amount of thorium tetrachloride could be supplied by batch operation. Continuous operation is considered quite feasible, however.

In two runs, two moles carbon monoxide per mole thorium were used in addition to chlorine and carbon tetrachloride. No benefit from carbon monoxide addition was realized during either of these runs.

Preparation of Thorium Metal by Calcium Reduction of Thorium Oxide

S. Cseplo and J.O. Davis
National Lead Company, Mount Healthy Station, Cincinnati, Ohio

The purpose of this project was to produce a quantity of thorium metal that could be hydraulically pressed into electrodes. These electrodes would then be arc-melted to form an ingot suitable for rolling and machining. Direct extrusion or swaging of pressed bars into rods was also considered a possibility. Adoption of this process looked favorable from an economic standpoint if the entire process were proven to be feasible.

The process for calcium reduction of thorium oxide to thorium metal was demonstrated on a 50-lb and a 100-lb scale in 10-in. and 14-in. high-chrome alloy steel pots. Critical purity specifications of ThO_2, iron, and carbon in the thorium metal product were equal to or better than in thorium metal currently made at NLO by the Ames process.

The average over-all yield predicted in production operation with good handling equipment is estimated to be about 90%. Water-leaching the primary residues from the reduction pot proved to be slow, even with a high-velocity water jet, the leaching time being 36 to 40 hr for the 100-lb reductions.

A thorium fire and explosion during a filter operation on one batch pin-pointed a serious process hazard and emphasized the importance of carefully controlled washing and handling techniques. The rest of the thorium powder produced appeared safe to handle. The thorium powder in the one batch was evidently activated so that it became pyrophoric. Extreme care and all safety precautions should be used when handling the thorium powder in the final stages of preparation (decantation or filtration of the wet thorium sludge, drying, and pressing).

Microscopic examination showed the thorium powder to be in the form of agglomerated fines and fused particles somewhat in the form of "clinker." The same "clinker" structure is exhibited regardless of method of leaching, acid washing, or powder concentration.

Pressing of the thorium powder into briquettes and electrodes was shown to be feasible. Electrodes 6 in. long by 1 in. in diameter were made. A rubber tube was filled with thorium powder, capped with rubber stoppers, and placed in a perforated steel tube, and the entire assembly was placed in the hydraulic oil chamber and pressed at 40,000 psi. The rubber stoppers and rubber tube were then stripped from the pressed electrode. The electrodes formed were straight and exhibited a dense and compact structure.

Thorium Production by the Sodium Amalgam Reduction of Thorium Tetrachloride

O.C. Dean
Oak Ridge National Laboratory, Oak Ridge, Tennessee

INTRODUCTION

The reduction of thorium tetrachloride by sodium in a mercury medium has many advantages in producing reactor grade thorium economically. All steps in which corrosion of equipment is a factor are carried out at low temperature. All steps up to the elimination of mercury are continuous. The metal is protected from loss and contamination by a coating of mercury during separation from by-products and impurities. The removal of the processing medium (mercury) leaves a nonpyrophoric massive metal which can be safely processed to billets and rods.

Two reduction procedures have been developed, either of which could be scaled up to pilot plant level for evaluation. In one, anhydrous thorium chloride is dissolved in propylenediamine before contact with sodium amalgam; in the other, the dry salt is mixed directly with the amalgam. Because the dry system required less equipment and promised more trouble-free operation, it was preferred over the solvent system. Continuous reduction, washing, and vacuum distillation on a scale up to 3.4 lb thorium per hr have been successfully demonstrated. Filter-pressing will require more development to make it a smooth operation. Sponge billets have been extruded directly to rod and evaluated, and have been arc-melted.

FLOWSHEET AND PROCEDURE

The basic feed material, thorium nitrate solution, is converted to hydrated thorium oxalate by precipitation with oxalic acid. The oxalate is pelletized, dried, and chlorinated with CCl_4 and Cl_2 at 675°C to produce anhydrous $ThCl_4$ of >90% purity.[1] In the schematic flowsheet of Figure 1, $ThCl_4$ and 4 *M* sodium amalgam are fed continuously to a high-shear mixer where they are contacted at 130°C for 20 min. The reduction reaction is

$$ThCl_4 + 4\ NaHg_4 + 60\ Hg \rightarrow ThHg_3 + 4\ NaCl + 73\ Hg + 20\ \text{kcal}.$$

The presence of small quantities of water or oxygen causes side reactions which produce oxides and oxychlorides. Sodium chloride, excess sodium, and side reaction products are separated from the amalgam in the wash column by contact with 3 *N* HCl, followed by 1% sodium versenate and then water. Thorium trimercuride is wetted and protected against reagents by the excess mercury. The washed product is a suspension of $ThHg_3$ in mercury of about 1% thorium content. Residual water and solid impurities are removed by bottom decantation from a phase separator whose walls are amalgamated. Approximately 60% of the mercury is removed by pressure filtration to produce a solid cake of 10 to 15% thorium content. The remainder of the mercury is removed batchwise by vacuum distillation, at temperatures from 25° to 1100°C. The thorium sponge billet of about 60 to 80% of the theoretical thorium density is nonpyrophoric and can be handled and pickled in air.

The feasibility and chemistry of the process were studied in the laboratory on a 30-g Th batch scale.[2] Further development of the reduction and washing steps was carried out at a 1-kg thorium batch scale. Finally, continuous reduction and washing were studied on a 3.5-lb thorium per hr scale.[3] Isolation of the thorium metal by filter-pressing and vacuum distillation were carried out batchwise on a 10-g to 20-lb scale. Thorium sponge billets have been extruded directly, and arc-melted and then extruded to rod for evaluation.

SMALL ENGINEERING SCALE DEMONSTRATION

In the large-scale continuous runs, reduction was carried out in a 1.5-gal Abbé Dispersall top-drive

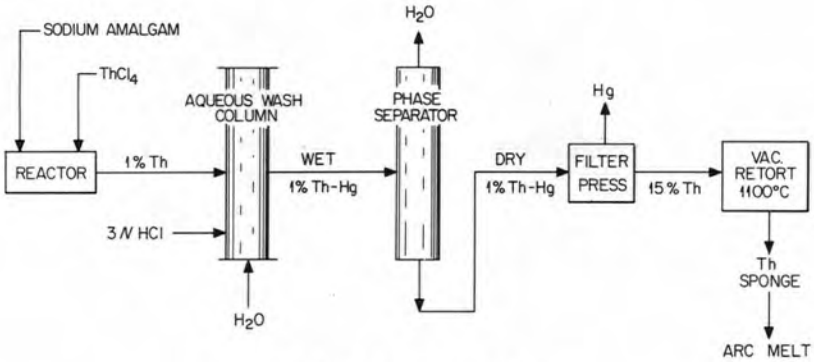

Figure 1. Metallex process flowsheet.

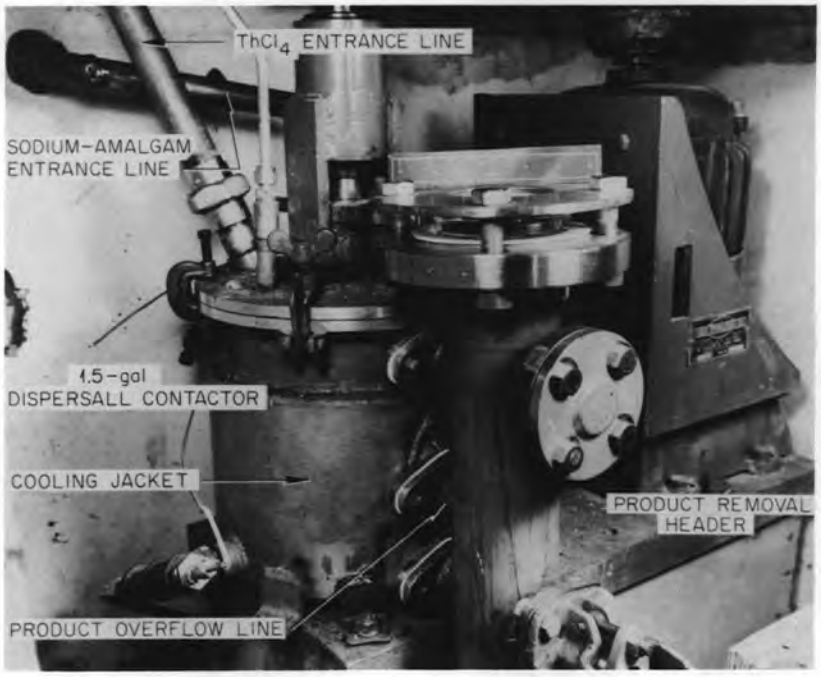

Figure 2. Reduction and product removal equipment for Metallex continuous process.

mixer with a Hastelloy C cup-rotary type impeller (Figure 2). The optimum temperature, agitator speeds, and contacting time had been established in batch tests at 130°C, 1160 rpm, and 20 min. The product was discharged through an overflow line (Figure 3) into the header, and through it vertically to the 4-in. by 6-ft wash column (Figure 4). The deflector cone and a helium purge through the reactor prevented backflow of gases from the wash column. Excess sodium amalgam was decomposed, and by-products were washed from the amalgam by an upflow of 3 *N* HCl introduced at midcolumn and then water introduced at the interface level. The amalgam was then passed through two amalgamated phase separators to remove water, and from them to a hold-up tank which was pressurized with helium to feed the filter press shown in Figure 5. Amalgam entered the filter press at 200 to 800 psi through the center of the bottom plate, and mercury filtered downward through a stainless frit in the bottom plate. When pressure built up to 800 psi, the amalgam flow was stopped and a pressure of 2000 psi was applied by the hydraulic ram. The cake was discharged by

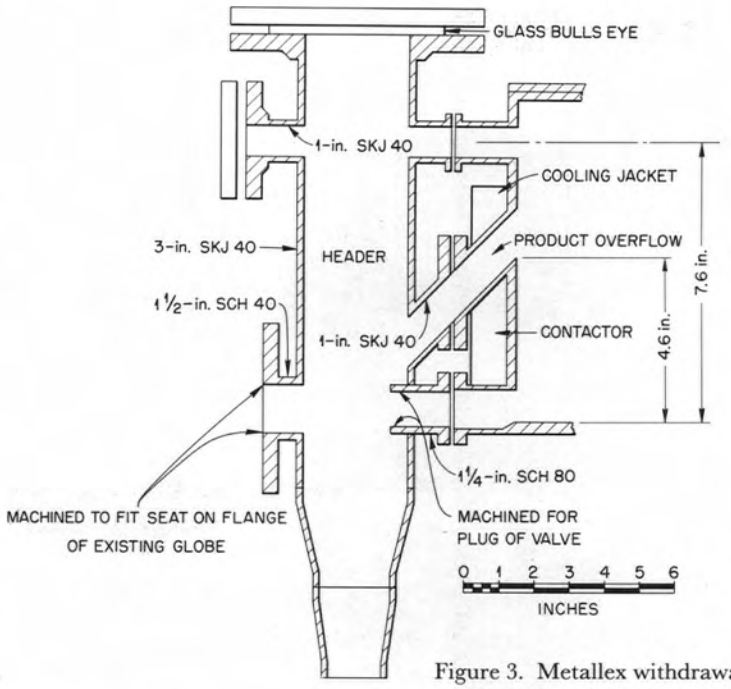

Figure 3. Metallex withdrawal header.

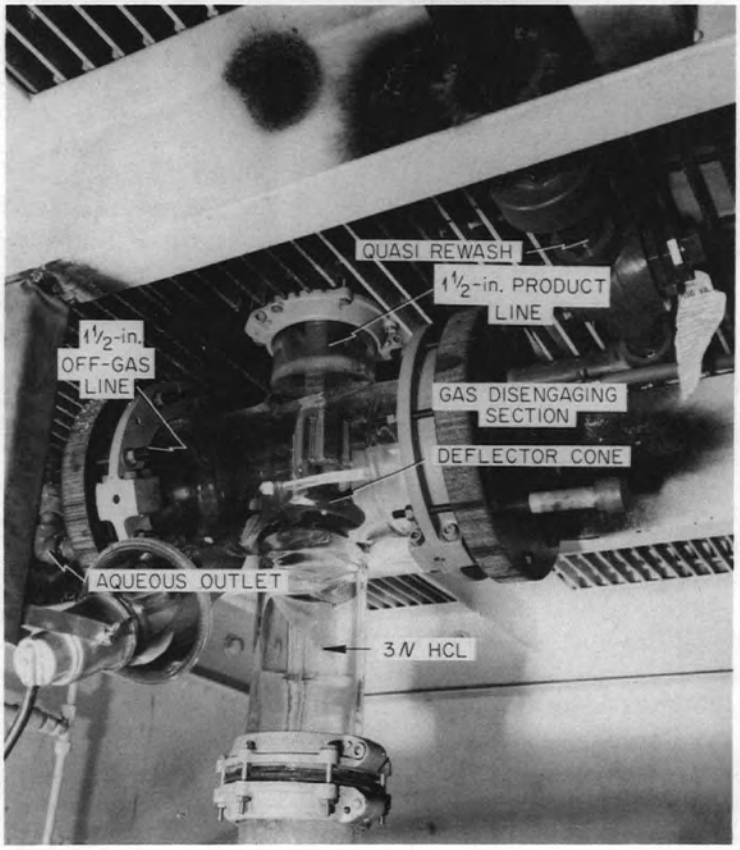

Figure 4. Wash column.

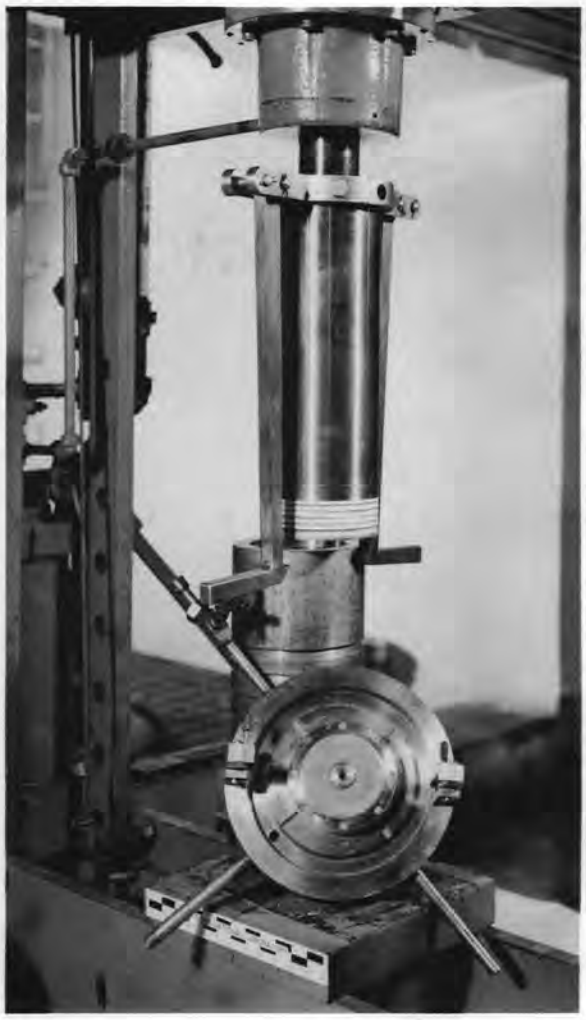

Figure 5. Filter press.

removing the bottom plate and applying pressure to the punch while holding the die with the ratchets. The cake and a vacuum-distilled sponge billet are shown in Figure 6. The billet had approximately ½ the dimensions of the cake. The cake was loaded into the retort, shown in Figure 7 without its associated furnace and vacuum equipment, which will hold 3 such cakes weighing about 55 lb each and roughly equivalent to 30 lb thorium. Vacuum was applied at 25°C, and the internal temperature was raised gradually over 6 hr to 1100°C and held for 1 hr. After 4 hr of cooling time the billets could be discharged.

Thorium rods were produced from sponge billets by three methods. Approximately 12 lb of billets 1 in. in diameter and 1½ in. long, produced in previous smaller-scale reduction operations, were sealed in steel cans 4 in. in diameter and 6 in. long. These were hot-pressed at 750°C after evacuation, outgassing, and back-filling to about ½ atmosphere with argon to produce an integral billet. The can was machined off, and the billet was again canned and preheated or preheated in a Houghton salt bath and extruded to rod. In other tests single 1-in. billets were extruded to ¼-in.-diameter rods. In still another test, sponge was comminuted to chips, which were nonconsumably arc-melted to a 3-in. billet. This was extruded bare at 800°C to rod.

RESULTS OF CONTINUOUS REDUCTION AND WASHING RUNS

Seven successful reduction runs were made, totaling 90 hr of operation, in which 225 lb thorium as $ThCl_4$ were reduced to $ThHg_3$. The results are summarized in Table 1. The longest runs were approximately 18 hr, and the highest yield was 92% of the thorium fed as $ThCl_4$ converted to $ThHg_3$ and remaining in the amalgam through the washing step. The yield over 7 runs was 82.5%. Sodium excess above 18.5% did not appear to be a definite factor in the reduction yield.

Experiments on a laboratory scale had shown that removal of water from the washed amalgam decreased the ThO_2 and hydrogen content of the sponge billets, and that bottom-decantation from an amalgamated container was as effective in removing water from the amalgam as vacuum drying. The optimum amalgam preparation sequence appeared to be 3 *N* HCl, washing, water-rinsing, then drying. The installation of a bottom-decanter to dry the amalgam from the continuous reduction runs caused a reduction in the average ThO_2 content of the large sponge billets from 1.14 to 0.5 wt %. The presence of residual chlorides, which collected on the cooler surfaces of the vacuum distillation retort, led to the suspicion that, although routine analyses reported no chloride residue in the washed amalgams, some was present, either because it had not been thoroughly rinsed out in the washing operation or because HCl had reacted with mercury to produce mercurous chloride. After some development in analytical methods, chloride was detected in thorium amalgams, and it was shown that the use of 1% sodium versenate in the rinse would remove it.

Figure 6. Billet (left) and cake.

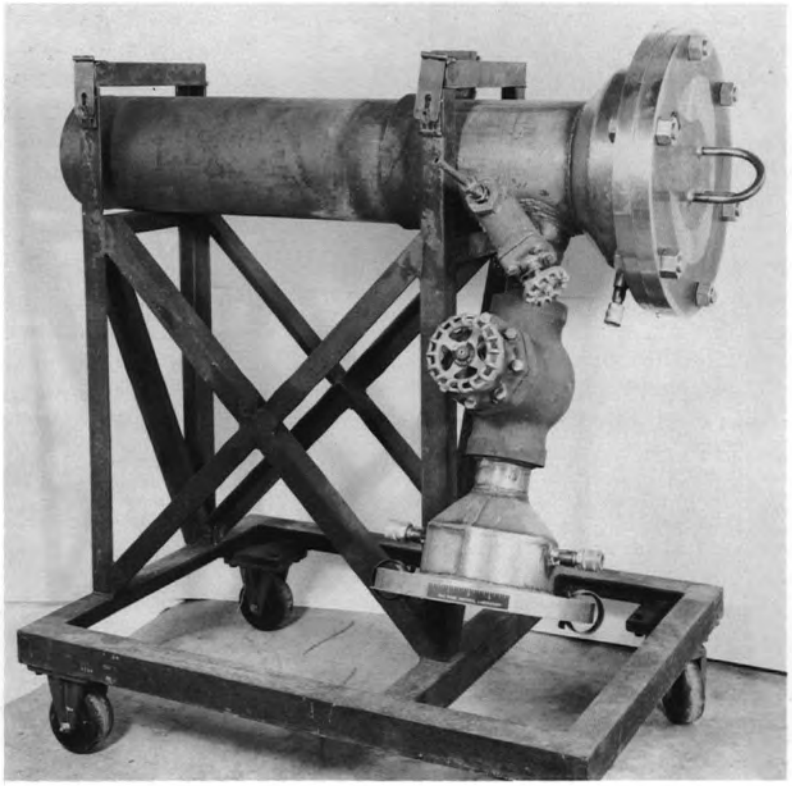

Figure 7. Retort.

Table 1

Thorium Production in Metallex Continuous Process

Conditions: 20-min residence time at 130°C±5°
Feed: $ThCl_4$, sublimed material containing <0.20% H_2O; Na-Hg, 2.5 to 3.8 *M*
Contactor: 1.5-gal Dispersall top-drive unit
Agitation speed: 1160 rpm

Run	Th metal produced, lb	Duration of run, hr	Sodium excess, %	Reduction efficiency, %
7	7.07	5.0	89	66.4
8	25.5	12.75	Variable	83.0
9	22.4	9.5	43	83.3
10	28.3	12.83	25	70.5
11	29.1	13.33	25	75.2
13	63	18.33	51(av)	92
14	50	18.0	18.5	87
Totals	225.4	90		

Average reduction=82.5%.

THE EVALUATION OF METAL PRODUCED BY THE METALLEX PROCESS

The sponge billets produced in the demonstration runs just described, and the metal fabricated by consolidation and extrusion were analyzed for impurity components affected by production methods. In Table 2 the range of impurity concentration in the various analyzed metals is compared to specifications recommended by the Thorium Quality Working Committee.[4] Factors which appeared to affect the ThO_2 content of the sponge metal were temperature in the reduction step, thoroughness of amalgam washing, residual water in the amalgam prior to vacuum distillation, and the bulk density of the sponge billet produced by vacuum distillation. The hydrogen content was dependent on the residual water content of the dried amalgam. Iron content is probably due to corrosion of the vacuum distillation retort by residual volatile chlorides (i.e., Hg_2Cl_2) in the amalgams which were not washed out. Iron, nickel, and chromium were not detected in amalgams which had not contacted steel subsequent to washing. Carbon was picked up by most metal specimens during direct extrusions, probably from the graphite lubricants used. Oxygen was introduced in most metal processing from imperfect atmospheres. Arc-melting tended to reduce all process impurities except iron, nickel, and chromium.

In Table 3 the ranges of bulk density and hardness for the sponge and fabricated metal are summarized and compared with those for similarly treated Ames metal. The density and hardness of sodium amalgam reduced metal compared favorably with those of Ames metal except in the case of the cold-worked specimens.

Tensile test specimens of ¼ in. diameter were prepared for each fabricated metal sample, and the mechanical properties are compared with val-

Table 2

Chemical Properties of Amalgam-Reduced Thorium

Metal source and consolidation method	Impurity concentration range					
	ThO_2, %	H_2, ppm	C, ppm	Hg, ppm	Na, ppm	Fe, ppm
Specifications[1]						
working	2.5	—	800	—	—	250
target	1.0	10	400	39*	—	100
Sponge billets	0.25 to 1.81	4 to 80	200 to 1100	10 to 75	10 to 360	25 to 1530
Small billets consolidated by hot-pressing, then extruded at 800°C	1.04 to 2.48	—	200 to 2200	5 to 59	25 to 186	520 to 2432
Single sponge billets, extruded directly at 700°C	1.4 to 2.5	36 to 130	300 to 3600	10 to 170	50 to 105	30 to 3020
Arc-melted, then extruded	0.58 to 0.76	8 to 13	400 to 440	9 to 21	10 to 12	650 to 1200

*Calculated from boron specification and relative cross sections.

Table 3

Density and Hardness of Amalgam-Reduced Thorium

Metal source and consolidation method	Bulk density range, g/cm³	Hardness range*	
		BHN	VHN
Ames, induction-melted,[5] cast, annealed	11.5 to 11.6	45 to 65	75
Metallex sponge billets	6.9 to 9.8	—	—
Metallex sponge, 50% cold-worked, annealed	9.4 to 11.7	23 to 48	—
Metallex, arc-melted, annealed	11.63 to 11.67	65	62 to 73
Metallex, hot-pressed, directly extruded, 800°C	11.56 to 11.66	56 to 74	—
Metallex, single billets directly extruded, 700°C	11.2 to 11.7	—	45 to 64

*BHN = Brinell hardness number, 500-kg load; VHN = Vickers hardness number, 10-kg load.

Table 4

Mechanical Properties of Amalgam-Reduced Thorium at Room Temperature

Metal source and consolidation method	Range of mechanical properties			
	Ultimate tensile strength, psi	Yield point, psi (0.2% offset)	Elongation, %	Reduction in area, %
Ames, induction-melted,[5] wrought, annealed	25,500 to 32,500	17,200 to 32,900	46 to 59	72 to 76
Ames, chopped, hot-pressed, extruded at 800°C	27,000 to 33,800	15,400 to 23,800	34 to 50	63 to 75
Amalgam-reduced, many pieces, hot-pressed, extruded at 800°C	26,300 to 38,200	17,300 to 25,000	28 to 38	37 to 55
Amalgam-reduced, single billets, extruded at 750°C	15,000 to 19,000	—	10 to 20	—
Amalgam-reduced, arc-melted, cold-rolled, 72% annealed	30,000	22,000	35	—

ues for wrought Ames metal in Table 4. Ultimate tensile strength and yield point of the amalgam reduced samples, except for those extruded from a single sponge billet, were in the same range as the values for Ames metal. A few of the specimens fabricated by hot-pressing and direct extrusion separated axially on rupture, which seemed to indicate that individual pieces were not well bonded. Specimens fabricated from single sponge billets showed low tensile strength, and appeared to rupture at junctions where oxide-coated void walls were pressed together.

Because small sponge billets were not consistently well bonded by hot-pressing and direct extrusion and because arc-melting produced purer metal, the recommended procedure for consolidation of sponge billets to rod is arc-melting followed by extrusion.

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Horizons, Inc., Production of High Purity Thorium Metal by Fused Salt Electrolysis*

BERTRAM C. RAYNES
Horizons, Inc., Cleveland, Ohio

Horizons, Inc., under a four-year research and development contract with the United States Atomic Energy Commission, has successfully piloted a completely integrated process for the production of high quality thorium metal by the continuous fused-salt electrolysis of thorium chloride dissolved in sodium chloride.

Two procedures for the preparation of electrolyzable thorium chloride from thorium nitrate have been piloted; other thorium compounds can be adapted for use as starting materials for cell feed production. An electrolytic cell design has been piloted to accommodate the electrolytic process. Metal recovery procedures are simple and effective.

The finely divided crystalline thorium produced by the process is a free-flowing powder readily adapted to cold consolidation and arc-melting, and to warm extrusion to billets approaching 100% theoretical density. Warm extrusion and subsequent warm-working may obviate the necessity for arc-melting for effective fabrication from electrolytic thorium powder. Arc-melted hardnesses of ingots produced from electrolytic thorium are in the range of 40 to 70 Brinell.

The fused-salt electrolytic process can produce a high quality thorium metal containing $<0.05\%$ total metallic impurities, $<0.20\%$ O_2, 0.003% N, 0.03% C, and $<0.5\%$ HCl insolubles. It is noted that when concentrations of thorium ion are sufficiently high in the electrolytic bath (i.e., of the order of 5 to 15%) rare earth ions remain in the electrolyte, effecting an electrorefining decontamination.

A cost estimate, including amortization but not including the cost of thorium nitrate, has been made for a facility producing 1000 tons/year of thorium metal by this fused-salt electrolytic process. On this production basis, total conversion costs are estimated to be $1.07 per pound of product thorium. In making this estimate an over-all process yield of 90% was conservatively used.

*This work was carried out under the auspices of the United States Atomic Energy Commission under Contract AT(30-1)-1335.

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SESSION IV

FUEL PREPARATION

AND

RADIATION EXPERIENCE - SOLID FUELS

The Fabrication of Thoria and Thoria-Urania

J.H. Handwerk
Argonne National Laboratory, Lemont, Illinois

Thoria (ThO_2) has been fabricated by the ANL Ceramic Group by the conventional methods of slip casting or dry pressing. From the pure oxide, ware has been produced having a density range from 8.0 to 9.9 g/cc. The effect on density of certain additives in ThO_2 was investigated at Armour Research Foundation,[1] and materials such as CaF_2, SrF_2, SnO_2, Bi_2O_3, and U_2O_5 were found to aid the densification of ThO_2, while materials such as Pb_3O_4, PbF_2, and UO_2 were found to retard densification. This work also indicated that vacuum sintering improved the densification of thoria, and that thoria ware fabricated from course thoria was more resistant to thermal shock.

In an effort to improve the thermal shock resistance of thoria, compacts were fabricated from thoria mixed with varying amounts of powdered metals such as aluminum and zirconium. The use of these powdered metals did not appear to improve the thermal shock resistance of the thoria bodies. However, as an additional effort to improve the thermal shock resistance and thermal conductivity, metal fibers were substituted for the metal powder.

The placement of refractory metal fibers[2] in thoria results in compacts with thermal shock resistance vastly superior to that of thoria. Such metals as molybdenum, niobium, and zirconium were incorporated in thoria and fabricated into dense compacts by hot pressing. The best results were obtained with short, thin fibers of molybdenum or niobium. Quantities as low as 5 wt % of these fibers impart to the body excellent thermal shock resistance. Other ceramic and metal fiber combinations have been fabricated that also have excellent thermal shock resistance. Preliminary room temperature thermal conductivity measurements of molybdenum fiber reinforced thoria compacts indicate that the compacts have thermal conductivities approaching those of the metal. The resistance of thoria compacts reinforced with fibers of molybdenum and of niobium to various corrosive environments at elevated temperatures was studied, and compacts containing either molybdenum or niobium fibers were found to be corrosion resistant to water at 400°F. However, because of the presence of numerous cracks and the continuous nature of the network fibers, these compacts were thoroughly oxidized in air at 1000°C.

Thoria-urania mixed crystal bodies were investigated,[3] and it was found that compacts of ThO_2 and U_3O_8 could be formed and sintered in air. Compositions containing up to 30 wt % U_3O_8 could be easily fabricated by incorporating a small amount of an organic binder in the mix and cold pressing. Densities of 90 to 95% of theoretical could be obtained by sintering at temperatures of 1700° to 1800°C. It is now apparent that the organic binder is a detriment to the fabrication of high density bodies containing more than 30 wt % U_3O_8. However, these bodies can be successfully formed by dry pressing a mixture of the pure oxides and sintering in air at temperatures of 1400° to 1500°C. By this procedure bodies containing up to 75 wt % UO_2 can be fabricated to densities of 9.5 to 10.0 g/cc.

Two compositions, one containing 2.5 and the other 10 wt % enriched UO_2, were irradiated in the MTR and CP-5 reactors.[4] These irradiation tests indicated that a thoria body spiked with sufficient enriched UO_2 to cause criticality would be suitable as a nuclear fuel. On the basis of these irradiation tests, a solid solution thoria-urania body containing $\approx$6.0 wt % enriched UO_2 was fabricated into pellets. These pellets were encased in aluminum – 1% nickel alloy tubes and used as a fuel for the BORAX-IV reactor.[5]

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Effects of Irradiation on Thorium-Bearing Fuels

J.H. Kittel
Argonne National Laboratory, Lemont, Illinois

Irradiation experiments at ANL on thorium-bearing fuels have been done on both metallic and ceramic materials. Except for a few irradiations by Reactor Engineering in CP-5 autoclaves, all irradiations have been made by the Metallurgy Division using NaK capsules in the MTR.

METALLIC FUELS

Swaged thorium metal and alloys of thorium with 0.13, 1.39, and 5.53 wt % uranium have been irradiated to total atom burn-ups ranging up to 4%. Irradiation temperatures were low, ranging from 50° to 200°C. The specimens all showed excellent dimensional stability under irradiation. For 1 atom % burn-up, they elongated from 0.06 to 0.3%, increased in diameter from 0.3 to 0.6%, and decreased in density from 0.3 to 1.3%. These changes are much less than those noted in uranium-base alloys.

Specimens now being prepared for irradiation are alloys of thorium with 10, 15, 20, 25, and 28 wt % uranium. Because of fabrication difficulties, the alloys have been cast to size rather than rolled or swaged. Specimens of these alloys will be taken to burn-ups of several atom % at temperatures ranging up to 800°C or higher.

CERAMIC FUELS

Pellets composed of solid solutions of ThO_2 with 2.5 and 10 wt % UO_2 have been irradiated to burn-ups ranging up to 0.42 atom % (including oxygen). Irradiation temperatures have ranged from 120°C to above the melting point (3200°C). All specimens showed dimensional stabilities surpassing those of the best metallic fuels. For example, dimensional changes, if any, in a specimen of the ThO_2 – 2.5 wt % UO_2 composition ¾ in. long and ¼ in. in diameter were less than 0.0002 in. after a total atom burn-up of 0.29%. Lead bonding was shown to be an effective method of preventing movement of fragmented pellets in aluminum jackets.

Specimens now under irradiation include a group of ThO_2 – 6.36 wt % UO_2 pellets lead-bonded in aluminum jackets. These specimens are directly water-cooled in the MTR and have achieved a burn-up of about 1% of all atoms with no difficulties being apparent.

Additional specimens just placed under irradiation in NaK capsules include ThO_2 with 4.1, 10.0, 12.7, and 25.4 wt % UO_2. Irradiations will start soon on a group of ThO_2 specimens containing a wide range of UO_2 contents and also niobium and molybdenum fibers to aid in improving the thermal conductivity of the material.

Review of Thorium Metal Properties and Thorium Fuel Plate Manufacture

J. CUNNINGHAM
Oak Ridge National Laboratory, Oak Ridge, Tennessee

MECHANICAL PROPERTIES

The mechanical properties of thorium and its alloys have been studied rather extensively during the past decade. Unalloyed thorium holds little attraction as a structural material because of its low strength, poor corrosion resistance, moderately high density, and relatively high cost.

By far the greatest amount of data exists for material produced by reduction of ThF_4 with calcium. Considerable data have also been obtained on arc-melted high purity thorium prepared by thermal decomposition of ThI_4. The mechanical properties of material prepared by powder metallurgy techniques, by comparison, have received only limited attention.

In general, the properties of thorium are extremely sensitive to small amounts of impurities, particularly those which dissolve interstitially, such as carbon, oxygen, and nitrogen. Of these carbon shows the greatest effect; 500 ppm more than doubles the hardness. It is also known that fabrication variables as well as certain testing conditions can have a marked influence on the mechanical properties of thorium. Important in this connection are the single or combined effects of such things as method of fabrication, temperature and time of annealing of the cold or warm forming, rate and temperature of extrusion, and rate of straining during testing.

For unalloyed metal, data are given below on the results of tensile (Table 1), compression, fatigue, impact, and hardness tests, including the effects of temperature. Some similar data on thorium alloys and the effect of heat treatment are also available.

Under conventional tensile testing conditions, bomb-reduced metal in the cold-worked and annealed condition often yields without increase in load and exhibits definite upper and lower yield points similar to those observed in mild steel. This phenomenon has been shown to be strain-rate dependent.

Both iodide and bomb-reduced thorium harden rapidly under relatively small degrees of cold work and only slowly in the latter stages. This effect, however, usually does not prevent an extreme degree of cold working.

Hardness measurements have been used extensively in studies of the effects of metallurgical variables and impurities in thorium. The hardness of arc-melted thorium that has been cold-worked and annealed ranges from 32 to 42 on the Vickers scale. The Vickers hardness of wrought annealed bomb-reduced material has been observed as low as 65 and as high as 111.

The effect of temperature on conventional tensile properties of bomb-reduced material has been studied in some detail. The tensile strength of wrought annealed material drops from 37.5×10^3 psi at room temperature to 24.5 at 200°C and to 17.5 at 500°C. The data show an initial decrease in percent elongation before an increase with temperature, an effect which has been observed for other metals which exhibit a yield point at room temperature.

A transition in the hardness curve as a function of temperature is noted at 400°C and is believed to be associated with a shift from one predominating deformation mechanism to another.

Early work on the impact properties of wrought annealed bomb-reduced thorium indicated a ductile-to-brittle transition for this material in the temperature range 100° to 200°C. Tests on iodide thorium, however, have shown that the iodide metal behaves more like f.c.c. metals and does not exhibit a transition temperature on impact. Further studies revealed that the transition temperature on calcium-reduced material is due to the impurity carbon.

The addition of most elements tends to strengthen thorium, but not to a very large extent. Small

Table 1

Conventional Tensile Properties of Thorium at Room Temperature in the Arc-Cast, Wrought Annealed, and Cold-Worked Condition

	Tensile strength, 1000 psi	4S 0.2% offset, 1000 psi	Elongation, %	Reduction in area, %
Iodide (wrought annealed)	17.3 – 19.7	6.9 – 11.2	36 – 44	60 – 62
Bomb reduced (wrought annealed)	33.7 – 39.6	26.3 – 30.3	55	52 – 69
Bomb reduced (arc-cast)		23.2	30	38
Bomb reduced (cold-worked)				
25%	58.7	54.8	11	39
50%	65.4	61.6	5	16

Modulus of elasticity: values at r.t. range from 10.0 to 10.4×10^6 psi.

Poisson ratio values have been determined by various measuring techniques at r.t. A representative value of this property for engineering calculation is 0.27.

additions ($<1\%$) of Nb, Mo, V, and Ti as well as Zr (2 to 5%) however, act as softeners. The mechanism is believed to be one of simply tying up the carbon impurity.

THORIUM FABRICATION

Despite its high melting point, thorium is characterized by low strength and high ductility. Arc melted iodide thorium deforms readily over a wide range of temperature. Impurities tend to impair somewhat the cold-working characteristics of arc cast bomb-reduced metal, but at elevated temperatures the metal can be readily formed into most desirable shapes.

Pure thorium can be cold rolled continuously without intermediate anneals to a reduction of 99% in thickness without cracking. The resistance to deformation can be sharply diminished by heating. The temperature for hot working thorium lies in the 932° to 1292°F temperature range. The practice generally followed for fabrication of bomb-reduced metal into plate, for instance, is to hot breakdown the ingot in order to refine the cast structure, and then to cold roll to finished size.

Thorium is amenable to fabrication by most of the conventional fabrication operations such as rolling, forging and swaging, extrusion drawing, machining, etc. Oxide and slag inclusions tend to abrade the die materials in operations such as extrusion and drawing.

The reactivity of thorium presents a problem during heating for hot working. The metal tarnishes in the ambient atmosphere and reacts readily with carbon, nitrogen, and hydrogen at elevated temperatures. Thorium oxidizes at a faster rate than either Ti or Zr. Much heat is evolved during the reaction of Th and H_2 at 300° to 400°C. Precautions must therefore be taken to prevent contamination during heating for hot working.

Massive pieces of thorium can be heated in air or nitrogen for hot working by forging and rolling when the formation of scale is not particularly important. The flaking of oxide scale presents a radiological health hazard, however. Protection can be achieved by the use of inert gases such as helium and argon, but the method is expensive and does not afford the necessary protection once the metal is removed from the heating furnace.

Protection of thorium during heating for hot working is best accomplished by the use of a molten salt bath. The salt acts as an excellent protective cover and promotes rapid transfer of heat, and the thin layer which adheres to the billet affords protection during transfer from the furnace to the fabrication equipment. Salt mixtures commercially available are generally employed. The bath is usually heated by gas or immersion type heaters and is contained in stainless steel or ceramic pots.

Thorium can be successfully fabricated into rod plate and tubing by the direct extrusion method. In the initial work the material was contained in copper jackets, but bare extrusion with salt bath heating is now widely employed. Initial breakdown can be accomplished by forging, rolling, or

extrusion, but extrusion offers the best method because of the high reduction rates that are possible.

The chief problem in the extrusion of thorium is to find a suitable die material that will stand the abrasive action of the metal. Scale and refractory inclusions tend to abrade or wash the die and limit the life of die material. The peculiar flow pattern and the high coefficient of friction of thorium are two important factors which contribute to the problem.

Fabrication procedures have been developed for hot and cold rolling, forging and swaging extrusion, and drawing. In cold drawing it is important to minimize the carbon content in order to reduce the resistance to deformation, and to employ suitable die lubricants.

Some effort has been directed toward protection of thorium for reactor service by roll and extrusion cladding. The major effort has been concentrated on cladding with Al and Zr.

The problem of cladding thorium with Al is difficult because of the dissimilar nature of the metals. The constitutional diagram shows the presence of 5 intermetallic compounds. Differences in thermal conductivity and expansion lead to warpage and weld breakage during the preparation of composites. The dissimilar flow characteristics between low-melting aluminum and high-melting thorium complicate the problem.

In order to avoid formation and growth of intermetallic layers at the cladding-core interface, the temperature of working must be carefully controlled. At 500°C, the compound $ThAl_3$ invariably forms; the thickness of compound layer formed naturally is diminished with temperature until 400°C is reached, at which point the compound is usually not observed. Al-clad thorium composites are prepared in the 250° to 400°C range with reduction in thickness greater than 5 to 1. At lower temperatures "dog boning" or a differential thickening of the Th core and a corresponding thinning of the Al cladding at the plate ends is encountered. This defect can be minimized by employing a grade of Th low in carbon and high-strength aluminum alloys. This practice tends to match the plastic flow properties of the Th core with those of the aluminum cladding.

Composite plates and tubing have been successfully prepared. The products have limited application however, because of thermal instability at service temperatures above 200°C. Long-time heating above this level results in compound formation and rapid degradation of the product.

The combination of Zr and Th on the other hand is ideal for solid state bonding. Both have high melting points and fairly well matched mechanical and thermal properties. There are no compounds in the system.

The only disadvantage of the combination is the strong tendency for both metals to adsorb gas. Surface oxidation is observed on Zr at a temperature as low as 500°F, but the rate is not rapid until about 1100°F is reached. Thorium tarnishes on exposure to ambient atmosphere. In the preparation of composites by rolling, the compacts are contained in Ti Namel jacket and evacuated for hot working.

Bonding can be achieved by hot working in the 1200° to 1500°F range. Higher temperatures are not employed because of the low melting eutectics in the FeTh and FeZr systems. After hot working at 1200°, it is necessary to resort to a diffusional annealing treatment to enhance bonding. Reductions in thickness of the order of 8:1 are required.

Composite rods, plate, and tubing have been successfully prepared. Properly prepared products are excellent and can be further formed or deformed as though they were solid metal without any deleterious effects.

Calcination of Thorium Oxide for Slurries and Suspensions

C.E. Curtis
Oak Ridge National Laboratory, Oak Ridge, Tennessee

In the development of thorium oxide with properties favorable for use in the H.R.P. slurry blankets, the Ceramic Department has been working in cooperation with Dr. Briggs' group. A wide range of calcination times and temperatures has been investigated. A minimum particle sizing, close to 1 μ, seems to be necessary to keep down the abrasion of pumps and tubes, while low surface area with its attendant surface activity is required if caking is to be avoided. These properties are being obtained at present by a calcination at 100°C for 4 hr. Gas fired kilns of the periodic type are being loaned by the Ceramic Department to aid in this calcination.

As further aid to the H.R.P. group, calcination of ThO_2 in an oxyacetylene torch and in a carbon arc were investigated. Both methods were found unsuitable because the pellets, spheres, and bubbles obtained did not break up readily in loop circulation (Figure 1).

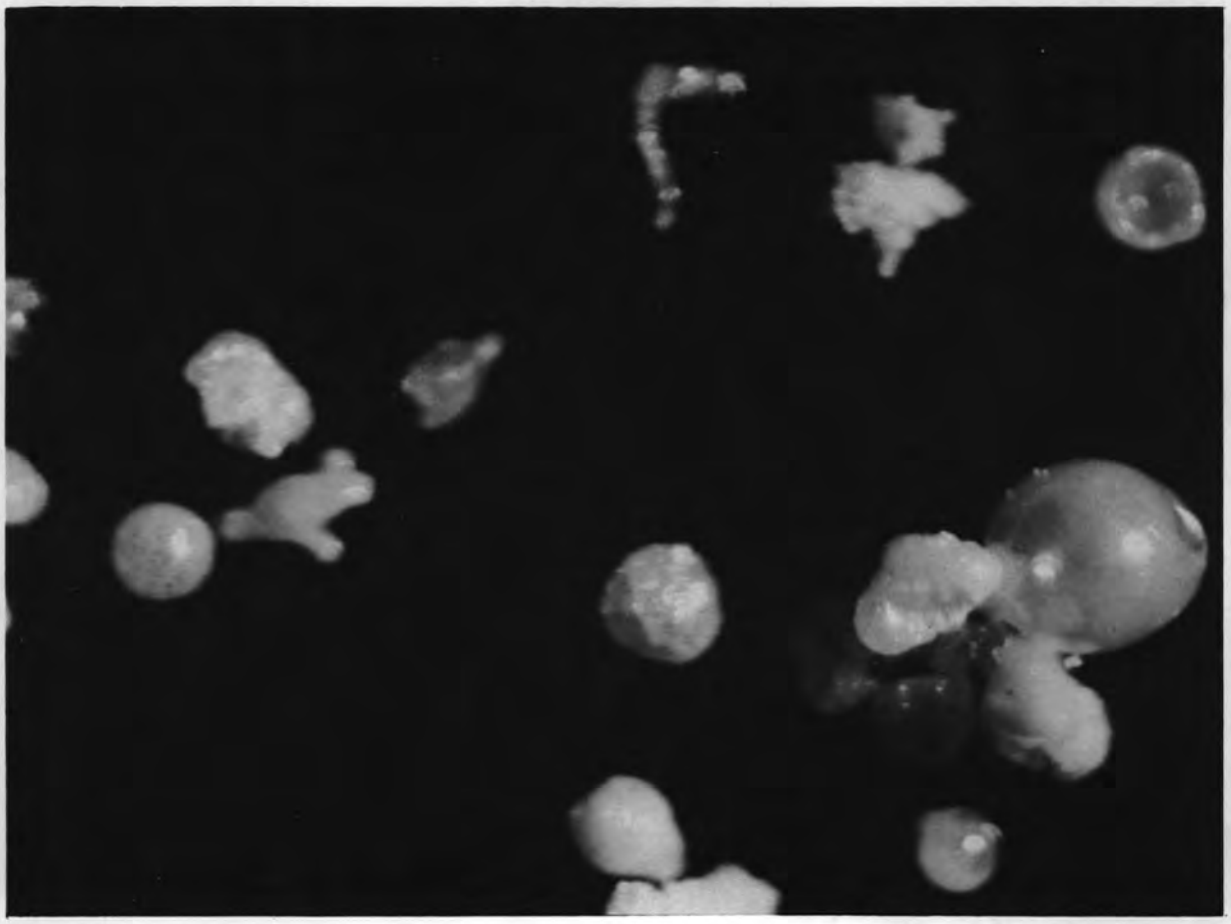

Figure 1. Spheres and bubbles of ThO_2 obtained by calcination in a carbon arc.

SUSPENDING AGENTS FOR THORIUM OXIDE SLURRIES

Dr. E.D. Lynch, a summer participant, found that the suspendibility of thoria slurries was improved by the addition of montmorillonite and attapulgite clays. These materials, in concentrations of 3% and at a *p*H of 7.5 to 9.0, improved the suspendibility markedly, and imparted easy resuspendibility of settled material.[1]

FABRICATION OF THORIUM OXIDE CERAMICS

Thoria powder has been fabricated into ceramics by all of the seven common methods: slip casting, dry pressing, isostatic pressing, jiggering, extrusion, and hot pressing; firing has been tried in air, hydrogen, and argon, and many of the properties of these products have been determined. Furnaces available for this work include propane and oxyacetylene types, electric resistance (silicon carbide, graphite, and molybdenum resistance types), and induction heated.

By isostatic pressing of 1-μ ThO_2 at 10,000 psi and firing at 1750°C for 1 hr, densities of 94 to 96% of theoretical (=100) have been obtained.

It has been found that ½ wt% CaO added as the carbonate or fluoride will increase the density of either coarse or fine ThO_2 to 99 to 100% under the same conditions as above. The effect is probably due to solid solution of the CaO in ThO_2 although no change in the size or structure of the ThO_2 is observable. The CaO leaches out slowly in hot water. The effect is lost if the firing is done in hydrogen. SrO has a similar but lesser effect than CaO.[2]

PHASE DIAGRAMS

The ThO_2-SiO_2 system has one compound, $ThO_2 \cdot SiO_2$, which can be synthesized from the respective oxides at 1500°C. It is unstable above 2200°C, which is below its melting point.

Investigations of syntheses and properties of such compounds as the nitrides, carbides, and hydrides of thorium are under way. Vapor pressure measurements of some of these are being made. It is planned to study triaxial combinations including ThO_2.

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High Temperature Irradiation of Thorium-Uranium Alloys

C.C. Woolsey
Atomics International, A Division of North American Aviation, Inc., Canoga Park, California

Interest in the use of the thorium-U^{233} cycle as a possible thermal neutron breeder cycle in sodium graphite reactors led to the performance of several experiments in the MTR. Since the proposed use would involve surface temperatures of the order of 1000°F and central fuel temperatures of 1200°F and higher, these experiments were designed to achieve such temperatures; further, the fuel slug central temperatures were measured.

The fuel slugs used in these experiments were ⅜ in. in diameter by 1½ in. long. Nominal composition was thorium with 10 wt % fully enriched uranium. The design of the irradiation capsule is shown in Figure 1. An important feature is the use of thermal shields within the capsule to allow the achievement of fuel slug surface temperatures as high as 1000°F when the outer surface of the capsule is cooled by the MTR process water. A thermocouple was placed in each slug ½ in. from the lower end. A tantalum foil prevented reaction between the fuel material and the stainless steel sheath of the chromel-alumel thermocouple. Temperatures were recorded on a six-point recorder throughout the irradiation.

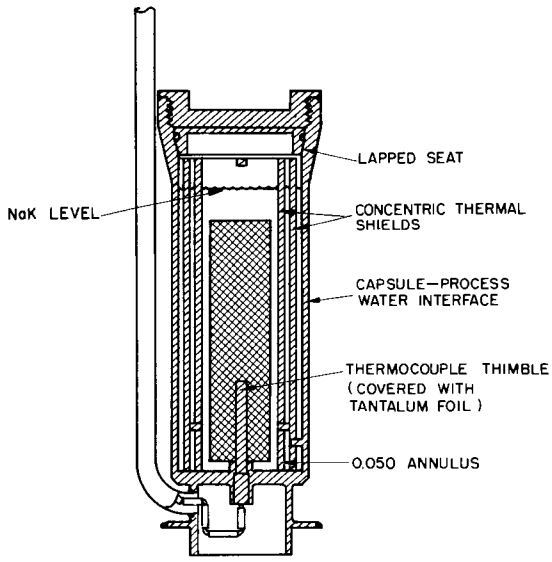

Figure 1. Irradiation capsule design.

Type 304 stainless steel was used for the capsule and inner thermal shield; Invar was used for the outer thermal shield. The lower end of one capsule was placed into the upper end of another and joined with a weld. Five capsules were stacked to form an experimental assembly approximately 13 in. long.

Six experimental fuel slugs have been irradiated and examined. The first achieved a lower temperature than expected, reaching a maximum of only 550°F. The experiment was terminated after a burn-up of only 0.05 atom %. The other five slugs, irradiated as a single series of capsules, achieved temperatures of 1000° to 1230°F and were carried to burn-ups of about 0.35 total atom %. Two additional series of slugs are in the MTR at present, one operating at about 1250°F, the other initially operating at about 1450°F but dropping to about 1250°F by the end of the first cycle. Both will be carried to burn-ups of 0.65 % or more.

Results of these irradiations are shown in Table 1. It will be noted that the low burn-up, low temperature sample showed essentially no dimensional change; any change found was within the experimental error of the measurements.

In the higher temperature irradiations, an effect has been noted at the upper end which leads to the belief that appreciably higher temperatures existed there than those measured by the thermocouple. A greater swelling is noted, leading to a "nail-head" or "mushroom" appearance at that end. This effect has been noted by others in elevated temperature irradiations and is thought possibly to be due to the Wilkins effect, named after the author who explained similar end effects in Hanford slugs in terms of higher heat generation at the corners of cylinders of fuel due to differences in self shielding. Figure 2 (sample NAA-15-5-2) shows a typical slug with this end effect. In tab-

Table 1

Sample No.	Estimated burn-up (%)	Measured temperature maximum (°F)	Average Δd (in.)	Δl (in.)*	ΔV,* Calculated (%)
NAA-15-2-6	0.05	550	0	0	0
NAA-15-5-1	0.35	1155	0.004	0.003	2.4
NAA-15-5-2	0.35	1230	0.003	0.038	4.3
NAA-15-5-3	0.35	1230	0.005	0.029	4.8
NAA-15-5-4	0.36	—	0.007	—	—
NAA-15-5-5	0.35	1000	0.004	0.023	3.9

*May be affected by "mushroom" at top end of specimen.

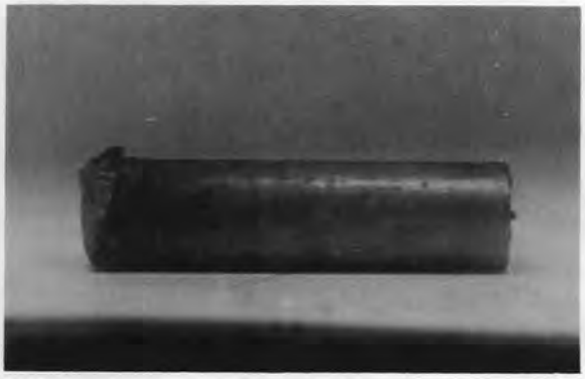

Figure 2. Sample NAA-15-5-2. Estimated burn-up, 0.35%; maximum measured temperature, 1230°F. Typical of slugs showing "mushroom" effect.

Figure 3. Sample NAA-15-5-1. Estimated burn-up, 0.35%; maximum measured temperature, 1155°F; volume increase, 2.4%.

ulating the average change in diameter, the increases due to these end effects were ignored; however, the length changes did necessarily include the end effect. It will be noted that no such end effect was observed in NAA-15-5-1 (see Figure 3) and that the length increase was small. Since the calculated volume increases depend on the length changes as well as the changes in diameter, it is probable that the actual volume increase for the measured temperature is smaller than reported for those slugs showing this "mushroom" effect.

Figure 4. Sample NAA-15-5-4. Estimated burn-up, 0.36%; thermocouple lost early in test. Fracture of specimen occurred in removal from capsule.

One of the samples, NAA-15-5-4 (Figure 4), showed a large enough growth of the upper end to cause difficulty in removing it from the inner thermal shield. The large end was held so firmly that the sample was fractured in attempting to remove it. Subsequently, the thermal shield was slit and the swelled end was released. An attempt was made to obtain some small samples of this swelled end by applying a 5000-lb load and thus causing it to fracture. It was found to be quite ductile; it was reduced to a flat plate less than ⅛ in. in thickness, with no fractures resulting. It is interesting to note that a substantial amount of NaK was squeezed out of the sample during this pressing; it

is estimated that this amounted to about 10% of the volume of the sample. Attempts to squeeze NaK out of the less swelled, lower end of the sample were not successful.

On the basis of these rather limited tests, it is concluded that thorium-uranium alloys of interest for sodium graphite reactors can be operated with central temperatures up to 1250°F, to burn-ups of the order of ⅓%, with resulting volume increases of the order of 3%. Further tests under way at present should give additional information on the behavior at higher burn-up and at higher temperatures.

Thorium Alloy Systems

F.A. Rough
Batelle Memorial Institute, Columbus, Ohio

The temperatures of the thorium alpha-to-beta transformation and melting point have been revised on the basis of studies performed by Chiotti.[1] Carbon is found to exhibit a pronounced effect on these temperatures; by extrapolating the melting and transformation temperatures determined for thorium with varying carbon contents to zero carbon content, corrected values were obtained. These are 1360° ±10°C for the alpha-to-beta transformation and 1775° ±10°C for the melting point.

Much work has been done over a period of years on thorium alloy constitution. While little work has been done recently on thorium for reactor use, there has been some progress in our knowledge of its alloys.

Thorium constitution has been reviewed by Wilhelm[2] and by Saller and Rough[3] covering work available up to about 1955. At that time, data were reported for a total of 35 systems. Of these, complete or partial diagrams were available for 16 systems and miscellaneous information on the remaining ones.

Upon the basis of recently obtained information, revised versions of the systems thorium-aluminum,[4,5] thorium-bismuth,[6] thorium-carbon,[1] thorium-lead,[6] thorium-magnesium,[7] and thorium-zirconium[8] are available. In addition, the thorium-uranium diagram has been revised to include new solid solubility data for uranium in thorium.

The systems of thorium with cerium,[9] hafnium,[8] plutonium,[10] selenium,[11] and tungsten[12] have been determined recently.

The total number of systems for which data are available is currently 38. The status of these data is summarized in Table 1.

Essentially, thorium forms alloys in a manner very similar to uranium, with its large atomic diameter (3.59 A) and different crystal structure accounting for the major differences.

Unlike uranium, it has limited solubility with the refractory elements even at high temperatures; therefore, improvement by alloying tends to be limited. In spite of this, a great deal has been done, and still further accomplishments appear feasible by alloying.

First, thorium forms alloys readily with the rare earths, and it is apparent that the potential of these alloys has not been fully realized. Studies have also been made of numerous alloys to determine mechanical properties and corrosion behavior. The effects of higher additions of alloys on mechanical properties need to be studied. A more intensive study of corrosion resistance would also be profitable, and should include the effects of impurities. In both areas, ternary alloying should be included.

Table 1

Status of Thorium Alloy Systems

Known	Partially known
Aluminum	Boron
Beryllium	Cobalt
Bismuth	Hydrogen
Carbon	Iron
Cerium	Lanthanum
Chromium	Manganese
Copper	Mercury
Gold	Molybdenum
Hafnium	Nitrogen
Lead	Oxygen
Magnesium	Phosphorus
Nickel	Silicon
Niobium	Sodium
Plutonium	Sulfur
Selenium	Tantalum
Silver	Tellurium
Titanium	
Tungsten	
Vanadium	
Uranium	
Zirconium	

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Summary of Development Work on Thorium at Sylcor

J. ZAMBROW
Sylvania-Corning Nuclear Corporation, Hicksville, New York

INTRODUCTION

The development work on thorium at Sylcor was done over a period of several years under the sponsorship of the Washington AEC and other AEC installations. Initally, the work was undertaken as an exploratory program for the Washington office, but as the scale of the work increased the sponsorship was transferred to the Oak Ridge Operations Office and finally to the Savannah River office. The work covered four general phases: 1) production of powder, 2) arc melting, 3) powder metallurgy, and 4) canning.

PRODUCTION OF POWDER

Hydride Methods

The first work undertaken at Syclor was on the powder metallurgy of thorium. Since no powder was available commercially, it was necessary to develop a method for making thorium powder on a laboratory scale. Facilities had been established for the preparation of uranium powder by the hydride method, therefore it was decided to use the same method for the preparation of thorium powder. Ames billet was used as the starting material. Powder of good quality was made in this way.

Calcium Reduction of Thorium Oxide

There were two reasons for the study of the calcium reduction of thorium oxide. First, difficulty was encountered in other reduction processes in obtaining metal of adequate purity. It appeared that the calcium reduction of the oxide might provide a simple means of obtaining metal of satisfactory purity. Second, since a powder was ultimately needed for powder metallurgy techniques, it was cheaper to reduce the metal directly to a powder than to convert massive metal to a powder.

A process was developed whereby thorium oxide was reduced directly to a metal powder by the use of calcium metal, and demonstrated on an 11-lb scale. The process was shown to be capable of producing metal for reactor application from high-purity raw materials without a significant pickup of harmful impurities.

The utilization of type 446 stainless steel as the reactor material of construction resulted in easy breakout of the reduction product without any adverse effect on metal quality. This solution was a major improvement over other versions of preparation of thorium metal from the oxide.

The following chemical analysis of thorium powder prepared on the 11-lb scale demonstrates the high purity attained at the conclusion of the program:

HCl insolubles:	0.15%	
Nitrogen:	60	ppm
Carbon:	190	"
Iron:	54	"
Chromium:	13	"
Calcium:	200	"

It should be noted that all other impurities, especially the high neutron absorption cross section elements in the metal, derive essentially from the thorium oxide feed material. The contribution of such impurities from other sources generally has been found to be insignificant. Thus powder of any reasonably high degree of purity may be produced by the use of an oxide of similar quality.

ARC MELTING

The consumable electrode arc melting of cold compacted thorium powder was developed to produce dense, clean, and soft ingots which could be hot rolled without cracking. By using a water cooled copper crucible, contamination was prevented and ingots cleaner than the original powder were produced.

The relationships of specific variables such as power at the arc, crucible size, electrode size, and argon pressure were determined relative to minimum requirements to obtain sound ingots. The

data were found to be applicable to other metals when reasonable corrections were applied. The following is the chemical analysis of a typical ingot melted from powder:

Nitrogen:	55 ppm
Carbon:	≈40 "
Hydrogen:	45 "
Calcium:	≈30 "
Magnesium:	8 "
Zinc:	Undetectable
HCl insolubles:	0.45%

The hardness of this ingot was 57 BHN and the density was 11.69 g/cc.

POWDER METALLURGY

The work on powder metallurgy covered the various powders that were available. These included powders prepared by Metal Hydrides Inc. and Horizons Inc. as well as those prepared at Sylcor. Studies included cold pressing, sintering, and hot pressing of thorium and also some work on thorium-uranium alloys.

Cold Pressing

It was possible to cold press thorium powder to fairly high densities with reasonable pressures. The maximum density obtainable appeared to be a function of the purity of the powder. For example, the powder made by calcium reduction of the oxide could be pressed to 95% of theoretical under a pressure of 75 tsi. Such compacts were quite strong (modulus of rupture 10,000 psi) and could be handled readily.

Sintering

Sintering of the various cold-pressed compacts was studied in the temperature range 1200° to 1600°C. Sintering was done in vacuum and in argon. Generally, the density increased with increasing sintering temperature except for the Horizons powder, which contained contaminants that appeared to cause porosity above 1400°C. Generally the samples sintered in argon appeared to be comparable to those sintered in vacuum.

Hot Pressing

Hot pressing variables of time, temperature, and pressure were studied for electrolytic, dehydrided, and calcium reduced thorium powders. All powders were found to yield high densities of about 11.5 g/cc when the variables were within the following ranges: temperature, 625° to 650°C; time at pressure, 10 to 15 min; pressure, 12 to 15 tsi.

A preforming procedure prior to hot pressing was found to be effective for thorium powders which had low apparent densities. Microstructure of typical hot-pressed samples showed that electrolytic powders contained large grains. Dehydrided and calcium reduced thorium showed a thorium matrix with a relatively uniform distribution of impurities believed to be mainly oxides.

Thorium-Uranium Alloys

Thorium-uranium alloys were made by cold pressing and sintering metallic powders. The alloys studied ranged up to 5 volume % uranium. There was found to be little interaction between the thorium and uranium. At temperatures above 1350°C the uranium was completely spheroidized.

CANNING

Considerable effort was put into the canning of thorium in aluminum. The work included slugs made from wrought thorium and slugs made by powder metallurgy. Canning was done by the hot pressing method in which the slug was bonded to the can and the can simultaneously sealed. It was found that with this technique the aluminum could be bonded to the thorium directly, that is, without the use of any barrier material. Techniques were developed for the cleaning of the thorium slugs and the aluminum cans.

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SESSION V

FUEL PREPARATION

AND

RADIATION EXPERIENCE – FLUID FUELS

U^{233} and Thorium Fuel Preparation and Radiation Experience

L.R. Weissert
The Babcock & Wilcox Company, Lynchburg, Virginia

OXIDE

As part of the core development program for the Consolidated Edison Project, the fabrication of pressed and sintered shapes containing mixtures of thoria and urania is now being investigated. The objective of the program is to produce high-density, close-tolerance pellets from commercially available powders by conventional ceramic techniques. The incorporation of burnable poisons, as either boron or rare earth compounds, in the fuel material is the subject of additional investigation.

IRRADIATION EXPERIENCE

The Babcock & Wilcox Company is completing a high pressure, high temperature, water-cooled loop to test the irradiation performance of thorium oxide for the Consolidated Edison Thorium Reactor. Testing of stainless steel clad, thoria-base-urania pelleted fuel elements will be initiated in the Materials Testing Reactor during the first quarter of 1958.

Molten Salts as Breeder Fuels

W.R. Grimes
Oak Ridge National Laboratory, Oak Ridge, Tennessee

GENERAL DESCRIPTION OF PROBABLE REACTOR

The ORNL-MSR program under the general direction of Dr. H.G. MacPherson has been in existence for somewhat more than one year, but at a very modest level of effort; therefore the MSR is in a preliminary planning stage, and some of the design conclusions must be considered tentative. It is likely that the first reactor of this family may be a simple U^{235} burner (or even possibly a plutonium burner). However, a considerable fraction of the design effort has been spent in examination of two-region breeders; some of these look moderately attractive.

A typical reactor under discussion would produce 600 Mw of heat with its fuel emerging from the core at 1250°F and returning at 1100°F. The reactor of spherically symmetric geometry would contain no additional moderator; the core diameter might be 5 to 10 ft. The blanket thickness is about 2 ft with the core vessel of ⅓-in. thickness of Inor-8 or Ni alloy with 7% Cr and 16% Mo; Inconel could almost certainly be used for this purpose.

The fuel carrier is a $LiF\text{-}BeF_2$ mixture probably containing 31 M % BeF_2; the Li used is to contain 0.01% Li^6. The fuel mixture will probably contain <0.3 M % UF_4 (93% U^{235}) and <1 M % ThF_4. The blanket may consist of 75 M % LiF – 25 M % ThF_4, but is more likely to be chosen from within the $Li^7F\text{-}BeF_2\text{-}ThF_4$ ternary system.

A secondary coolant of alkali metal, molten salt, or possibly He would transfer the heat to a steam generator, or possibly a molten-salt secondary coolant will drive a mercury turbine. In any case it would appear that conversion efficiencies above 40% could be realized.

CHOICE OF FUEL AND BLANKET SYSTEM

Molten fluorides as fuels for breeders are at a considerable disadvantage insofar as neutron economy is concerned in comparison with such fuels as heavy water solutions or fuels based on molten bismuth. They offer, however, among their several advantages the fact that high concentrations of thorium can be used in homogeneous solution. It seems obvious that no single set of fuel components will prove optimum for all reactor types, but it is likely that the optimum breeder fluids must be found in the $LiF\text{-}BeF_2\text{-}ThF_4\text{-}UF_4$ quaternary system.

Detailed investigation of the phase diagrams of the quaternary and its family of binary and ternary systems clearly reveals that melting points below 500°C are available over a wide range of compositions. The lowest melting point available in the quaternary system appears to be about 350°C at about 52 M % BeF_2 and 1 M % UF_4 and ThF_4. Heat transfer properties of mixtures of this family appear quite adequate for the purpose; but it is likely that the fuel chosen will melt well above the minimum described, since viscosity of the material increases considerably with increasing BeF_2 concentration.

The corrosion of Inconel and Inor by these materials at 1250° to 1100°F appears to be very slight. The corrosion is independent of the flow rate, does not depend on a protective film, and is apparently controlled by the rate of diffusion of Cr in the cooler region of the machine. Pump loop tests at Reynolds numbers of 5000 indicate corrosion to a depth of 2 mils/year and no "mass transfer."

FUEL PREPARATION

It is convenient to fuel reactors of this type by adding the barren carrier (probably with the ThF_4) to the heated fuel circuit and then bringing the reactor to critical concentration by addition of known increments of a uranium-rich liquid (a $LiF\text{-}UF_4$ mixture in this case) to the circulating fluid. Fuel is, accordingly, prepared as inert solvent and concentrate.

Nuclear poisons are not common contaminants of the fluorides of reactor interest. Purification processes are, accordingly, designed to insure absence of sparingly soluble oxygen compounds and to minimize corrosion rather than to effect marked improvement in neutron economy.

The process described below for $NaZrF_5$ and Na_2UF_6 (the solvent and concentrate for the Aircraft Reactor Experiment) has been shown to be applicable with only minor modifications to a wide variety of fluoride compositions.

The molten mixtures were purified at 800°C by alternate sparging with HF and H_2 in a closed system of Ni. $NaZrF_5$ was processed in 250-lb and Na_2UF_6 in 30-lb batches. The blended raw materials were melted and heated to 800°C under a flowing atmosphere of HF to remove water. Sparging with dry H_2 reduced penta- and hexavalent uranium compounds, sulfate, and extraneous oxidants. Subsequent HF sparging volatilized HCl and H_2S and converted any oxygen compounds to fluorides but dissolved considerable NiF_2 in the melt by reaction of the gas with the container. A final 24 to 30-hr sparging with H_2 reduced this NiF_2 and FeF_2 contained in the charge to insoluble metals. Partial pressure of HF in the H_2 emerging from the melt was measured to evaluate completeness of the reduction step. The purified melt was then forced through a transfer line, containing a filter of sintered nickel and a sampler, into a clean Ni receiver vessel where it was allowed to freeze under an atmosphere of He. By use of appropriate valves and connections the cold receiver was detached from the production assembly and attached to a helium-filled manifold for storage without exposure of the contents to atmospheric contamination.

The $NaZrF_5$ and Na_2UF_6 produced showed <1 ppm boron and <100 ppm Ni plus Fe; no trace of oxygen-containing phases was detectable under the petrographic microscope.

A transfer line built into the receiver permitted discharge of the remelted contents by use of He pressure; transfer of 250 lb $NaZrF_5$ into the reactor in this manner generally left <0.5 lb in the receiver. Na_2UF_6 was added to the reactor with simple equipment which drew a predetermined quantity (usually 1 to 10 lb) of the melt from the receiver and added this increment to the circulating system.

Subsequent experimentation has shown that Cu-lined steel is more satisfactory than Ni for the reaction vessel.

RADIATION STABILITY

A series of experimental irradiations of various molten fluorides has been carried out in Van de Graaff accelerators, in cyclotrons, and in nuclear reactors, the bombarding radiations including electrons, protons, deuterons, fast neutrons, and fission fragments. Both accelerator and reactor experiments were made on quasi-static samples of molten fluorides contained in small capsules of nickel, stainless steels, and Inconel. Four experiments have been made with molten fluorides circulated in closed loops, at least partially within the cores of test reactors. One experimental reactor has been operated.

Radiation effects on the fuels were searched for by attempts to measure gas evolution from capsule experiments and by chemical, mass spectrographic, and petrographic analyses. In no cases have molten mixtures of the fluorides of the alkali metals, beryllium, zirconium, trivalent uranium, and tetravalent uranium been observed to change chemically, beyond the introduction of fission and corrosion products. No analytical evidence has been obtained for an acceleration by radiation of the corrosive attack by these molten salts on their containers. Corrosion of the containers was studied by metallographic examinations of fuel-metal interfaces. No reliable evidence has yet been found for enhancement of the rate of corrosion by irradiation.

Molten fluoride fuel mixtures have been shown to withstand accumulation of considerable quantities of fission product compounds without adverse effect. The noble gases are very sparingly soluble and are readily removed by sparging with He. The alkalies, alkaline earths, and zirconium form fluorides which are very soluble at operating temperatures. The rare earth fluorides are sufficiently soluble to avoid precipitation during reasonable uranium burn-up. Such elements as Mo, Nb, and Ru probably appear as metals which are very insoluble in the melt and which tend to alloy with the container metal.

The Preparation of Thorium Oxide for HR Blanket Slurry

D. Ferguson
Oak Ridge National Laboratory, Oak Ridge, Tennessee

The aqueous homogeneous thorium breeder reactor being developed at ORNL will use a blanket of ThO_2 slurried in D_2O. In many respects thoria is an ideal slurry material. It is insoluble and has adequate chemical stability. In addition, when properly prepared, thoria as an aqueous slurry maintains its initial physical properties under prolonged pumping and neutron irradiation and gives negligible erosion and corrosion.

The principal method of preparation of thoria for the tests at ORNL has been the thermal decomposition of thorium oxalate. With this method, the particle size and, to a certain extent, particle shape may be controlled in the thorium oxalate precipitation, since the oxide retains the particle size of the oxalate. The specific surface area, the chemical nature of the surface, and particle integrity are controlled by the firing temperature used for the oxide.

Large quantities of oxide prepared from oxalate precipitated at 70°C with 1 *M* $Th(NO_3)_4$ and 1 *M* $H_2C_2O_4$ used as reagents and fired to 800°C have been tested. This oxide is in the form of platelets, on the average 5 μ on edge and 1 μ thick. In this form, the particles break up readily on pumping as an aqueous slurry and in many cases reagglom-

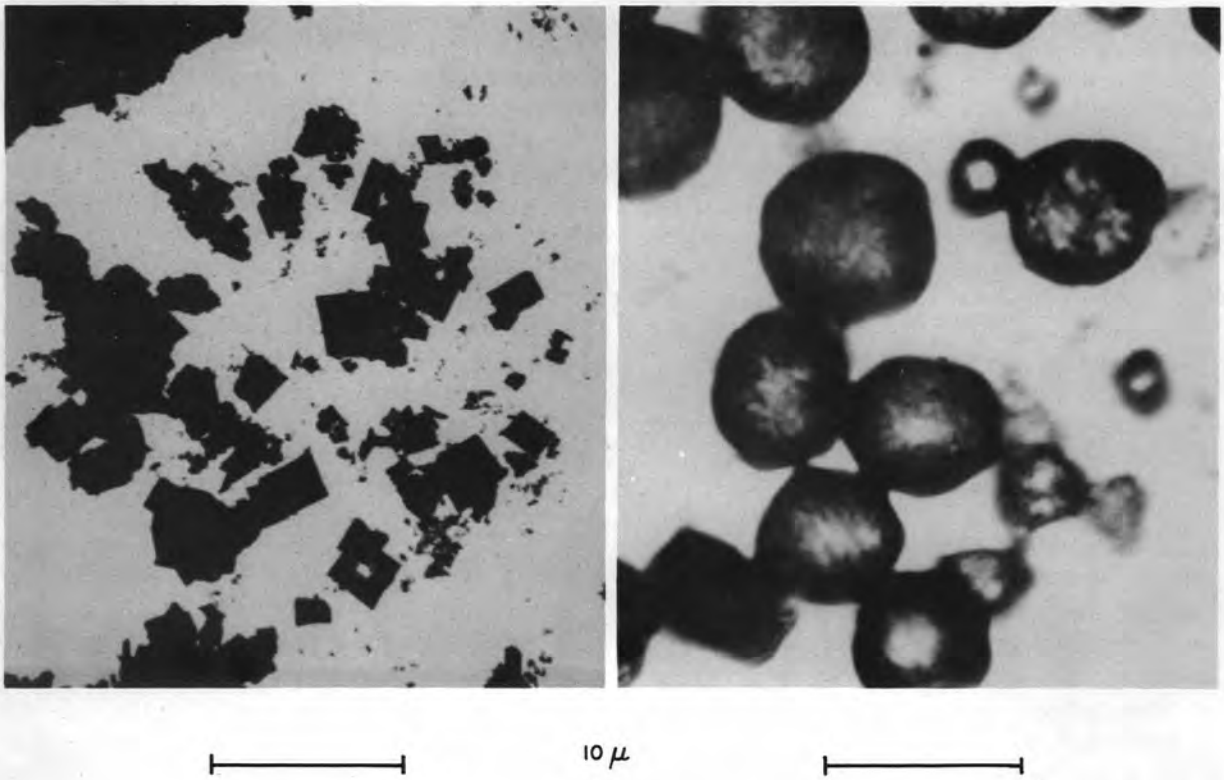

Figure 1. ThO_2 before and after pumping.

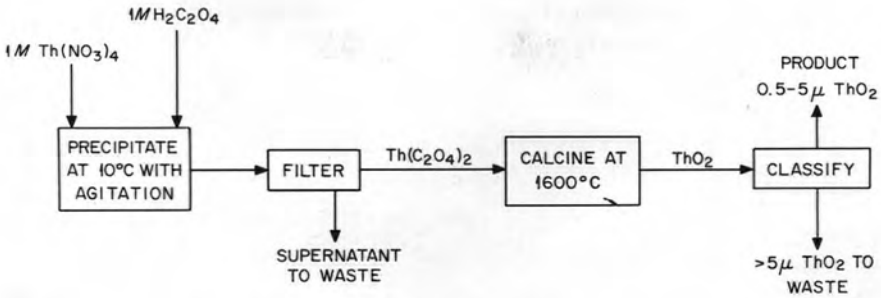

Figure 2. Preparation of 1-μ ThO_2, 1600°C calcined.

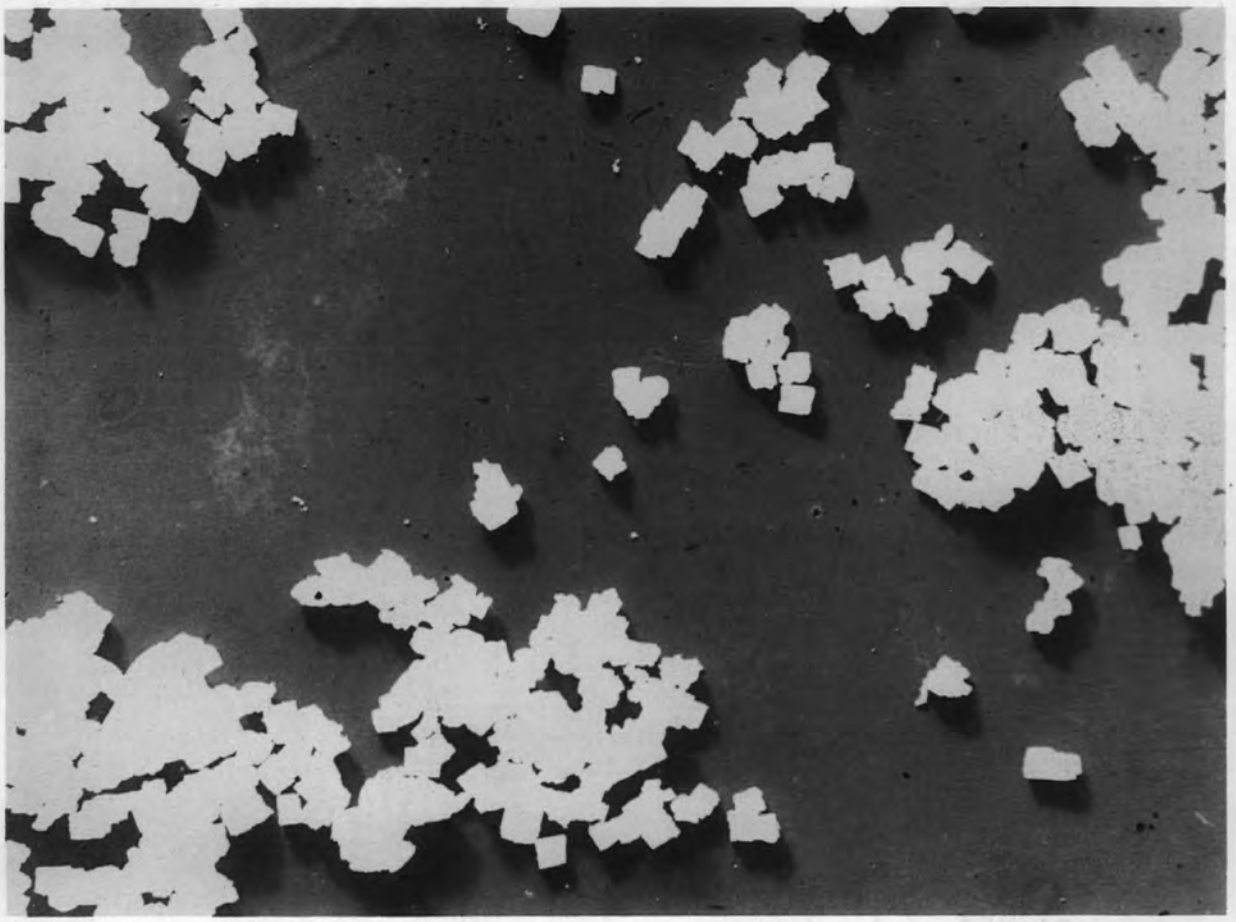

Figure 3. Cubical thorium oxide.

erate to cakes in pumps and piping, form large spherical particles, and in general give a slurry whose rheological properties are far from ideal (see Figure 1). In addition, severe erosion is encountered during the degradation of the 5-μ particles.

The degradation of the oxide particles and accompanying erosion can be avoided by making the particles smaller and firing them to 1600°C. There are several ways of reducing the size of the original thorium oxalate particles: precipitating with violent agitation, lowering the precipitation temperature, and increasing the reagent concentration.

Several hundred pounds of oxide have been made with an average particle size of 1 μ by batch

precipitation with 1 *M* reagents at 10°C and firing to 1600°C (Figure 2). The final oxide must be classified to remove oversized particles, which are extremely erosive. The product oxide is in the form of 1-μ cubes (Figure 3) and has given excellent results in all tests to date. A slurry of this material has low yield strength, is essentially nonerosive, and appears to be unchanged by prolonged pumping at elevated temperatures and by neutron irradiation.

It is possible to prepare a more uniform material by precipitating under conditions of violent local agitation (Figure 4). To accomplish this in a large tank, the agitator is mounted in a draft tube into which the oxalic solution is introduced. With this arrangement, the very fine particles made during the initial part of the precipitation are recirculated through the precipitation zone and grown to the desired particle size. This is an extension of a jet precipitation method (which was not successful for this preparation because it gave an oxide particle size range which sintered badly on firing even to 1200°C). Thorium oxalate precipitated by this method can be fired to 1600°C without a large fraction of oversize particles being formed. The average particle size of the oxide can be varied at will from 0.9 to 2.5 μ by varying the rate of oxalic acid addition and stirring speed.

Houdry Laboratories has prepared test quantities of spherical, controlled particle size ThO_2 by atomizing a fast-setting thoria gel into oil and subsequent drying and firing. Tests on this material are just beginning.

A slurry of high-fired ThO_2 or mixed uranium-thorium oxide can be made catalytically active for the recombination of radiolytic hydrogen and oxygen formed in the reactor. The addition of 0.048 *M* MoO_3 to 1600°C fired ThO_2 containing 0.5% U gave a slurry capable of recombining 75 to 85 moles H_2/hr-liter of slurry (Figure 5), more than seven times the required rate for a reactor blanket.

Results of neutron irradiation of slurry in the LITR at a flux of 2.3×10^{13} n/cm^2-sec for periods up to 300 hr for stirred slurry and 2000 hr for settled slurry have shown no effect of irradiation on apparent viscosity, particle size, crystallite size, or settled density (Figure 6). The *G* value for H_2 production has been measured as 0.5 molecules H_2 per 100 ev of energy absorbed. These in-pile experiments have also demonstrated the effectiveness of MoO_3 as a catalyst in the presence of the expected level of fission and corrosion products.

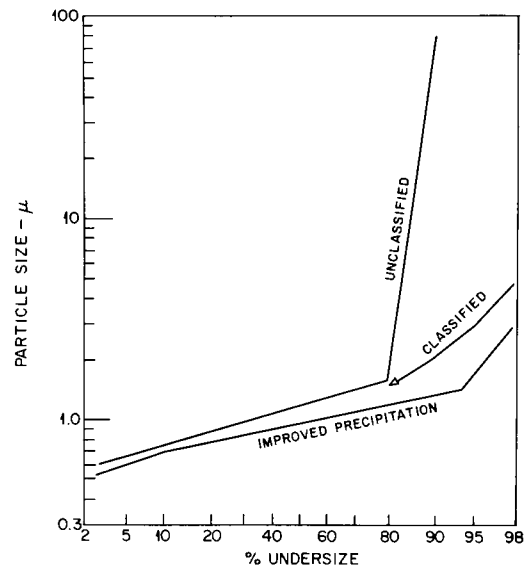

Figure 4. ThO_2 particle size.

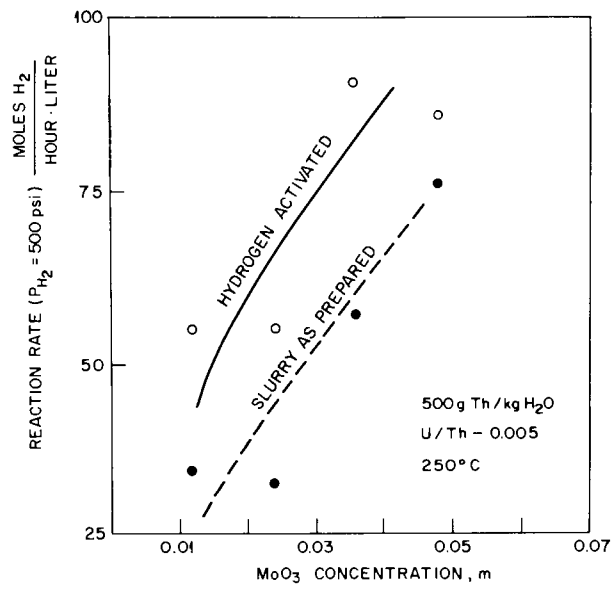

Figure 5. Hydrogen-oxygen reaction in thorium-uranium oxide (1600°C) slurries containing molybdenum oxide catalyst.

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TEMPERATURE : 300 °C

FLUX: 2.7 X 10^{13} n/cm^2·sec

EXPOSURE TIME: TO 385 HR STIRRED-2090 HR UNSTIRRED

RESULTS INDICATE:

(1) NO CHANGE IN
- (a) APPARENT VISCOSITY
- (b) SETTLED DENSITY
- (c) CRYSTALLITE SIZE
- (d) PARTICLE SIZE

(2) FISSION PRODUCTS (EXCEPT Cs) AND CORROSION PRODUCTS ARE WITH SOLID PHASE

(3) G VALUE: ~0.5 MOLECULES H_2/100 ev

Figure 6. Irradiation of ThO_2 slurries.

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Thorium Suspension in Liquid Metals

JOSEPH S. BRYNER
Brookhaven National Laboratory, Upton, New York

Suspensions of thorium in liquid metals are being considered for use as fluid breeder blanket materials in thermal reactors with a U^{233}-Th^{232} fuel cycle. Such suspensions would be expected to possess most of the advantages of fluid materials for reactor use. They could be circulated outside the blanket region for removal of heat and bred products by pumping through closed containers. This facilitates the handling of the highly radioactive materials and minimizes the possibility of spreading contamination. The liquids do not require expensive mechanical fabrication and are not subject to radiation damage. In addition, the liquid metals are stable at high reactor temperatures, thus avoiding the problem of high-pressure containment. In a Liquid Metal Fuel Reactor, the use of a liquid metal blanket system permits balancing the liquid pressure across the wall separating the fuel and the blanket material.

The liquid metal which might be used in such blanket materials must have low melting temperatures and low thermal neutron absorption cross sections. These considerations limit the possibilities to bismuth and lead. The low solubility of thorium in liquid bismuth, lead, or bismuth-lead mixtures prohibits the use of liquid metal solutions. It is therefore necessary to use suspensions of thorium-bearing solids in these liquids to achieve thorium contents sufficiently high for efficient breeding.

The solids that can be used may be divided into two classes. One class contains the intermetallic compounds in the Th-Bi-Pb system which are in equilibrium with the low-melting, bismuth-lead liquids at reactor temperatures. Phase diagram studies have indicated that the following examples are possibilities: 1) $ThBi_2$ (in bismuth or in lead-bismuth eutectic), 2) Th_3Bi_4 (in 92 wt % Pb – 8 wt % Bi), 3) $ThPb_3$ (in lead). The other class of solids

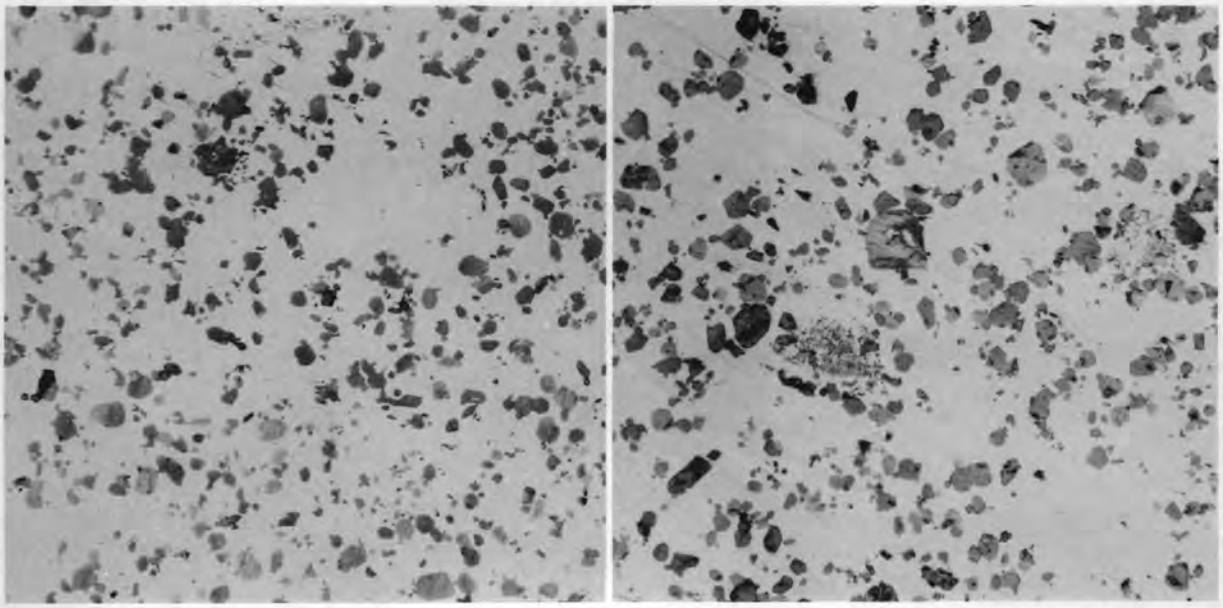

Figure 1. Suspensions of equiaxed $ThBi_2$ particles in Bi produced by heating Th and Bi at 500°C for 2 hr. 5 wt % Th – 95 wt % Bi. 150 ×. (a) Left: Th added as 325-mesh powder. (b) Right: Th added as 0.01-in.-thick chips.

contains the ionic or nonmetallic compounds formed between thorium and other elements of low cross section. Typical examples of these solids are ThO_2, ThF_4, and ThC.

For high fluidity in such suspensions, the volume concentration of solids may not exceed $\approx$25%. The maximum concentration is favored when the solid particles have equiaxed shapes and are larger than colloidal in size. In the case of the intermetallic compound suspensions, this consideration limits the thorium content of the $ThBi_2$ suspensions to 10.0 wt % Th, of the Th_3Bi_4 suspension to 12.4 wt % Th, and of the $ThPb_3$ suspension to 6.7 wt % Th. In the case of the nonmetallic compound suspensions, the maximum thorium contents are in the neighborhood of 20 wt % Th.

In order to permit a possible breeding gain, the thermal neutron utilization factor ($\mathcal{N}_{Th}\sigma_{Th}/\sum\mathcal{N}\sigma$) of such a suspension must approach 1 as closely as possible, and almost certainly must exceed 0.9. This limitation eliminates all the intermetallic compound suspensions except $ThBi_2$ in bismuth (TNUF=0.96) and possibly $ThBi_2$ in Pb-Bi eutectic (TNUF=0.89) unless low cross section isotopes of lead are used in place of natural lead. The nonmetallic compound suspensions meet this requirement without difficulty.

For ease in maintaining suspensions, the densities of the liquids and solids should be close. This condition is met by all the systems listed. In addition, the solids must be wetted by the liquids. The intermetallic compounds are perfectly wetted by the liquids in equilibrium with them. Although nonmetallic compounds are not normally wetted by liquid bismuth or lead, wetting may be achieved by minor additions of other elements in solution in the liquids.

METHODS OF PREPARATION

Intermetallic Compound Suspensions

Several techniques have been developed for preparing suspensions of essentially equiaxed intermetallic compound particles in liquid bismuth, lead, or lead-bismuth mixtures. In one technique, called the "exfoliation method," metallic thorium in the form of powder or thin chips is heated in contact with the liquid under an inert atmosphere at temperatures between 500°C and the temperature of complete solution. The intermetallic compound forms at the thorium-liquid interface and exfoliates into the liquid as extremely fine particles ($\approx$1 μ). These grow rapidly into equiaxed single crystals with a maximum dimension of $\approx$50 μ at 500°C. The time required for complete reaction increases with the dimensions of the thorium, but the ultimate particle size is only slightly affected. For example, 325-mesh thorium powder reacts completely with bismuth in 5 min at 500°C, thorium chips 0.10 in. thick require 2 hr at 500°C for complete reaction in bismuth, and chips 0.20 in. thick require 13 hr. Comparison of a suspension produced from 325-mesh powder with one produced from 0.010-in. chips, both shown in Figure 1, reveals very little difference in particle size. Increasing the temperature decreases the time required, but increases the particle size. The reaction becomes more sluggish as the lead content of the liquid is increased. If the thorium is added to the surface of the liquid at the desired temperature, it must be mechanically stirred through the surface; otherwise a crust of intermetallic compound forms at the surface which is strong enough to support subsequent thorium additions and thus slow down and even prevent complete reaction. During the reaction, which is exothermic, an appreciable evolution of an unidentified gas has always been observed. It is necessary to stir the suspensions under vacuum in order to remove entrapped bubbles of the gas. The exfoliation method has been used to produce suspensions of $ThBi_2$ in bismuth in batches of up to 90 lb. It could be readily adapted for initial preparation of suspensions on a tonnage scale.

An electrolytic method of preparing thorium intermetallic compound suspensions has been studied. In this method, finely divided thorium is electrodeposited upon a liquid metal cathode from a supernatant mixture of fused chlorides. The thorium must be stirred into the liquid, where it reacts as in the exfoliation method. Suspensions of $ThBi_2$ in bismuth satisfactory with respect to thorium content and particle size and shape have been produced in batches of up to 10 lb under the following range of conditions.

Voltage: 4 to 5 v.
Current density: 25 to 163 amp/decimeter^2.
Temperature: 525° to 710°C.
Salt composition: Various proportions of anhydrous NaCl, KCl, and $ThCl_4$ above 650°C; various proportions of NaCl, KCl, $CaCl_2$, and $ThCl_4$ below 650°C; Th content from 10.0 to 31.6 wt %.

Unfortunately, the necessary stirring introduces salt inclusions which are difficult to remove com-

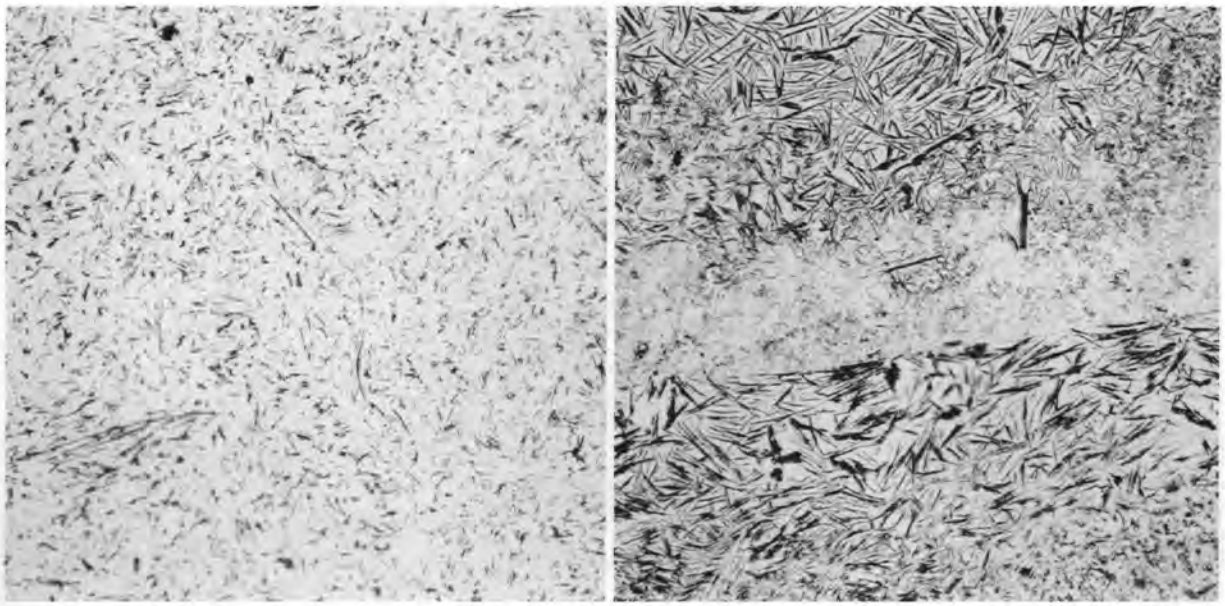

Figure 2. Suspensions of small $ThBi_2$ platelets in Bi produced by rapid cooling of solutions of Th in liquid Bi. 150×. (a) Left: 5 wt % Th, cooled from 1000°C. (b) Right: 10 wt % Th, cooled from 1100°C.

pletely. These would impair the neutron economy of the suspensions because of the high thermal neutron absorption cross section of chlorine. The method is therefore not yet considered satisfactory.

A preparation method has been developed primarily for reconstitution during or after the processing of an irradiated Th-Bi suspension for removal of bred products. In this method, the thorium is completely dissolved in the bismuth by heating to a sufficiently high temperature (>950°C for 5 wt % Th, >1060°C for 10 wt % Th). Cooling the solution very rapidily at a rate in the neighborhood of 1000°C/sec causes precipitation of $ThBi_2$ in the form of platelets $\approx 50\ \mu$ in diameter by $1\ \mu$ thick. Figure 2a shows the size of the platelets formed by pouring a solution of 5 wt % Th in Bi from 1000°C into a graphite crucible at room temperature. Very rapid cooling is necessary, because the platelet size increases as the cooling rate is decreased. This effect is demonstrated in Figure 2b, which shows the size of the platelets formed by pouring a solution of 10 wt % Th in Bi from 1100°C into a graphite crucible at room temperature. The layered structure is due to individual drops of solution which flattened and froze before the following drop landed. The increase in platelet size from the bottom to the top of each layer shows the extreme sensitivity of the dependence of platelet size upon cooling rate. These platelet dispersions are extremely viscous when the thorium content exceeds 3 wt %. Reheating the suspensions at temperatures above 500°C causes the platelets to grow thicker and approach an essentially equiaxed shape at a rate which increases with temperature. Treatments for 5 min at 900°C or 20 min at 800°C reduce the diameter-to-thickness ratio from >50:1 to ≈5:1. Suspensions of particles of this shape are fluid at thorium concentrations up to 10 wt %. Figure 3 shows a fluid 10 wt % Th-Bi suspension formed by quenching the solution and reheating to 800°C for 20 min. This method has been demonstrated on a 250-g scale. Experiments are in progress to develop techniques for handling tonnage quantities.

Another preparation method which may be suitable for reconstitution involves first dissolving the thorium in the liquid metal and then applying ultrasonic energy during cooling at a moderate rate. Application of 1000-w, 20-kc energy to a 163-g, 5 wt % Th-Bi alloy in cycles of 30 sec on, 30 sec off during cooling from 1000° to 500°C over a period of 1 hr produced a suspension of essentially equiaxed $ThBi_2$ particles $\approx 50\ \mu$ in maximum dimension. The optimum conditions for this method have yet to be determined, and large-scale feasibility has yet to be demonstrated.

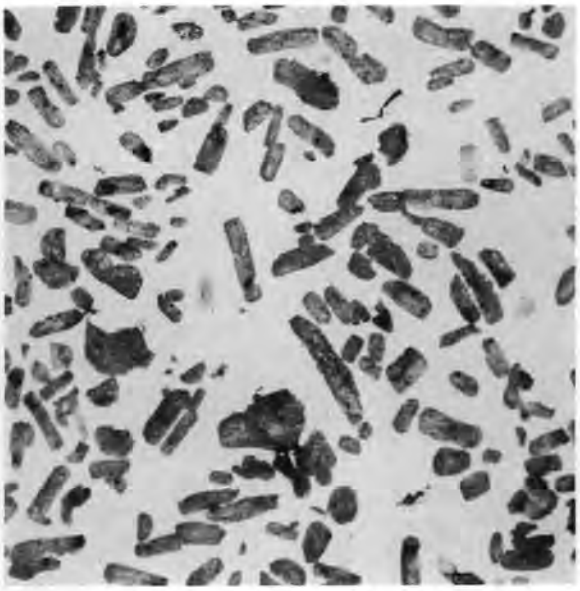

Figure 3. Suspension of $ThBi_2$ particles in Bi produced by rapidly cooling a Th-Bi solution to form a suspension of small platelets and then reheating at 500°C for 20 min. 10 wt % Th – 90 wt % Bi. 150×.

Nonmetallic Compound Suspensions

Very little work has been done on methods for preparing suspensions of nonmetallic thorium compounds in liquid bismuth or lead. Preliminary experiments have shown that ThO_2 particles can be wetted by liquid bismuth containing dissolved minor additions of thorium, calcium, or magnesium. Further study of these systems is planned.

RADIATION EXPERIENCE

No attempts have been made as yet to study the effects of irradiation or reactor conditions upon the suspensions of nonmetallic thorium compounds in liquid metals. Radiation experiments have been carried out on suspensions of $ThBi_2$ in bismuth and in lead-bismuth eutectic. Since irradiation generates protactinium-233, uranium-233, polonium, and fission products, specimens must be handled remotely. The pyrophoric compound must be protected from oxidation. Specimens contained in graphite crucibles are sealed under vacuum in aluminum capsules for exposure in the BNL reactor. Copper capsules plated with cobalt-free nickel are used for higher-temperature, higher-flux exposures in the MTR.

Specimens have been prepared in this manner and irradiated for study of the mechanical effects of irradiation. These specimens have not yet been examined, because the equipment for remote metallographic examination is being repaired. It appears possible that fission of U^{233} in the solids may cause some particle breakup. If this phenomenom does occur, it should have little effect upon the usability of the suspensions.

Most of the experiments with irradiated suspensions have been concerned with determination of the effects of subsequent heat treatment upon the distribution of protactinium between the solid and liquid phases. Pa^{233} and U^{233} are generated almost entirely in the solids because almost all the thorium is in the solids. The suggested method of blanket processing for these suspensions involves separation of a portion of the liquid phase for bred-product removal. Therefore information on the distribution of Pa and U between the phases is important in determining the rate of Pa^{233} and U^{233} removal during blanket processing.

Irradiated capsule specimens are heated at the desired temperature for the desired length of time with agitation. They are then held stagnant to allow the solids to settle to the bottom, and then cooled rapidly. The capsules are scanned from top to bottom by a collimated pulse height analyzer to measure the 0.35-Mev gamma radiation from Pa^{233} as a function of height in the specimen. From the data thus obtained, it is possible to calculate the ratio

$$\frac{\text{atoms Pa per g } ThBi_2}{\text{atoms Pa per g liquid}}.$$

It has been observed that the rate of transfer of Pa from the solids into the liquids is extremely slow at 550°C and at lower temperatures above the melting point. The amount of Pa transferred at these temperatures can be accounted for quantitatively by the mechanism of isothermal particle growth, which indicates that the rate of diffusion of Pa through solid $ThBi_2$ is negligible at these temperatures. The rate of transfer increases as the temperature is increased. With time at constant temperature the distribution ratio approaches a constant equilibrium value. The equilibrium ratio varies with temperature. In $ThBi_2$-Bi suspensions the equilibrium ratios are 205, 88, and 51 at 350°, 450°, and 550°C respectively. These ratios do not change appreciably with Th content or with Pa content over the ranges studied.

The effect of heat treatment upon the distribution of uranium between liquid bismuth and solid $ThBi_2$ has been studied with unirradiated suspen-

sions containing U^{238} in amounts low enough to be completely soluble in liquid bismuth containing no thorium. These suspensions are filtered after the desired heat treatment, and the filtrates and residues are analyzed chemically. From the results of these analyses, it is possible to calculate the ratio

$$\frac{\text{g U per g } ThBi_2}{\text{g U per g liquid}}.$$

It has been observed that the uranium distribution approaches a constant equilibrium ratio at constant temperature. Equilibrium ratios of 4.8 and 3.7 have been measured at 400° and 600°C respectively. These ratios do not vary appreciably with Th or U content over the ranges studied. The rate of approach to equilibrium at 550°C and lower temperatures is extremely slow as in the case of Pa.

Other work which might be termed simulated radiation experience has been concerned with the determination of the effects of anticipated thermal conditions in a reactor blanket system upon the behavior of $ThBi_2$-Bi suspensions. Isothermal particle growth studies on unirradiated suspensions have shown that equiaxed, 50-μ particles of $ThBi_2$ in bismuth grow as single crystals at reactor temperatures. The average rates of increase in particle diameter observed are 22 μ/month at 500°C, 58 μ/month at 550°C, and 130 μ/month at 600°C. It has been found that minor additions of tellurium in amounts as low as one part by weight tellurium to 100 parts by weight thorium inhibit isothermal particle growth at temperatures as high as 800°C.

Since heat must be removed from a reactor blanket, it is likely that a fluid blanket material would be circulated through heat exchangers, and thus be subjected to thermal cycling. Suspensions of $ThBi_2$ in bismuth have been subjected to thermal cycling by causing a molten specimen to flow back and forth in a periodically tilted tube, one end of which is hotter than the other. In a specimen cycled between 350° and 580°C at 10 sec/cycle for 500 hr in a graphite tube, the maximum particle dimension increased from 50 to 225 μ. This rapid rate of growth was caused by particle agglomeration rather than by growth of single crystals. In a similar specimen containing a small amount of tellurium which was subjected to an identical treatment, no particle growth or agglomeration was observed. The mechanism by which minor tellurium additions inhibit $ThBi_2$ particle growth is not yet understood.

A $ThBi_2$-Bi suspension was cycled between 350° and 550°C at 10 sec/cycle for 500 hr in a Croloy 2¼ steel tube. A similar suspension containing 0.025 wt % zirconium to inhibit corrosion and mass transfer of the Croloy was subjected to an identical treatment. In both specimens it was found that the $ThBi_2$ particles had formed plugs at the cold ends of the tubes. Microexamination of the plugs revealed that a layer of iron-chromium particles had precipitated on the tube surface before the $ThBi_2$ plug started to form. Evidently the amount of zirconium added was insufficient to prevent mass transfer of the Croloy. This observation seemed to indicate that the roughening of the tube surfaces due to mass transfer of the Croloy may have been instrumental in starting the formation of the $ThBi_2$ plug. Formation of a $ThBi_2$ plug has been observed when a $ThBi_2$-Bi suspension has been pumped through a Croloy loop under a temperature differential. The problem of $ThBi_2$ plug formation in heat exchangers must be solved before the $ThBi_2$-Bi suspension can be accepted as a breeder blanket material.

Session VI

CHEMICAL REPROCESSING

Introductory Remarks on Chemical Reprocessing

F. R. Bruce
Oak Ridge National Laboratory, Oak Ridge, Tennessee

Table 1

Thorium and U^{233} Use in Power Reactors

Reactor	Fuel	Blanket	Clad
LMFRE	Bi-U	Bi-Th	None
MFR	$LiF-BeF_2-UF_4-Th_4$	$LiF-BeF_2-UF_4-ThF_4$	
HRE No. 3	$UO_2SO_4-D_2O$	ThO_2-D_2O	None
PAR	$ThO_2-UO_2-D_2O$	None	
SRE (Core 2)	90% Th – 10% U	None	SS
SGR	95.9% Th – 4.1% U	None	SS
Borax IV	93.7% ThO_2 – 6.3% UO_2	ThO_2	Al-Ni
EBWR (Core 2)	96% ThO_2 – 4% UO_2	None	Zircaloy-2
Rural Cooperative	75% ThO_2 – 25% UO_2	None	Zircaloy-2
Consolidated Edison	94.4% ThO_2 – 5.6% UO_2	None	SS

INTRODUCTION

The object of this session is to review the chemical reprocessing methods for power reactors employing U^{233} or thorium as fuel and blanket materials (Table 1). In general, the fluid fuel reactors including the Liquid Metal Fuel Reactor, the Molten Fluoride Reactor, the Thermal Breeder Reactor, and the Pennsylvania Advanced Reactor employ chemical reprocessing methods which are being developed as an integral part of the reactor system. The reprocessing of the first three of these reactors will be discussed in separate papers. PAR reprocessing requirements are similar to those of the Thermal Breeder Reactor blanket processing.

The reactors employing thorium or U^{233} as the metals may be reprocessed either by conventional solvent extraction, which will be described in the two discussions of the Thorex process, or by pyrometallurgical techniques which will be presented separately.

Several reactors including the Consolidated Edison Reactor, the Experimental Boiling Water Reactor, Borax IV, and the Rural Cooperative Reactor employ ThO_2-UO_2 as fuel. The reprocessing of these fuels will be accomplished by the Thorex process. The only unusual problems they present arise from the necessity of dealing with either zirconium or stainless steel cladding, and from the fact that we have had only limited experience in the dissolution of the ceramic mixtures to be employed. Tentatively, Oak Ridge National Laboratory has been assigned the responsibility for the development of processes for these fuels and for constructing a pilot plant to be used on an interim basis for the recovery of the spent fuels. Pertinent development programs which have been carried out both at Oak Ridge and at other sites consist of investigations of chemical and mechanical methods of removing cladding materials and dissolution of the oxides.

ThO_2-UO_2 SOLID FUEL PROCESSING

Mechanical Processing

As in the case of other power reactor fuels, it seems likely that mechanical processing will play an important part in reducing the size of fuel as-

semblies to a more manageable form for shipping and charging to a chemical dissolver. Mechanical processing, through separation of diluent from fuel, also effectively reduces the volume of solution to be processed for fissionable and fertile material recovery, and minimizes the volume of waste to be stored.

Two mechanical processing operations show special promise in the case of ThO_2-UO_2 fuels. Zirconium or stainless steel clad elements may be sheared to expose the acid soluble core material to a dissolution reagent. Shearing experiments at KAPL have shown that simulated slugs consisting of stainless steel clad aluminum oxide, 0.5 in. in diameter, could be sheared at the rate of 35 cuts/min. At ORNL 1.1-in.-diameter uranium slugs clad with 0.035-in. stainless steel were successfully sheared. Cutter life was found to depend primarily on the thickness of the cladding and was estimated to be about 10,000 cuts for the case studied.

High-fired thoria-urania is very refractory, and dissolves only about one-tenth as fast as thorium metal. It is therefore desirable to increase the surface area exposed to dissolution in order to obtain high dissolving capacity. The Mackintosh-Hemphill Rotary Straightener and Derodder may be used to accomplish this purpose (Figure 1). In the operation the cladding is worked on passing between rollers, and the brittle core material is crushed. It is expected that the resultant powder may be poured out after shearing the element.

Stainless Steel Dejacketing

Stainless steel jackets are removed from ThO_2-UO_2 fuel elements by refluxing in 4 *M* sulfuric acid. The resulting solution, which is 2 *M* in sulfuric acid, is saturated when it contains 100 to 110 g/liter of stainless steel. The dissolution rate remains constant at about 4 mg/cm^2/min throughout the dejacketing operation. Uranium and thori-

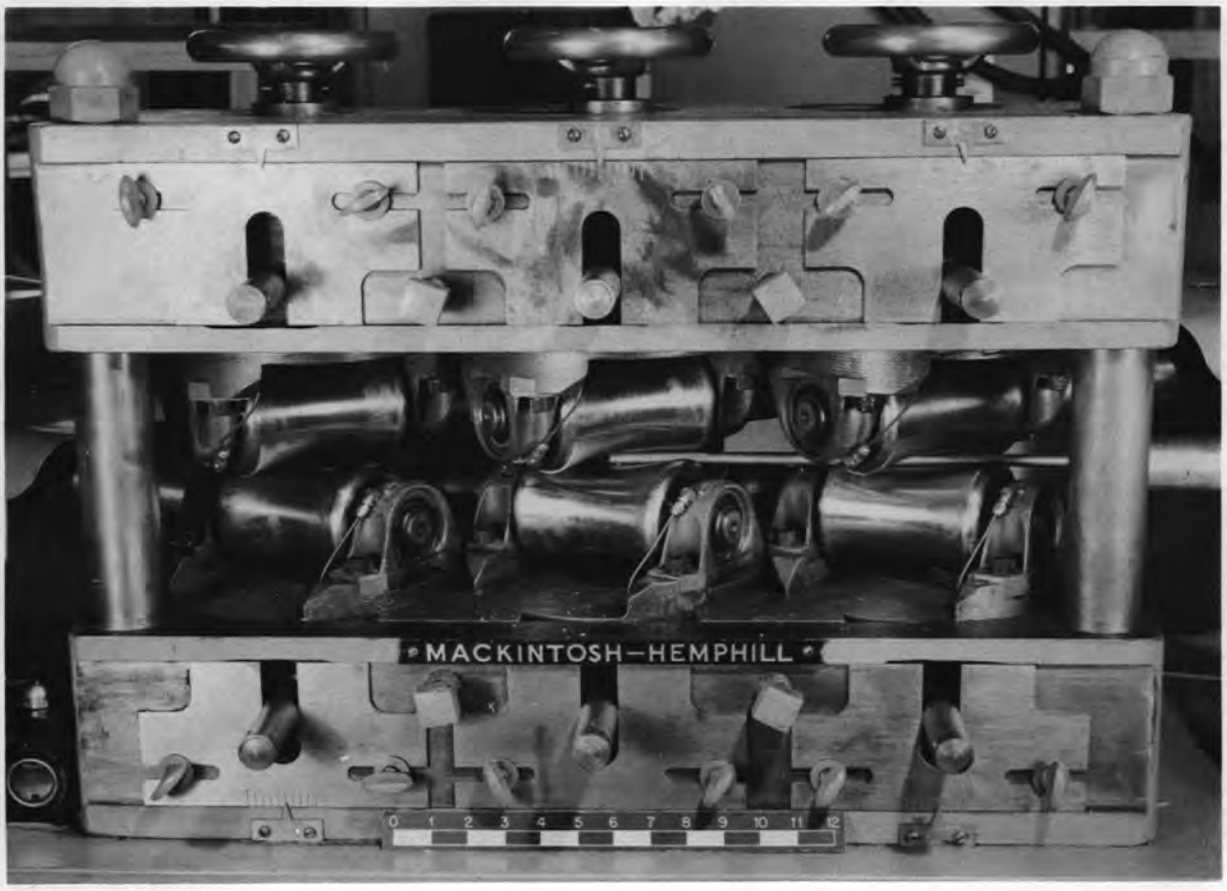

Figure 1.

um losses in the dejacketing step have not yet been investigated.

Zirconium Dejacketing

Nine *M* HF or 6 *M* NH_4F may be used to remove zirconium cladding. In the former case a fluoride:zirconium ratio of 4.5:1 is employed, and in the latter 6:1 to 7.5:1. Ammonium fluoride dejacketing may be carried out in conventional 347 stainless steel equipment for which a corrosion rate of 6 mils/year is observed. Carpenter 20 may be an adequate structural material for HF dejacketing, since preliminary indications are that a corrosion rate of 6 mils/year is obtained on cyclic treatment with 8 *M* HF – 8 *M* HNO_3. Losses of core material during the dejacketing of zirconium clad fuels are uncertain.

ThO_2-UO_2 Dissolution

The most promising dissolvent for ThO_2-UO_2 ceramic has the same composition as that used for dissolving thorium metal in the Thorex process, namely, 13 *M* nitric acid containing 0.04 *M* sodium fluoride as catalyst. Fluoride ion concentration has little effect on dissolving rate over the range 0.01 to 0.5 *M*. The most important factors influencing the dissolution rate are thorium nitrate concentration and nitric acid concentration (Figure 2). When the dissolver acidity falls below 8 *M* nitric acid, the dissolution rate is about proportional to the third power of the hydrogen ion concentration for solutions containing no thorium, and to the fourth power of the hydrogen ion concentration for solutions containing 0.3 to 1 *M* thorium nitrate. In dissolvent having >8 *M* nitric acid the dissolution rate shows a fourth power dependence on hydrogen ion concentration. The most rapid dissolution cycle is realized when 13 *M* nitric acid is used as dissolvent, and the dissolution proceeds until the acidity reaches 8 to 9 *M* nitric acid and the thorium nitrate concentration is 1 *M*. The two most important problems remaining are determination of the dissolution rate of irradiated thoria-urania and the dissolution rate of the 2% heel which is present at the end of the recommended dissolving cycle.

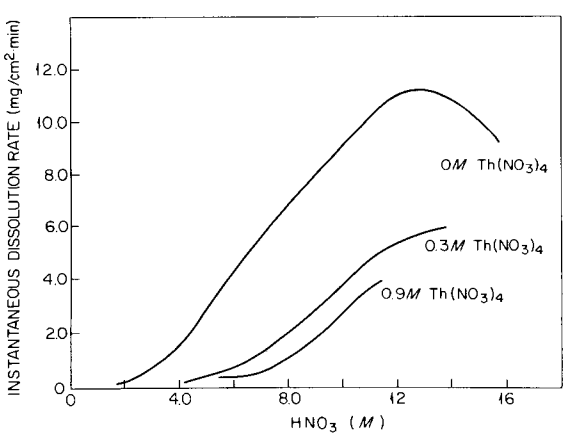

Figure 2. Dissolution rate of 1700°C fired 96% ThO_2 – 4% UO_2 pellets in HNO_3 – 0.04 *M* NaF, at the boiling point.

The solution resulting from fluoride-catalyzed nitric acid dissolution of thoria-urania then passes to the feed adjustment step of the Thorex process.

Dissolving studies with simulated Consolidated Edison core material, 96% ThO_2 – 4% UO_2 calcined at 1700°C, showed that with 13 *M* nitric acid – 0.04 *M* sodium fluoride 98% dissolution occurred in 5.3 hr. The resulting dissolver solution contained 8.6 *M* nitric acid and 1 *M* thorium nitrate, and the over-all dissolution rate was 3.4 mg/cm²/min. When the pellets were pulverized to about 1200 μ diameter, complete dissolution was obtained in about 1 hr.

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Thorex Process Development at Savannah River

T.H. Siddall
E.I. du Pont de Nemours & Co., Aiken, South Carolina

In this paper selected topics are discussed in SRL and KAPL development work in the processing of irradiated thorium. Extensive data and detailed results may be found in reports from these sites.

BRIEF PROCESS DESCRIPTION

The outlines of the Thorex process are the same as those of the Purex process. Two products, one in bulk and the other as a minor component, are to be isolated from each other and from extraneous radioactivity. Dissolution of thorium in nitric acid is different only in that a small amount of fluoride ion is needed as a catalyst. In most concepts of the Thorex process dissolution is followed by a feed treatment step. This step at ORNL consisted of holding the feed at high temperature in order to coagulate silica by dehydration and to improve the behavior of ruthenium in subsequent processing. At KAPL and SRL a head end step which consisted of precipitation of manganese dioxide was proposed. This step, in addition to clarifying the feed, gave some decontamination from fission products and substantial decontamination from protactinium.

The treated feed is adjusted in concentration and fed to pulse columns or mixer-settlers. The flowsheets for solvent extraction are quite similar to those for Purex. The principal differences are the use of more or less aluminum nitrate as a salting agent and at ORNL the use of 42% tributyl phosphate (TBP) rather than 30%. The first cycle of solvent extraction employs three contactors in cascade as in Purex. Second cycles of solvent extraction are used as required. Finishing steps for the products after solvent extraction are more or less analogous to those in Purex.

Factors of decontamination from fission products are not required to be as high as in Purex. Thorium itself does not fission significantly, and the fission products must come from U^{233} fission as it is formed during irradiation. However, Pa^{233} as the intermediate between Th^{233} and U^{233} is usually present in quantity. Depending on the decay period, very large decontamination from protactinium may be required. The relatively small separation required from fission products has stimulated a very considerable effort to achieve the desired separation without the use of second cycles of solvent extraction.

A major difference in process problems is brought about by the presence of U^{232} in irradiated thorium. This isotope is formed by *n*,2*n* reactions. U^{232} will follow U^{233} in chemical processing and because of its 75-year half-life will not decay appreciably. Th^{228} and its gamma active daughters start to grow in with a 1.9-year half-life immediately after separation of U^{233}. The Th^{228} which is already present in irradiated material follows the thorium product. Since Th^{228} is part of the decay chain of natural thorium, the net effect is to increase the natural activity of thorium. The effect may be so great as to interfere seriously with direct handling of the thorium. The growth of Th^{228} into irradiated thorium is the incentive for processing thorium as soon after pile discharge as possible. The lapse of the smallest possible fraction of 1.9 years is desirable. However, the processing of short-cooled material introduces severe complications, some of which are discussed below.

DISSOLVING AND CORROSION DURING DISSOLVING

The dissolving process, as visualized from SRL data, would have been a two-step process. In the first step the aluminum jackets would be removed in a solution of sodium nitrate and sodium hydroxide in a manner substantially the same as in the Purex process. In the next step thorium would have been dissolved at reflux in 10 *M* HNO_3 – 0.05 *M* HF. This choice of nitric acid and hydrofluoric acid concentrations possesses no unique feature except that use of these concentrations was computed to give the desired time cycle for dis-

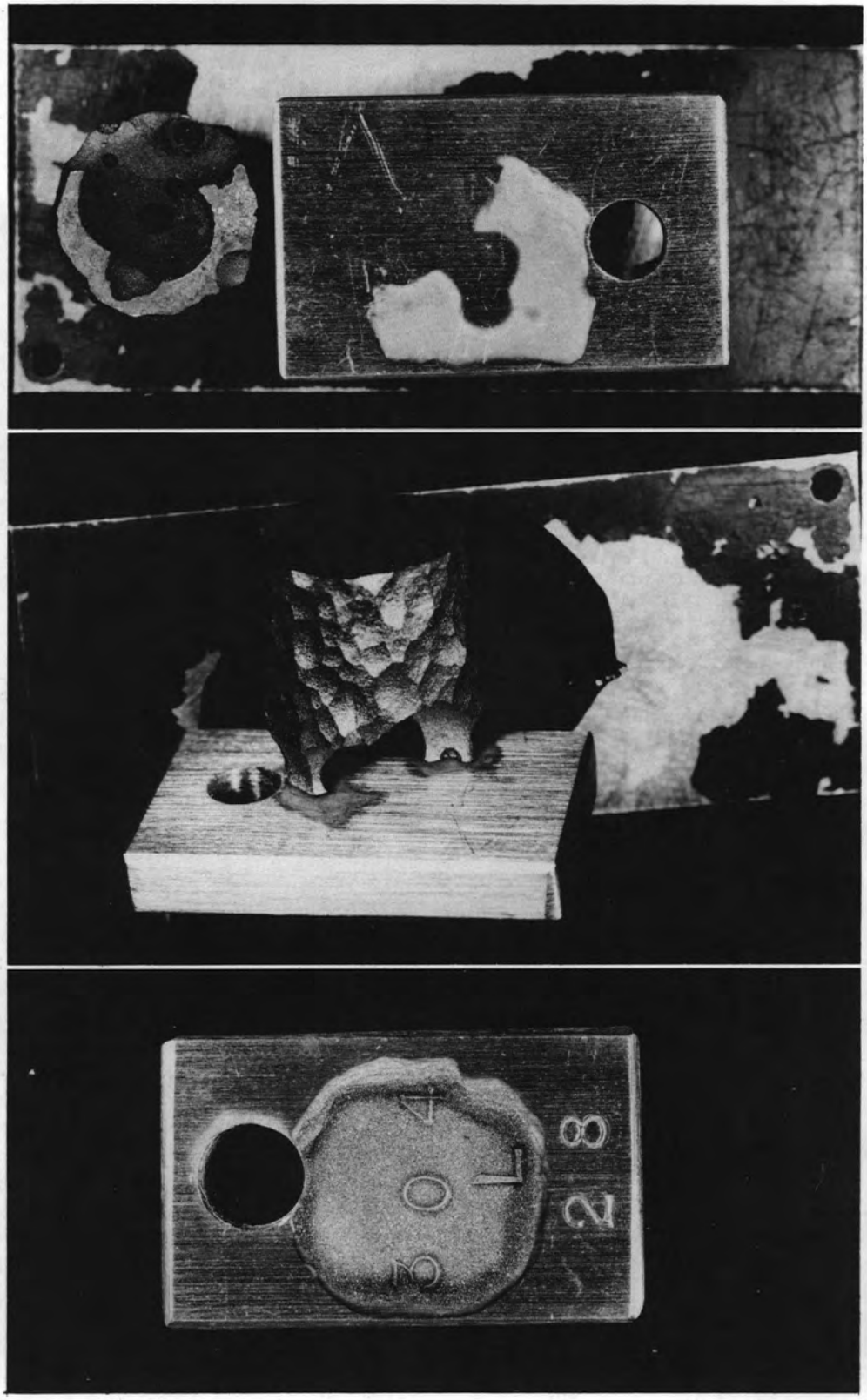

Figure 1.

solution. From the laboratory work such a dissolving scheme seemed feasible, and corrosion rates by ordinary mechanisms appeared to be quite acceptable.

However, serious contact corrosion was observed when thorium slugs which had been bonded with Al-Si were dissolved while in contact with stainless steel coupons. Examples of this corrosion are shown in the accompanying photographs (Figure 1). Attack was intergranular in nature and in some cases the rate amounted to as much as 5 in./year. Fortunately contact corrosion was limited to those areas where Al-Si had been incompletely removed from the thorium slug. Further experiments showed that when Al-Si was completely removed during the dejacketing step, contact corrosion did not occur.

HEAD END WITH MANGANESE DIOXIDE

Precipitation of a manganese dioxide cake is particularly effective in removing protactinium from Thorex dissolver solutions. Decontamination factors from protactinium of 100 are typical of experience in the laboratory. The efficiency of protactinium scavenging is much greater than that of fission products. Consequently a head end step with manganese dioxide has a more important potential than it does in the Purex process, for example.

One important potential of manganese dioxide lies in its use with short-cooled material. Aside from the extra load that protactinium places on decontamination during solvent extraction, a very large part of irradiation damage to the solvent is due to the protactinium in short-cooled feed. If the bulk of the protactinium were removed from the feed, it is probable that solvent damage would remain at an acceptable level except in cases of cooling times of much less than 30 days.

The protactinium held up on the manganese dioxide could be processed very easily after a few months to allow for decay to U^{233}. The intense radiation field would reduce the insoluble MnO_2 to soluble Mn^{++}. The decayed material might be returned continuously to the main process or might be processed separately as a source of isotopically pure U^{233}.

The high radiation field might impose restrictions on the manner of performing the precipitation. Otherwise complete redissolution of the cake could occur in process. However, this effect should impose no serious restriction, and techniques of continuous formation of cake are now available and should permit very short processing time. According to an experiment at KAPL the rate of reduction of MnO_2 is 5.0×10^{-4} moles/mole Th/hr with dissolver solution from slugs irradiated to 2400 g/ton and cooled for 66 days. Their experiment was performed with a mole ratio of manganese to thorium of 0.03. Even after half the MnO_2 had been reduced, only about one-tenth of the protactinium was released. Even with 30-day cooled feed one-half the cake would still be present after about 7 hr of exposure.

The conditions for obtaining the best scavenging of protactinium and cake of good physical character for centrifugation were explored at KAPL and at SRL. The maximum desirable thorium concentration was found to be 0.9 to 1.0 *M*. Above this concentration decontamination from protactinium fell sharply, and cake volume and carryover of cake into the centrifuge effluent rose sharply. Decontamination decreased above an acidity of 0.4 *M*, but the best physical characteristics were not obtained until acidity was raised to 0.6 *M*.

The major experimentation was done with the forward strike head end (addition of Mn^{++} to MnO_4^- after a simmer period). The reverse strike procedure was found to be acceptable but with the loss of a factor of about two in decontamination from protactinium.

SOLVENT EXTRACTION

It is reasonable to expect that high decontamination factors from fission products will be more difficult to achieve in a TBP-thorium (Thorex) system than in a TBP-uranium (Purex) system. The presence of protactinium can only add difficulty. Thorium is generally less extractable than uranium by a factor of about ten. It follows that separation factors from fission products will be a factor of ten smaller. It does *not* necessarily follow that decontamination will be poorer by a factor of ten in each stage of the 1A contactor, which would result in poorer over-all decontamination by many powers of ten. Still, it must be anticipated that successful operating conditions cannot exist over so wide a range in Thorex as they do in Purex, and that the best operation may not produce spectacular results.

The occurrence of a second organic phase at high concentrations of thorium when paraffinic hydrocarbons are used as a diluent would also be

expected to limit decontamination. Although there is little experimental proof that the appearance of a third phase would seriously interfere with contactor performance, there is general agreement among mixer-settler experts that serious trouble would follow. If flowsheets are designed to limit the thorium concentration in order to avoid the third phase, then only a low percentage of TBP is complexed by thorium in the organic phase. One of the chief devices to improve decontamination in the Purex process has been to complex as much of the TBP as possible.

The general experience of KAPL and SRL may be summed up by saying that head end plus one cycle of solvent extraction usually gave adequate decontamination from protactinium and all the fission products except ruthenium. Ruthenium decontamination to both products was usually insufficient by a factor of ten. KAPL was able to get adequate ruthenium decontamination only by operating at 70°C. Unfortunately operation even at about 50°C was accompanied by the gradual accumulation of solids in the partition and stripping contactors. After a number of hours the contactors became inoperable. The solid material was identified as a compound of thorium and dibutyl phosphate.

With the temperature limitation imposed by the solid compound, there remains no straightforward approach to improving ruthenium decontamination in the TBP-thorium system. The detailed knowledge of ruthenium chemistry which might suggest a cure for the trouble was not available at that time, nor is it yet. The only obvious recourse is to include a second cycle of solvent extraction.

It is interesting to observe that the best decontamination factors for ruthenium in the uranium stream at 70°C were only 3×10^3. In Purex runs in miniature mixer-settlers at SRL and KAPL, decontamination factors of 1×10^6 from ruthenium have been obtained routinely even without benefit of head end.

The Thorex process development work at KAPL is conveniently summarized in KAPL-1306, May 1956, by Haas and Smith. This report also describes runs made in miniature mixer-settlers to compare the then current flowsheets as proposed by KAPL, ORNL, and SRL. The results with the SRL flowsheet are quite representative of the best results obtained at SRL in miniature mixer-settler runs.

SUGGESTION FOR FUTURE DEVELOPMENT IN THOREX SOLVENT EXTRACTION

An alternative to continued efforts to overcome the natural handicaps in the TBP system is to

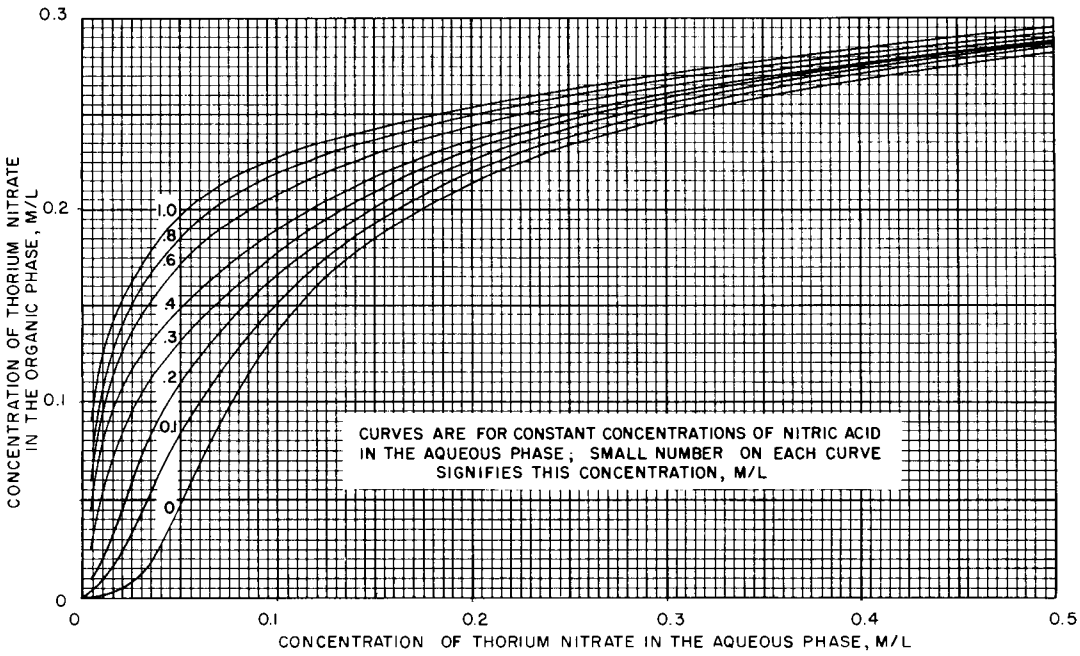

Figure 2. Equilibrium diagram of thorium nitrate – nitric acid – water – 1.09 *M* DAAP in *n*-dodecane at 30°C.

Table 1

Comparison of TBP and DAAP at 30°C

Extractant	% of Uncomplexed* extractant in the solvent effluent from the 1A contactor	Minimum % of uncomplexed* extractant inside the 1A contactor
TBP	51	37**
DAAP	33	14

*Complex with thorium assumed to contain three extractant molecules.
**Formation of second organic phase at 45% uncomplexed extractant ignored.

abandon TBP and search for new extractants. A limited effort to find extractants superior to TBP for general application to processing nuclear fuels has been under way for some time at SRL. This work has consisted almost entirely of batch equilibrations with uranium, plutonium, thorium, and tracer levels of zirconium. No work with full level feeds has been done. However, this work has indicated extractants which may be more suitable for processing irradiated thorium.

Di-*n*-amyl *n*-amylphosphonate (DAAP) merits serious consideration as a replacement for TBP in thorium processing. Until this compound is actually tested with full level feed, its potential advantages cannot be stated as though they were actual advantages in practice. However, specifically the equilibrium separation between thorium and zirconium is at least ten times greater than is the case with TBP. Also, DAAP has a definite general advantage. Flowsheets can be devised in which almost all the extractant is complexed by thorium. Sufficient salting to achieve a high degree of complexing is provided even by rather dilute nitric acid. No second organic phase is formed except at very high concentrations of thorium which lie outside any conceivable process range. The compound is available commercially and is quoted at prices very close to those for TBP.

An equilibrium diagram is given in Figure 2 for the system $Th(NO_3)_4$-HNO_3-H_2O-1.1 *M* DAAP in *n*-dodecane at 30°C. This diagram may be compared directly with the comparable diagram for TBP given in DP-181. A 30% solution of TBP is 1.1 *M*.

The degree of complexing which could be obtained with DAAP in the 1A contactor is compared in Table 1 with that which could be obtained with TBP. A flow ratio of seven volumes solvent (1.1 *M* extractant) to one volume scrub was used in the calculations. A scrub stream containing 1.0 *M* HNO_3 was assumed for the DAAP, and containing 3.0 *M* HNO_3 for TBP.

The avoidance of a second organic phase is not unique to the use of DAAP. Apparently all trialkyl phosphates and dialkyl alkylphosphonates which contain at least 14 carbon atoms share this advantage. Although it is true that the second organic phase may be avoided even with TBP by the use of an aromatic diluent or diluent with condensed structure, replacement of TBP still may be preferred. The increased chemical reactivity, higher viscosity, and density of these diluents as compared to paraffins weigh heavily against them.

A closing thought is that it may be a mistake to continue to force TBP to serve so many tasks in such a variety of situations met in processing irradiated fuels. There are many other conceivable extractants, some of which may occupy the preferred position in individual situations. Other trialkyl phosphates and dialkyl alkylphosphonates have been suggested as alternates in the special situation of processing thorium. Even this increase in the range of alternatives is only a beginning.

Pilot Plant Processing of Irradiated Thorium

E.M. SHANK
Oak Ridge National Laboratory, Oak Ridge, Tennessee

INTRODUCTION

The Thorex flowsheet has been developed to process irradiated thorium for the separation of thorium and U^{233} from each other and from fission product activities and Pa^{233}; to recover the thorium and uranium as aqueous products suitable for further direct handling; and to recover isotopically pure U^{233} after decay storage of the Pa^{233}. The initial flowsheet included a single solvent extraction cycle for both the thorium and the uranium, followed by ion exchange purification for the uranium. Increased interest in nuclear power, along with the problems of U^{232} daughter activities, directed the emphasis to high irradiation levels and short decay periods. Consequently, the Thorex flowsheet has been expanded to include two solvent extraction cycles for the thorium and three solvent extraction cycles plus ion exchange for the uranium. Although thorium oxide has not been processed, the Thorex process is considered satisfactory for recovery of HR thorium blanket and cores.

This paper contains a summary of the status of the Thorex program, a review of the process flowsheet as it now stands, a discussion of 30 months of pilot plant operation during the processing of long-decayed and short-decayed thorium, and a summary of the work still required to conclude the development of a short-decay Thorex flowsheet.

DISCUSSION

The evaluation of the Thorex process has been completed with the use of thorium irradiated to levels as high as 3500 g/t and decayed as long as 400 days. Tentative activity specifications established for both products have been met consistently, and both products have been sufficiently pure chemically for subsequent needs. Extraction losses are not considered satisfactory, and chemical means of reducing these losses are being investigated.

The evaluation of the Thorex process for short-decayed thorium has been terminated, but is incomplete. The uranium product will meet tentative activity specifications after a third solvent extraction cycle. The thorium product does not meet activity specifications, exceeding them by about 200; Ru is still the limiting contaminant.

Recent flowsheet modifications incorporated for the processing of short-decayed thorium include 1) the continuous metering of potassium iodide and air sparging during dissolution to remove I^{131}; 2) the use of a caustic scrubber for I^{131} removal from the dissolver off-gas; and 3) the addition of sodium bisulfite to the first and second cycle feeds for ruthenium decontamination.

Plant operation has been accomplished without excessive mechanical difficulties and without excessive personnel hazards except during the recently completed short-decay processing. Corrosion in the feed preparation system, initially of great concern, has not been excessive as determined by corrosion specimens and equipment inspection.

Decontamination factors during long-decay processing have been sufficient to provide thorium and uranium products meeting tentative specifications, but those during short-decay processing have not. The decontamination factors for products are shown in Table 1. The gross gamma decontamination factors observed for thorium irradiated to 3500 g/t and decayed 30 days averaged 4×10^4 for thorium and 5×10^7 for uranium. With the decontamination factors shown above, the thorium product exceeded specifications for all constitutents except rare earths, and the uranium product met specifications (the radiation specification for uranium is currently the controlling specification).

CONCLUSIONS

Preliminary conclusions from the processing of short-decayed thorium are as follows.

Table 1

Thorex Pilot Plant Product Decontamination Factors (Thorium Decayed 30 Days)

Constituents	Decontamination factors	
	Thorium	Uranium
Gross γ	4×10^4	5×10^7
Pa	7×10^6	5×10^{10}
Ru	200	4×10^6
Zr-Nb	3×10^4	7×10^6
TRE	2×10^6	3×10^8
I	1×10^4	3×10^7

1. Ruthenium continues to be the major contaminant in both the uranium and thorium products.

2. The addition of sodium bisulfite to first and second cycle feeds was apparently effective in increasing the ruthenium decontamination by a factor of about 10 for each cycle over that obtained in the previous short-decay scouting run.

3. Approximately 85% of the I^{131} estimated to have been in the thorium slugs was removed from the dissolver. The caustic scrubber was effective for decontaminating the dissolver off-gases from I^{131}.

4. The decontamination factor for I^{131} across the solvent recovery column was not as high as expected.

5. Solvent degradation during short-decay processing presented no problems during the radive portion of the first two runs. Solvent degradation during the third run appeared greater as evidenced by solids in the uranium product stream, decreased partitioning efficiency, and a more rapid build-up of thorium phosphate gel in the strip columns. The good performance of the solvent initially was attributed to pretreatment of the Amsco diluent with oleum.

6. Pa^{233} losses from the system amounted to $<1\%$ with an over-all material balance of 109%. U^{233} losses were obscured by Pa^{233} decay. Thorium losses were comparable to those in long-decay runs.

7. Personnel radiation exposure during the runs increased significantly. Shielding throughout the plant operating areas proved to be inadequate.

8. Elaborate off-gas handling facilities will be required for I^{131}, Pa^{233}, and $Xe^{131-133}$ removal, and adequate process ventilation must be provided to prevent air contamination.

SUMMARY OF SOME OF THE WORK REQUIRED TO COMPLETE THE THOREX FLOWSHEET FOR SHORT-DECAY PROCESSING

A process has been developed and demonstrated during extended operating periods for the processing of long-decayed thorium to give products meeting activity and ionic specifications. Full evaluation of short-decay processing cannot be completed until extended operating periods (30 to 60 days) have been demonstrated.

The problem of how to improve decontamination has been studied, but additional effort will be required, particularly for ruthenium; means of reducing the decomposition rate of bisulfite are being investigated. The problems of solvent degradation and recovery have been partially solved. Runs completed suggest that serious deleterious effects may be expected after 10 to 20 beta-watt-hr/liter of exposure. Means of eliminating the thorium phosphate gel formed in the uranium stripping columns must be developed to permit continuous operation.

Analytical procedures for the activity levels encountered need improvement for Pa^{233} and fission product determinations. A third uranium cycle flowsheet is needed with increased separation for thorium and U^{233} and greater specificity for U^{232} decay daughters. The chemistry of short-lived fission products is obscure and requires additional investigation.

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Experiments in Low Decontamination Processing of Metallic Thorium-Uranium Fuels

G.E. Brand, E.W. Murbach, and A.G. Buyers
Atomics International, A Division of North American Aviation, Inc., Canoga Park, California

INTRODUCTION

Experiments are being conducted at Atomics International to develop economical methods of reprocessing thorium reactor fuels. Emphasis has been placed on the development of compact low decontamination processes, which yield a relatively small volume of highly radioactive wastes. Although remote fabrication is required for fuel reprocessed by this method, it is felt that this additional cost may be more than offset by savings in the decontamination process. Some of the more promising processes which have been investigated include direct volatilization by arc and induction drip melting, extraction with molten salts, and fused salt electrolysis. One of the difficulties associated with high temperature decontamination of thorium-uranium alloys is containing the molten metal. The experiments were designed to minimize the thorium container contact time at or above the melting point of the alloy.

DIRECT VOLATILIZATION[1]

The melting point of thorium is sufficiently high that a number of elements would be expected to volatilize readily from molten thorium. The vapor pressures of the most harmful fission elements (Table 1) are higher than that of thorium, which is lower than that of uranium. Examination of these data indicates that Cs, Te, and Sr, as well as the rare gases and halogens, should be effectively removed by melting thorium. Cerium and the other rare earths would be only partially evaporated, and no appreciable volatilization of zirconium and ruthenium should take place. Very little loss of thorium, uranium, or protactinium should occur.

Table 1

Vapor Pressures of Some Elements at 1680°C

Element	Vapor pressure, atmos	Element	Vapor pressure, atmos
Cs	90	Pu	10^{-4}
Te	60	Y	2×10^{-5}
Sr	4	U	8×10^{-7}
Ba	1	Zr	2×10^{-7}
Ce	3×10^{-3}	Ru	10^{-10}
La	6×10^{-4}	Nb	10^{-11}
Pr	3×10^{-4}		

These expected results have been essentially verified in three types of small-scale laboratory experiments, with crucible-contained molten thorium, nonconsumable-electrode arc-melted buttons, and induction drip melted rods.

In the crucible experiments, the metal was melted in tantalum containers and held molten for periods up to two hours. Here, one of the problems

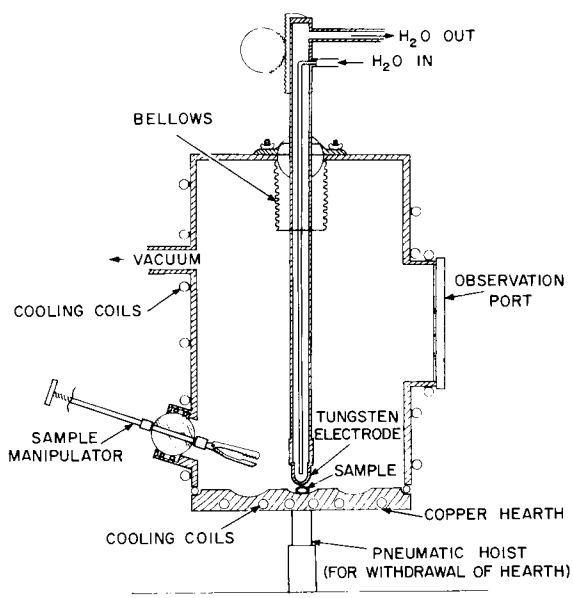


Figure 1. Arc-melting furnace.

Table 2

Nonconsumable Arc Melting of Th-(3 wt %)U Alloy

Experimental conditions				Percent fission product removed								
Time, min	Temp, °C	Wt, g	Current, amp	U	Ce	R.E.	Cs	Sr	Te	Zr	Pa	Ru
2	16-1700	2.8	19	6	25	52	99	100	20	0	8	0
4	18-1900	2.9	25	4	31	53	99	100	52	0	10	0
8	18-1900	2-3	25	9	95	98	99	99	55	16	20	0
12	18-1900	2-3	60	—	85	78	95	99	89	0	31	0

involved in pyrochemical processing of thorium is evident. The tantalum containers were attacked by the molten metal as are most of the common refractories.

The chief advantage of the arc-melting method is that no container is required (Figure 1). The metal is melted in contact with water-cooled copper so that the molten metal in reality is contained in a frozen skin of the same metal. In the small-scale experiments run to date, the thorium was melted by a water-cooled tungsten electrode. The results of these investigations (Table 2) show that almost all of the Sr, 99% of the Cs, and appreciable quantities of rare earths can be removed. Attempts to increase the decontamination of these elements by longer heating at higher temperatures resulted in a 25% loss of Pa and some loss of U, perhaps from local overheating (Figure 2). It can be seen that if most of the rare earths are to be removed some U and Pa losses must be accepted. This Pa loss is serious since it will decay to U^{233}. This loss is not important if the fuel has been cooled several months as the Pa (half-life 27 days) would have decayed to U^{233}. As expected, Ru and Zr were not removed by evaporation.

Another promising method for melting thorium without crucible contamination is the drip-melting process (Figure 3). The thorium slug is suspended in vacuum in the field of a high-frequency induction coil. Power is supplied at a rate such that the metal slowly melts and drips from the end of the rod. The induction coil is moved by a motor-driven saginaw screw so that the most intense heating is near the end of the slug. The product is collected in a copper mold. The resultant high surface area to weight ratio is produced without local overheating. Indications are that fission product removal will be similar to that with arc melting but with less danger of uranium losses.

FUSED-SALT ELECTROLYSIS

The results of theoretical calculations indicate that fission products can be removed from irradiated thorium by electrolysis.[2] It can be shown that at one throughput, i.e., when the thorium content of the bath has been replaced just once, the decontamination factor, D, for impurity metals less noble than thorium is given approximately by the following equation:

$$D=\exp\left[\frac{nF}{RT}(E_m^{\circ}-E_{Th})\right]$$

where

n = valence of metal ion,

F = Faraday's constant,

R = gas constant,

T = absolute temperature,

E_{Th} = decomposition potential for thorium salt, and

E_m° = standard decomposition potential for metal.

Decontamination factors based on this formula have been calculated for chloride salt baths (Table 3). Metals more reactive than thorium dissolve readily at the anode, but do not plate out at the cathode. These metals accumulate in the salt bath. Metals less reactive than thorium by about one-half volt or more have large decontamination factors because they do not dissolve in the salt bath as ions to any appreciable extent. A metal such as uranium, with an E^0 value close to that of thorium, plates onto the cathode at the same time that it dissolves after equilibrium is reached.

The production of pure thorium by electrodepositing the solid metal from molten salt baths has not been used extensively because of the den-

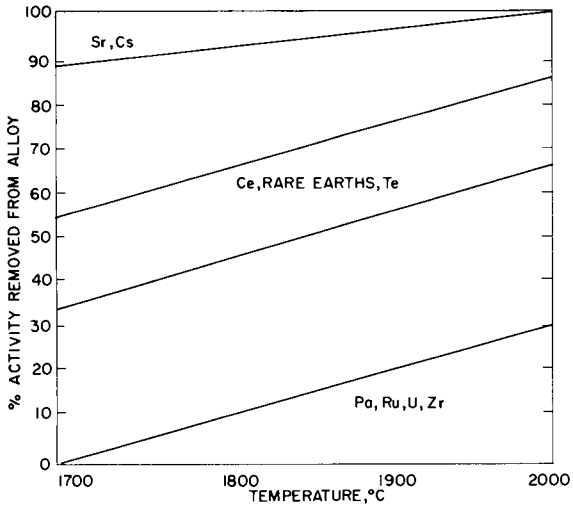


Figure 2. Fission product evaporation from molten irradiated Th-(3 wt %)U alloy. Time = 10 to 120 min.

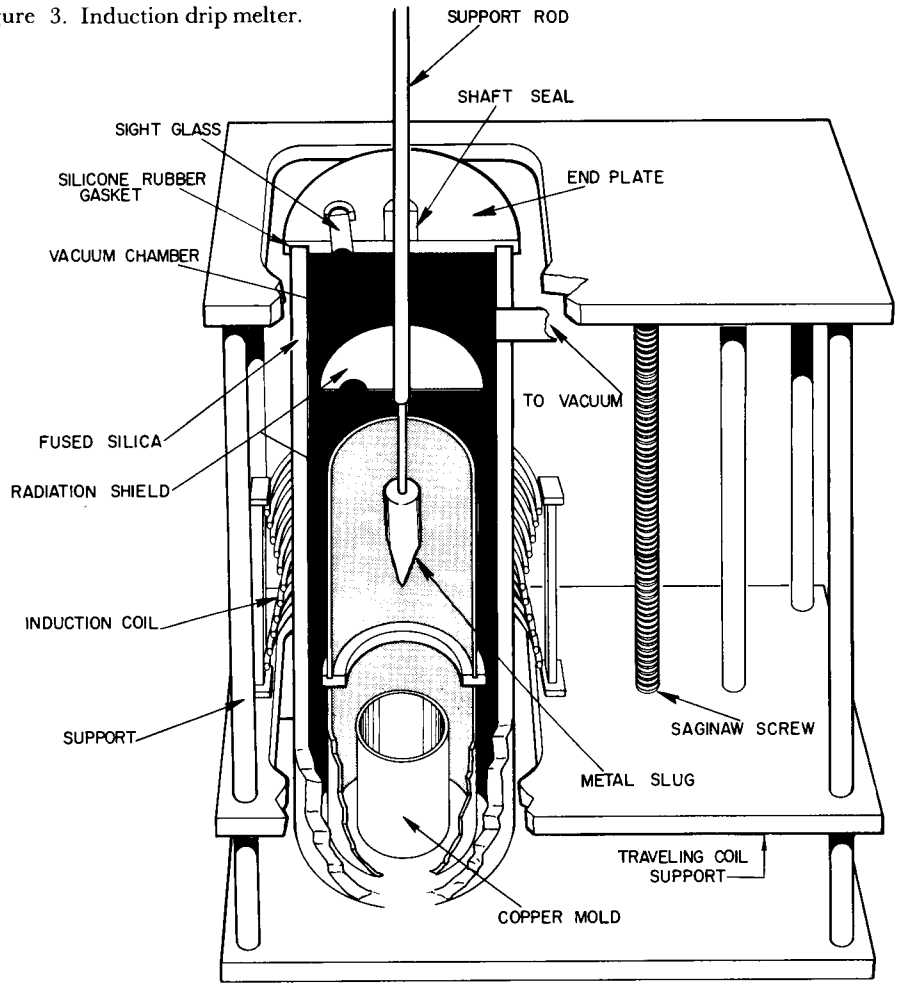
Table 3

Theoretical Decontamination Factors for Removal of Various Metals from Thorium by Electrolysis

Metal ion	Standard* emf's for chlorides, v at 800°C	$\Delta E = (E_m^{\circ} - E_{Th})$, v	Decontamination factor, $D = \exp(n\Delta E/0.21)$
Ba^{+2}	3.58	0.83	8×10^7
Sr^{+2}	3.45	0.70	5×10^6
Ca^{+2}	3.32	0.57	3×10^5
La^{+3}	3.05	0.30	2×10^4
Ce^{+3}	2.97	0.22	1.3×10^3
Cs^{+1}	3.36	0.61	8×10^2
Nd^{+3}	2.93	0.18	4×10^2
Th^{+3}	2.75	0.0	—

*ANL 5107.

Figure 3. Induction drip melter.



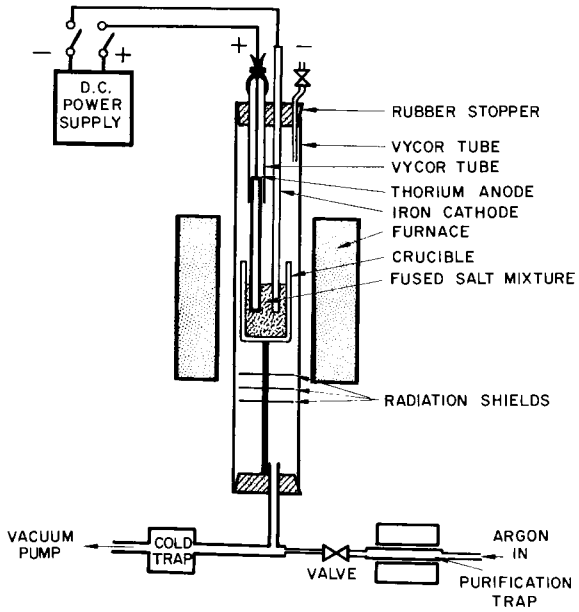


Figure 4. Molten salt electrolysis apparatus.

dritic nature of the deposits obtained, which requires an elaborate process to remove impurities from the porous deposit. This latter step would be especially tedious if the impurities contained radioactive fission products. The deposition of pure molten thorium would produce a satisfactory material; however, there is no known material that will contain molten thorium and the fused salt above 1700°C for the extended periods of time required for electrolysis.

In the case of uranium, which is similar to thorium with respect to dendrite formation, deposits have been avoided by using a nickel rod as a cathode and operating at such a temperature that the uranium metal deposited forms an alloy with the nickel and drips from the rod to form a pool at the bottom of the container.[3]

Experiments similar to the above have been carried out with thorium in this laboratory.[4] Iron has also been used as the cathode in the molten salt electrolysis of thorium (Figure 4) carried out at about 1000°C. The cathode alloy formed and dripped to a molten pool in the bottom of the container with no evidence of dendrite formation. The attack of the container by the molten alloy and fused salt is much less severe at these reduced temperatures.

Pure thorium could theoretically be obtained from the cathode alloy by volatilizing out the iron, but in practice this is likely to prove difficult. This would also be true if nickel or manganese were used as the cathode. Apparently, there is no solid metal that can be used as a satisfactory cathode and yet be removed easily from the refined thorium.

Experiments were carried out to study the electrolysis of thorium into a molten zinc cathode (Figure 5). Temperatures maintained varied from 600° to 800°C. The amount of thorium in the zinc varied from 4 to 15%. The salt mixture used was 45 M % NaCl, 45 M % KCl, and 10 M % $ZnCl_2$. At the beginning of the electrolysis the zinc ions

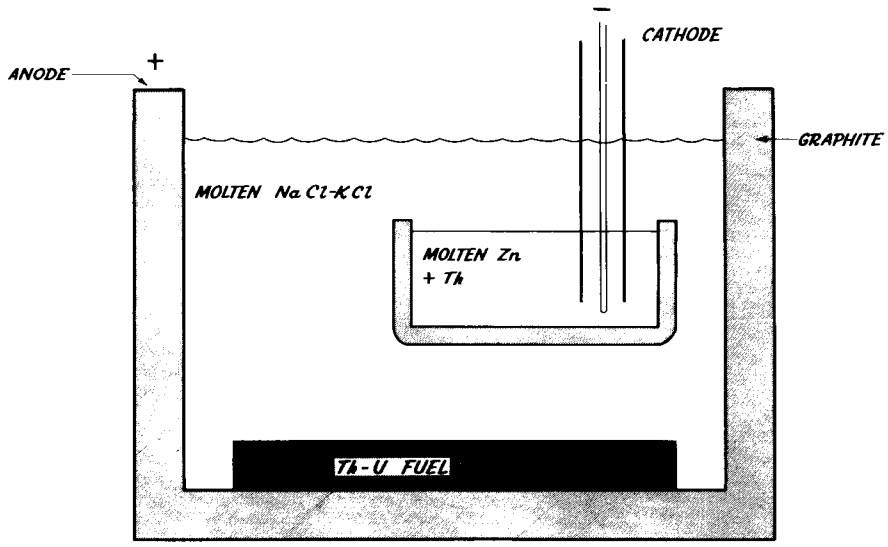


Figure 5. Apparatus for molten salt electrorefining of Th-U alloy.

are replaced by thorium ions. This eliminates the necessity of adding thorium salts to the original bath. The zinc is easily removed from the deposited thorium by volatilization.

The results of these experiments (Table 4) show that virtually all the Cs and Sr are removed. Appreciable quantities of rare earths, Ce, Ru, and Zr are removed. Improvement of the method should result in higher removals of Ce and the rare earths. It should be noted that Ru, Zr, and Mo are not removed by direct volatilization or by salt extraction. Although no Mo decontamination data are available, they should be similar to Ru data.

Table 4

Fission Product Removal from Irradiated Th-(10 wt %)U Alloy by Molten Salt Electrolysis

Element	% Removed
Cs	99.5
Sr	99.5
Ru	90
R.E.	85
Ce	79
Zr	60

Table 5

Standard Free Energies of Formation of Some Oxides at 1500°K

Oxide	$-\Delta F^{\circ}$, kcal/eq	Oxide	$-\Delta F^{\circ}$, kcal/eq
ThO_2	115	PuO_2	96
CaO	114	BaO	95
BeO	112	SiO_2	72
La_2O_3	112	NbO	66
Ce_2O_3	107	NbO_2	62
Nd_2O_3	107	Nb_2O_5	57
MgO	103	MoO_2	38
SrO	102	Cs_2O	4
Al_2O_3	102	TeO_2	5
UO_2	99	RuO_2	−3
ZrO_2	97		

Table 6

Standard Free Energies of Formation of Some Fluorides at 1500°K

Salt	$-\Delta F^{\circ}$, kcal/eq	Salt	$-\Delta F^{\circ}$, kcal/eq
SrF_2	116	ZrF_4	90
CaF_2	115	ThF_4	88
BaF_2	115	CsF	87
LaF_3	113	UF_4	85
LiF	112	UF_3	84
CeF_3	111	PuF_4	81
NbF_3	109	AlF_3	80
MgF_2, KF	100	NbF_5	74
PuF_3	96	BiF_3	45
		TeF_6	32

SALT-BED[5]

Oxide drossing has proven a very successful method for removing fission products from irradiated metallic uranium. In this method the molten uranium is contacted with UO_2. The more active fission products such as the rare earths react with

Table 7

Distribution of Fission Products Between Th-U-Mn and Molten Halides (Percent activities measured)

	$CaCl_2$ at 1050°C; time=30 to 60 min; graphite and tantalum crucibles; av. of 2 experiments	
Element	Metal	Salt
Ce	7	87
R.E.	5	67
Cs	8	79
Sr	9	61
Te	87	5
Zr	100	trace
Ru	80	trace
Pa	66	1
U	100	trace
Th	100	trace

	ThF_4 at 1150°C; time=50 min; graphite crucibles; av. of 3 experiments	
Element	Metal	Salt
Ce	22	54
R.E.	11	78
Cs	56	34
Sr	46	40
Te	96	3
Zr	100	trace
Ru	—	—
Pa	96	1
U	100	trace
Th	—	—

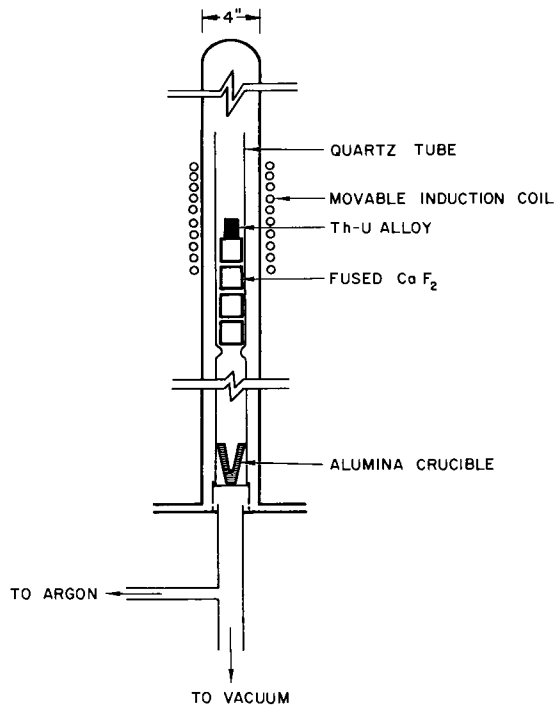


Figure 6. Salt-bed apparatus.

UO_2 to form oxides and separate in a layer on the surface of the uranium. The rare gases, as well as strontium and cesium, are lost by volatilization.

Since the free energy of formation of ThO_2 (Table 5) is more negative than that of the fission products, very little decontamination should be achieved by contacting with oxides. The standard free energy of formation of ThF_4 (Table 6), however, is less negative than that of many fission products. Therefore, it would be expected that appreciable decontamination could be achieved by contacting irradiated thorium with fluorides.

Experiments have shown (Table 7) that fission products are extracted from molten thorium by contacting with molten calcium fluoride. No suitable crucible for containing this mixture above 1700°C has been found. A Th-U-Mn alloy with a melting point much lower than that of pure thorium was used in these investigations.

The container problem was avoided by developing the salt-bed process (Figure 6). In this process thorium-uranium alloy is placed on top of a vertical bed of prefused CaF_2. As this metal is heated by induction it melts the surrounding salt and sinks into the bed. The induction coil is lowered, and the thorium melts its way through the column, continually contacting fresh salt. The molten metal melts only its salt environment and avoids all contact with the container until it breaks free from the bottom of the vertical column of salt and falls from the induction field into an alumina crucible. The metal freezes on or before contacting the crucible (Figure 7). Decontamination achieved by application of this technique to irradiated samples (Table 8) indicates that this process effectively extracts tellurium, cerium, rare earths, strontium, and cesium, while protactinium, zirconium, and ruthenium remain with the metal. Although thorium losses are high, it is possible that these losses could be decreased by increasing the weight of thorium and thus reducing the surface area to weight ratio.

SUMMARY

Comparison of these processes (Table 9) indicates that the simplest process is direct evaporation, and that the process giving the best decontamination is fused-salt electrolysis. Although the salt-bed process gives better decontamination than direct volatilization, it might prove almost as difficult to scale up as electrolysis. Electrolysis is the only method that will remove significant quantities of Ru, Zr, and Mo. No separation of thorium and uranium is obtained by direct volatilization, salt-bed, or electrolysis. These methods would therefore be most applicable for processing fuel from a single-region breeder reactor using thorium fuel enriched with a few percent U^{235} or U^{233}. It might be possible to modify the electrolysis process so that uranium could be separated from thorium.

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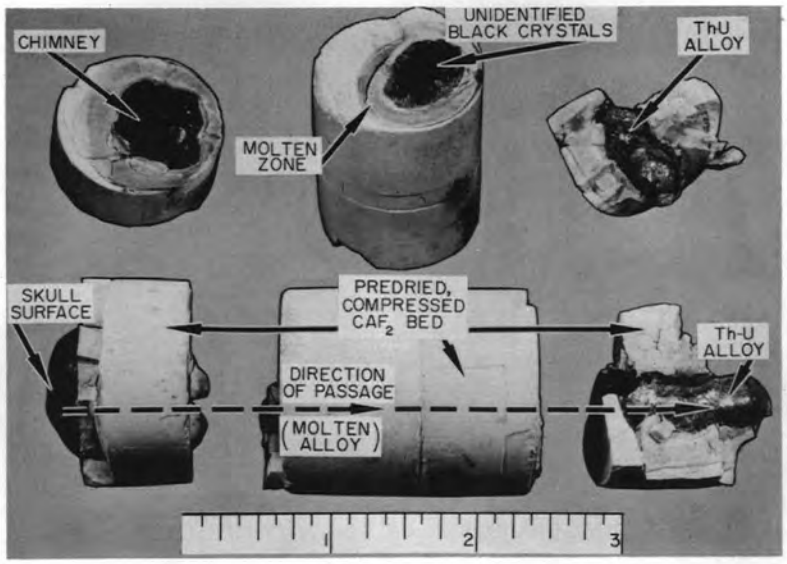

Figure 7. Molten thorium which has passed through calcium fluoride salt bed.

Table 8

Decontamination Data for Salt-Bed Processing of Th-(10 wt %)U Alloy
(Bed CaF_2 premelted)

Weight alloy, g	Bed length, in.	Heating time, min.	Percent of element removed									
			Ce	R.E.	Cs	Sr	Te	Zr	Pa	Ru	U	Th
11.1	1	3	35	37	35	59	69	8	7	0	—	1
11.6	1½	5½	75	73	45	70	82	7	10	0	3	2
12.5	2¾	10	84	75	39	62	—	2	11	0	0	4
11.2	4½	16	96	96	78	95	—	3	13	0	1	9
12.0	6⅛	28	98	98	92	97	—	0	13	0	2	12

Table 9

Comparison of Thorium Reprocessing Methods

Method	Removes	Leaves	Advantages	Disadvantages
Direct volatilization	I, Xe, Kr, Sr, Cs, some rare earths	Zr, Mo, Ru, U, ThU metal	Relatively simple	Difficult to condense active material
Salt-bed	I, Xe, Kr, Sr, Cs, rare earths, some Th	ThU metal mixed with salt	Better fission product removal	Th loss large; large volume of salt needed
Fused-salt electrolysis	Most fission products	ThU, some Zr	Good decontamination	Several steps required

Present Status of U^{233} Purification and Metal Production at LASL

J.A. Kircher
Los Alamos Scientific Laboratory, Los Alamos, New Mexico

INTRODUCTION

Impure U^{233} nitrate solutions originating from Oak Ridge Thorex product or from metal fabrication residues are separated from trace amounts of thorium isotopes with cation resin. After allowing time for decay of thorium daughters, beta-gamma activity is sufficiently reduced to permit conventional processing in unshielded equipment.

The U^{233} is chemically purified by one or more precipitations as uranium peroxide, which is calcined to U_3O_8. The U_3O_8 is reduced to UO_2 and converted to UF_4. Pure metal is prepared by bomb reduction of the UF_4 with calcium as the reducing agent.

Residues from the chemical purification steps, reduction, metal fabrication, and general cleanup are processed into nitrate solutions, solvent extracted, and concentrated for recycle.

SUMMARY

It has been the purpose of the U^{233} section at Los Alamos to produce pure metal for various purposes either from Thorex product solutions or from recycled metal fabrication residues.

On an experimental basis, both Thorex nitrate solutions and solutions from recycled metal have been successfully separated from the thorium isotopes due to alpha decay of U^{232} and U^{233} by use of small quantities of AG50-X8 (Dowex 50) cation resin. A shielded drybox has been built in which beta-gamma activity in all U^{233} can be reduced by this method, which results in lower personnel exposure. Work on a recovery scheme for the thorium isotopes is continuing.

After allowing time for decay of the thorium daughters and consequent reduction of beta-gamma activity, the U^{233} is processed to metal in conventional dryboxes without shielding.

Automatic titration, another device for decreasing personnel exposure, is used to precipitate uranium peroxide in order to remove other contaminating ions. Routinely, the UO_4 is heated to form a compound approximating UO_3 for easy dissolution in HNO_3, and the peroxide precipitation step is repeated. This UO_4 is calcined to U_3O_8 at 900°C.

The U_3O_8 is reduced to UO_2 with H_2 and converted to UF_4 with anhydrous HF in a nickel reactor.

U^{233} metal is made from the UF_4 by the bomb reduction method with calcium as the reductant. CaO, MgO, and CaO-lined MgO crucibles have been used. Total impurities in the metal are usually <500 ppm.

Residues originating from the various processes are treated to provide feed for a small solvent extraction system and subsequent return to the main stream.

A final report on these procedures is being prepared.

Core and Blanket Processing in the LMFR

O.E. Dwyer
Brookhaven National Laboratory, Upton, New York

CORE PROCESSING

In the Liquid Metal Fuel Reactor, the fission products fall into three main groups: the FPV's, which are volatile at the operating temperatures of the reactor and consist principally of Kr and Xe; the FPS's, which form chlorides more stable than UCl_3 and consist of the elements in groups IA, IIA, and IIIA of the Periodic Table and the rare earths; and the FPN's, the remaining fission products. The fuel itself is a dilute solution of U, Mg, and Zr in bismuth.

Because the LMFR is a thermal breeder reactor, the concentration of FVP's in the core must be kept very low for good neutron economy. For a 1% reactor poisoning level, the concentrations of 9.13-hr Xe^{135} and total Xe in the fuel are estimated to be about 1.5 and 13 parts per billion, respectively, for a full-scale plant.

Over 80% of the FPV's is xenon, and a very important factor governing its removal from the fuel is the chemical behavior of its decay precursor, iodine. Detailed analyses of the thermodynamics and chemical kinetics of the system show that the iodine should largely react with the alkali metals and alkaline earths present to form iodides of very low solubility. These iodides would be largely expelled from the fuel and would presumably adsorb on nonwetted surfaces. Experimental evidence obtained at Brookhaven supports this prediction.

Another important factor affecting the removal of Xe is its extremely low solubility in bismuth. Indications are that the solubility of Xe is so low that it will tend to collect on unwetted solid surfaces, rather than remain in solution until it is removed in a degasser. It thus appears that the Xe problem is not so much one of removal from the fuel in a desorber as of prevention of collection on core surfaces, particularly graphite. The design of FPV removal equipment must be based on a consideration of gas collection on solid surfaces and of removal therefrom to an external system.

The FPS's are removed from the fuel by extracting them, as chlorides, into fused chloride melts. It is proposed to use continuous extraction columns for this purpose, and the preferred salt mixture is the $NaCl$-KCl-$MgCl_2$ eutectic, with or without slight amounts of $BiCl_3$. Since the FPS's include Sr^{90} and Cs^{137}, there is a strong likelihood that this group of fission products will have to be removed from the fuel more for reasons of reactor safety than of neutron economy. For example, in a typical LMFR, a 10-day cycle time will keep the concentration of the FPS's to a level at which they contribute only 1% of reactor poisoning, but a one-day cycle time (which would be practical) would reduce this level by a factor of ten. A one-day cycle time for a 500-Mw (heat) plant would call for a continuous fuel processing rate of about 3 to 5 gpm.

It is planned to use three counter-current extraction columns for effecting material transfer between metal and salt streams. The number of theoretical stages required in any one column is small in most cases, usually five or less. The variation of solute concentration with column height for two of the columns is normal, but that for the third is most unusual. The concentrations reach high maxima in the middle of this column, because it operates on the "stoichiometric" system whereas the others operate on the buffer system. Fluid dynamical studies, in which mercury and water were used in place of bismuth and salt, indicate that the columns may be of either the disk-and-doughnut or packed-column design. Thus far, counter-current extraction columns have not been tested with bismuth and salt; a special out-of-pile loop is currently being built for this purpose. It is expected that the columns will be no more than 6 in. in diameter and 3 to 5 ft high.

The chemistry of the FPS removal process appears to be fairly well understood, reassuring information having been obtained on actual fission products in an in-pile loop. The emphasis now will be on engineering development.

Zr goes along with the U in the chloride system, which means that it must be removed by a special process. The fused chloride process can produce a Zr-U-Bi solution which can be treated by one of three possible methods. The method that looks most attractive at the moment is based on forming ZrC by contacting the bismuth solution with graphite at temperatures around 900° to 1000°C. Very little experimental work has so far been done on the problem of U-Zr separation.

The FPN's may be divided into two subgroups, FPN-I and FPN-II. The former is removed by salt extraction in a manner similar to that used for the FPS's; but the latter group, more noble than Bi, is removed by zinc "extraction." The solubility of Mo in bismuth is so low that it cannot be removed along with the other FPN-II fission products; for its removal, the "cold-finger" technique appears to be most practical.

BLANKET PROCESSING

The development of a processing method for an LMFR blanket is not nearly as advanced as that for the core, principally because relatively little effort has thus far been spent on the blanket problem. In fact, an entirely satisfactory blanket system is not yet apparent. Most work, however, has been done on the thorium-bismuthide/bismuth system, and the following process is postulated on the basis of available information.

The slurry would be a 28 wt % dispersion of $ThBi_2$ in bismuth, would be processed at the rate of 15 tons/day, and would be circulated through an external exchanger for heat removal. The preferred particle size is in the 50 to 100-μ range. The bred uranium and thorium are partially transferred to the liquid bismuth phase by dissolving the particles by a dilution-heating process and then reprecipitating the $ThBi_2$ particles by sudden cooling. A portion of the bismuth liquid containing uranium, protactinium, and thorium is then separated from the diluted slurry by centrifugal action for recovery of the bred species. This is accomplished by salt extraction with fused chlorides.

The bismuth solution will, of course, contain fission products in addition to Th, U, and Pa. These would be removed in the same manner as that described above for the core processing. Both the FPS's and FPN's could be removed in the same equipment as that used for the core processing. After the Th, U, and Pa are removed from the bismuth, the FPN's could be removed from both the blanket bismuth and the core bismuth at the same time, since both streams are identical in composition.

After the FPS's are removed, the Th, U, and Pa are extracted from the bismuth in a fused chloride melt by oxidizing them with $BiCl_3$. The oxidant would be carried by the KCl-$NaCl$-$MgCl_2$ eutectic mixture. The chemical stabilities of the chlorides of Th, U, and Pa are not far enough apart for a separation to be achieved between these materials by salt-metal contacting. From the salt, the three materials are reduced into a second, low-volume bismuth stream, in which the Pa is allowed to decay over a period of several months. The Th-U-Bi mixture is then cooled and centrifuged, the Bi-Th slurry mixture being returned to the blanket system and the Bi-U being either sent to the core or processed for uranium recovery.

The $ThBi_2$-Bi slurry blanket has many attractive features for use in the LMFR, one of the more outstanding being that its chemical processing is very similar to that of the core. This blanket has, however, one serious disadvantage, namely, its apparent tendency to precipitate Th-Bi compounds on cold surfaces. This tendency is peculiar to all soluble-type slurries. As alternate blanket systems not having this disadvantage, slurries of such compounds as ThO_2, ThF_4, and ThC in bismuth are proposed. Up to now, little experimental work has been done on these so-called insoluble slurries, although some work has been recently started on the ThO_2-Bi system.

As far as processing of this slurry is concerned, after separation of the ThO_2 from the bismuth, the Thorex process could be used; but a nonaqueous method would be more desirable, preferably one similar to that proposed for the core. The more alike the core and blanket processing are, the more favorable are the economics.

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Processing of the Aqueous Homogeneous Reactor and the Molten Salt Reactor

D.E. Ferguson
Oak Ridge National Laboratory, Oak Ridge, Tennessee

Two fluid fuel reactors are currently under development at ORNL: the aqueous homogeneous reactor and the molten salt reactor. These reactors present several unique features from the standpoint of chemical processing, which stem from the fact that the fuel and blanket mediums are fluids.

The aqueous homogeneous reactor on which the development at ORNL is primarily concentrated is a two-region thorium breeder reactor. It has a central region, or core, containing a dilute solution of $U^{233}O_2SO_4$ in D_2O. The outer region, or blanket, contains the fertile material in the form of ThO_2 slurried in D_2O. Processing of the fuel (Figure 1) consists in passing it through a hydroclone, a liquid-solid separator, to concentrate insoluble fission and corrosion products into a small volume of solution; for a 500-Mw reactor this is about 100 liters/day. This small volume of fuel may be combined with an equal volume of ThO_2 slurry from the blanket and, after recovery of D_2O by evaporation, processed by the Thorex process (see paper by Shank) for recovery of U^{233} and thorium for reuse in the reactor.

Of the nongaseous fission and corrosion products formed in the reactor, only cesium and niobium have a significant solubility. The withdrawal of 100 liters of fuel per day for comprehensive cleanup controls the build-up of these soluble impurities at a satisfactory level.

The effectiveness of processing by solids removal will be tested on the HRT, now in operation at ORNL. A solids removal experiment, the HRT Chemical Plant (Figure 2), has been built and will be operated with the 10-Mw HRT. This plant consists of a hydroclone for removing solids from the fuel, a dissolver to facilitate taking a representative sample of the slurry removed from the reactor, and storage tanks for the radioactive uranium solution. The enriched uranium from this experiment will be recovered and decontaminated in the Thorex pilot plant at ORNL.

With the aqueous solution fueled reactor it is possible to remove gaseous fission products – iodine, xenon, and krypton – continuously by gas stripping. However, to make reactor operation independent of gas removal may not be simple.

Under simulated reactor conditions iodine is predominantly in the elemental form (Table 1), and in this valence state favors the vapor phase over the reactor fuel solution. In addition, at reactor temperature and pressure iodine can be stripped from the same vapor phase with water. Iodine can be removed from the reactor system by first stripping it from the fuel with the pressurizing gases, O_2 and D_2O vapor, removing it from the gas by partial condensation of the D_2O vapor, and isolating it by fractional distillation to recover the D_2O. This process will accomplish two major objectives: control of Xe^{135} poisoning of the reactor by removing the parent I^{135} and control of the build-up of radioactive iodine, which is a serious radiation hazard of this reactor.

The molten salt power reactor under development at ORNL is also primarily a thorium breeder reactor (Table 2). It is a two-region machine fueled with U^{233} contained in $LiF\text{-}BeF_2$ with a thorium blanket contained in the same solvent salt. A comprehensive processing period of about one year is adequate for both blanket and core systems.

A fluoride volatility process has been developed for recovering uranium from such fuels and is now being studied on a pilot-plant scale. The method consists of volatilizing the uranium from the fused salt by fluorination with fluorine gas and decontamination by NaF adsorption (ORNL process) or fractional distillation (Argonne process).

The exclusive use of such a process has the disadvantage that discarding of $LiF\text{-}BeF_2\text{-}ThF_4$ contaminated with fission and corrosion products costs about $2,500,000 per year. This provides an incentive for a simple, cheap method of removing the

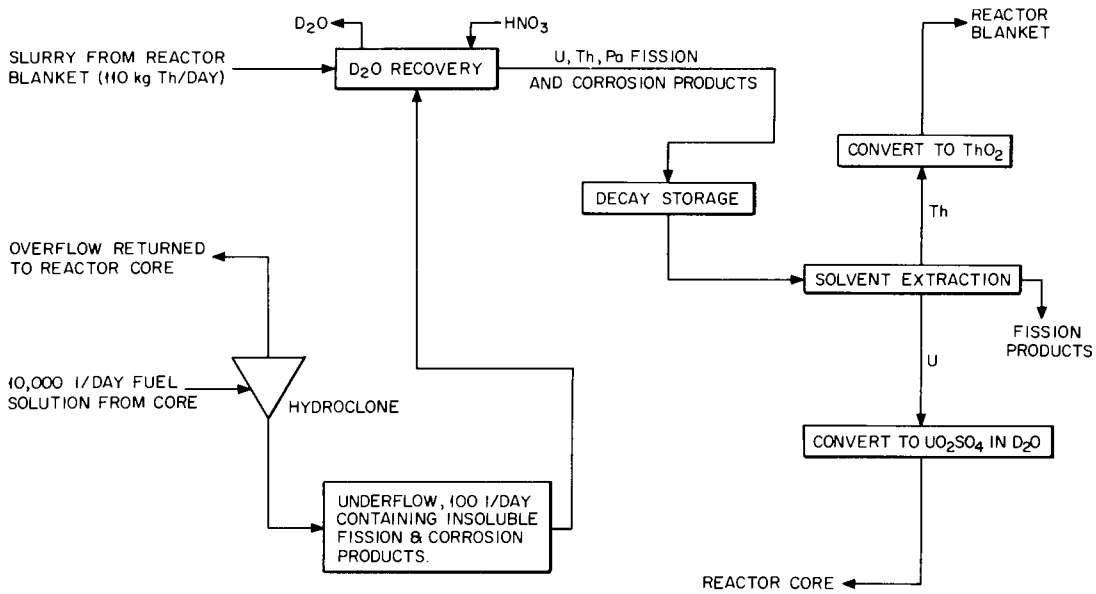

Figure 1. Schematic flowsheet for thorium breeder reactor processing.

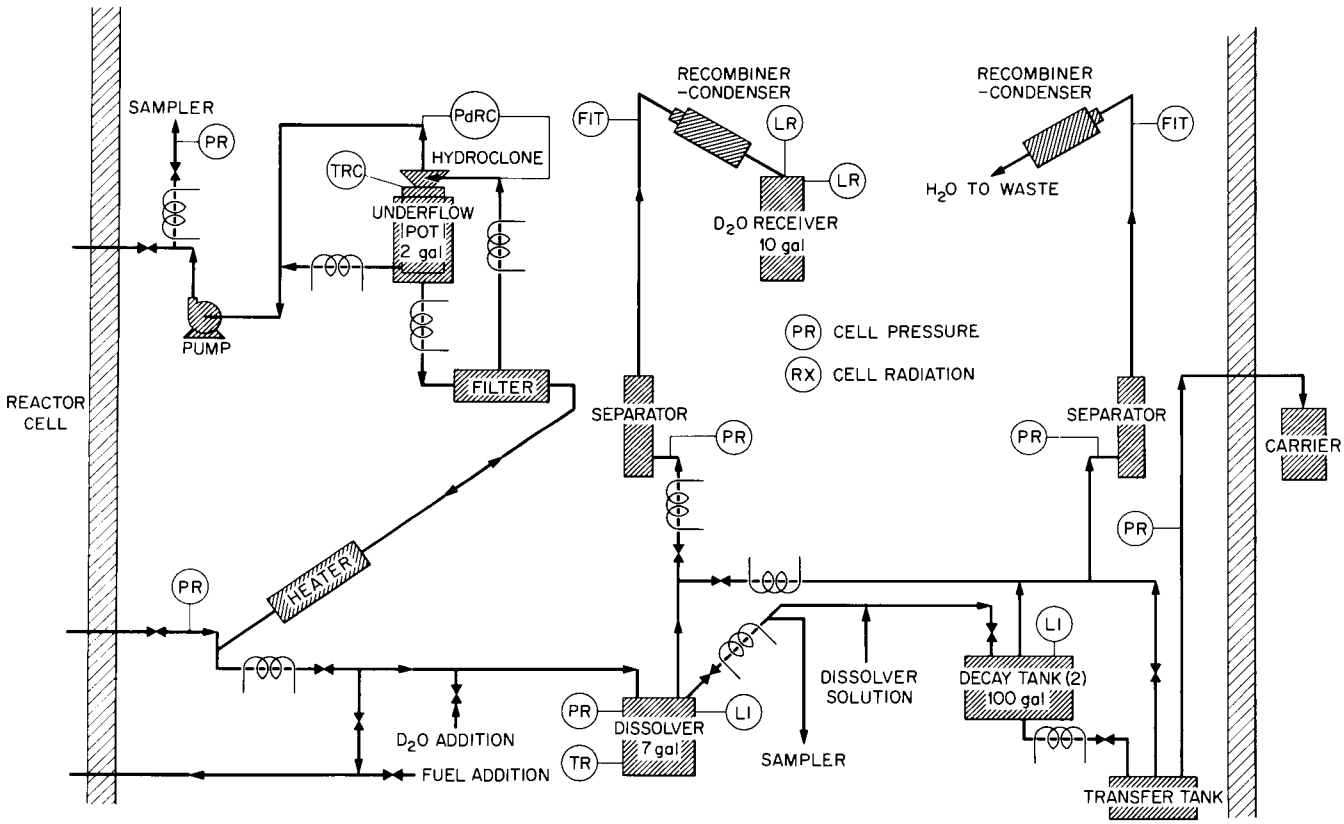

Figure 2. HRT core processing plant.

Table 1

Behavior of Iodine at 280°C

$$IO_3^-{}_{(l)} \rightleftharpoons I^0{}_{(l)} \rightleftharpoons I^0{}_{(g)}$$

In 0.02 *M* UO_2SO_4, 0.005 *M* H_2SO_4:

$$[I^0{}_{(l)}]/[IO_3^-{}_{(l)}] = 7,$$

$$[I^0{}_{(g)}]/I^0{}_{(l)}] = 7.$$

In D_2O at *p*H 4 to 9:

$$[I^0{}_{(g)}]/[I^0{}_{(l)}] = 0.2.$$

bulk of the fission and corrosion products from the salt so that it may be reused.

Scouting work has been carried out on the removal of fission products and corrosion products from fluoride melts, mainly $NaF\text{-}ZrF_4$ to date. Partial freezing leads to a concentration of rare earths, the major fission product neutron poison, in the liquid phase by a factor of 2 to 4. The addition of CaO also removes rare earths by metathesis to the insoluble oxides. The expected corrosion products – iron, nickel, chromium, and molybdenum – can be removed by hydrogen reduction. The extension of this work to the $LiF\text{-}BeF_2$ salts is just beginning.

Table 2

Molten Salt Thorium Breeder Reactor

Power:	
Heat	600-700 Mw
Electricity	235-280 Mw
Core:	
Volume	500-700 ft^3
Composition	62% LiF – 37% BeF_2 – 0.5% ThF_4 – 0.2% UF_4
Blanket:	
Volume	500-700 ft^3
Composition	71% LiF – 16% BeF_2 – 13% ThF_4
Required Processing Rate:	1 System vol/year

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Session VII

FUEL RECYCLE AND HANDLING

Health Physics Aspects of Handling U^{233} Feed Material

J. Lawrence
Los Alamos Scientific Laboratory, Los Alamos, New Mexico

Two distinct radiation problems exist in the purification and fabrication of uranium-233 feed material. These are the control of alpha and gamma radiation. The isotope U^{233} presents only a simple alpha control problem. However, the feed material currently encountered contains from 20 to 40 ppm of the isotope U^{232}. It is the daughters of the U^{232} which constitutes the gamma radiation problem. In the absence of either one of these, the remaining situation could be dealt with in a routine manner.

The concentration of the U^{232} isotope is so small that the specific activity of the total uranium in the U^{233} feed material is not appreciably changed. With no U^{232} the specific activity of the uranium isotopes in the feed material would be about 9.4×10^{-3} curies per gram; 40 ppm U^{232} raises the activity to only 10.3×10^{-3} C/g, considering only the uranium present.

At LASL, because of the high specific activity of this material as compared with the other uraniums encountered, it has been decided that all work with large quantities of U^{233} feed material will be done in dryboxes. In this connection the maximum permissible body burden q and the maximum permissible air concentration $(MPC)_{air}$ should be considered. In *NBS Handbook 52* both the soluble and insoluble forms of U^{233} were discussed. The q for the soluble was 0.4 μC with the bone as the critical organ, and for the insoluble 0.008 μC with the lungs as the critical organ. The $(MPC)_{air}$ for the soluble and insoluble were 1×10^{-10} and 1.6×10^{-11} μC/ml air, respectively, for continuous exposure. Recently the ICRP has prepared a more complete and revised table of q and $(MPC)_{air}$ for presentation at the 1958 Geneva Conference. This seems to contain the best figures available at this time. The q and $(MPC)_{air}$, as calculated by using the exponential elimination function, are 0.015 μC and 2.1×10^{-11} μC/ml air (47 dis/min/m^3), respectively (quoted here with their permission). These are based on the kidney as the first critical organ, a biological half-life (after fixation) of 300 days, and the assumption that only 0.0275 of the quantity inhaled actually becomes fixed in the kidney.

For occupational exposures the $(MPC)_{air}$ of 2.1×10^{-11} μC/ml air is unnecessarily restrictive. Assuming a 40-hr work week and a 50-week work year, the $(MCP)_{air}$ for occupational exposure becomes 6.1×10^{-11} μC/ml air (or 136 dis/min/m^3). For the years 1956 and 1957, in the area where U^{233} feed material is worked, the average air count has been 4 dis/min/m^3, which is substantially below the allowed value. In February 1957, a mild explosion occurred in the drybox line where the chemical purification of the U^{233} feed material is done. This resulted in the only *unexpected* above-permissible air concentration so far encountered. The high count at this time was 1400 dis/min/m^3 for an 8-hr period. Although the accident was not discovered until after the area was entered, the persons entering the area, without respirators, did not show excessive amounts in their urine.

This brings up the points of the use of respirators and the meaning of urine assays. It is the current practice at LASL to require the wearing of respirators when the average level of U^{233} in the air exceeds the occupational exposure permissible level. Unfortunately, the level of activity is not routinely determined until the day after the sample is taken. Therefore, special policies had to be adopted to insure a minimum of inhalation of U^{233}. It is the practice now to require the wearing of respirators whenever a high air count is expected, and then for a minimum of 1 hr afterwards when in the area. High air counts are expected whenever any of the following jobs are done: changing drybox gloves, performing maintenance on the dryboxes, decontaminating a spill, and performing air transfers into or out of the dryboxes. It is due to the preventive use of respirators that no person thus far, working with the material, has showed an excessive amount in the the urine.

It may be shown that, with no further exposure, the initial rate of excretion of a fixed permissible body burden in the kidney would be about 30 dis/min/liter in urine. With a continuing exposure the level to be expected is more nebulous. Since only 2.75% of that taken into the body by inhalation reaches, and is fixed in, the critical organ, the remaining 97.25% must be eliminated. Actually urinary excretion of the uranyl carbonate complex is the main method of excretion from the body, and 85% of an acute dose is eliminated by this process in the first 24 hr. For a working number, LASL has selected the level of 50 dis/min/liter as indicative of a significant exposure. Normally urine samples are required monthly from persons working the U^{233} line.

If a sample contains >50 dis/min/liter, the situation is investigated, and the cause is eliminated. LASL is in the process of changing over from a solvent extraction method of recovery of U^{233} from urine to an ion exchange method. The latter gives a better cleanup of the thorium and thorium daughters, and has about 90% recovery of the uranium, while the solvent extraction method had a recovery of only about 70%. The level of significance for U^{235} is the same as that for U^{233}, and no distinction is made in the analysis.

During the past two years the average urine count for persons working exclusively in the U^{233} chemical processing area has been about 13 dis/min/liter. The highest sample encountered thus far contained $\approx$75 dis/min/liter, but this level was not maintained.

The gamma problem in handling U^{233} feed material is not due to the U^{233} and its daughters, but rather to the U^{232} and its daughters. Although contamination to the extent of 20 to 40 ppm does not seem very significant, a comparison with natural thorium will illustrate the fallacy of this argument. U^{232} has a half-life of 74 years, and its immediate daughter is Th^{228} with a half-life of 1.9 years. Th^{228} is also the third daughter of natural thorium, Th^{232}. A little calculation will show that at equilibrium (i.e., the condition when the least quantities of both Th^{232} and U^{233} would be required) it would require 3750 times as much Th^{232} as it would U^{233} feed material (20 ppm U^{232}) to give the same rate of formation of the Th^{228}. By comparison there would be no appreciable radiation problem in handling natural thorium, because the much larger bulk would effectively shield and dilute the source of radiation.

In practice the gamma problem in handling the U^{233} feed material is one of growth of activity. The U^{232} itself presents no problem. However, the gamma activity of its daughters is another story. All the daughters after Th^{228} have half-lives of <4 days. However, as a result of the 1.9-year half-life of the Th^{228}, there will be an exponential build-up of gamma activity with a maximum at 10 years and subsequent decay with a 74-year half-life.

Some *calculated* data on the radiation output of U^{233} feed material will serve to illustrate the growth and to show that the predominance of activity comes from the U^{232} and daughters. The dose rates given are in r/hr at 1 cm from a ¼-in.-thick, 2-in. disk of U^{233} feed material (20 ppm U^{232}) at various ages.

	Age			
	1 Day	4 Weeks	32 Weeks	10 Years
U^{233} + daughters	0.0029	0.0032	0.011	0.15
U^{232} + daughters	0.019	0.37	3.2	14.0

Two disks of U^{233} feed material, ⅛ in. thick and 2 in. in diameter, were procured about a year and a quarter ago. The growth of radiation output of these has been followed. The emission rate from each is approximately the same, even though one is nickel coated and the other is sealed in a plastic envelope. The surface dose rates measured 28 days after casting were 6.5 rad/hr and 6.7 rad/hr. When measured a year and two months later, the surface dose rates were 53 rad/hr and 58 rad/hr, respectively, for the nickel coated and plastic bag encased pieces. This rate of build-up on the two pieces was verified by a series of Cutie Pie measurements extending over the same period. The Cutie Pie reading corresponding to the extrapolation chamber reading at one year and two months was 3.6 r/hr for a single piece and 5.1 r/hr for the two pieces stacked. The value for two pieces stacked corresponds to a rough theoretical calculation of the dose rates to be expected. The rates of build-up, i.e., observed rate and calculated rate, differ slightly. The observed rate is slightly less than the calculated, which indicates that some appreciable amount of Th^{228} and its daughters were present after casting.

The primary gammas from the U^{232} chain range from about 0.040 to 2.6 Mev. After emerging from U^{233} feed material ⅛ in. thick or more, the calculation mentioned earlier indicates that about ½ of

the total dose rate would be due to the 2.6-Mev gammas of Tl^{208}.

For gamma-rays of this energy, moderate amounts of lead shielding are not very effective. Some rough measurements made on the U^{233} feed material disks about 1¼ years after casting indicate that ¼-in. lead shielding reduces the roentgen output to ½ the unshielded value. Additional ¼ inches of lead reduce the dose rate by factors of about 0.7 each up to a total of 2 in. (measurements with thicker lead shields were not made). This indicates that the gammas emerging after the first ¼ in. of lead are essentially all 2.6 Mev in energy.

The emission rates experienced are a function of the degree of thorium cleanup in the last chemical purification or metallic casting and period of time since that operation. During the past two years, batches have been received reading from 0.1 to 3.0 r/hr (readings taken with hard-shell Cutie Pie in contact with plastic shipping bottles). Old material which has been reworked has also shown emission rates in this same range. These emission rates are for about 250 g material in about 2 liters solution.

During 1957, the radiation levels of material worked at LASL have averaged somewhat higher than in 1956. This is reflected in the total gamma exposure received by all persons working the material when the quantity of material worked is taken into account. Working the material consists of chemical purification, i.e., several peroxide precipitations, hydrofluorination, and reduction to metal. The total gamma exposure received, as measured by film badge, was about 44.0 rem in 1956 while working about 32 kg metal. In 1957, the total gamma exposure was about 18 rem while working only about 8 kg metal. The 1957 exposure rate was about 0.9 rem more per kg metal than in 1956.

During the past two years a total of nine persons have been involved to some extent in the chemical purification of U^{233} feed material. In 1956, two persons received about 11.0 rem each, while the others received about 4.0 each. A total of only two biweekly overexposures ($>$0.6 rem in 2 weeks) were experienced in 1956. In 1957, an attempt was made to keep all operators' exposures below 5.0 rem/year, in accordance with the NCRP recommendations. By judicious use of personnel rotation, only one person received $>$5.0 rem, in this case only 5.3 rem. One other received almost 5.0 rem, and the others averaged about 1¼ rem. Only one biweekly overexposure was experienced in 1957. The fact that so few biweekly overexposures were experienced for this operation during the past two years is attributed to the excellent cooperation of the operators, who have kept their own weekly records of pocket dosimeter exposures and have governed their work accordingly.

To date very little shielding has been used. The filtrate bottles have been shielded with ½ in. of lead, and an external, portable ½-in. lead shield was constructed and used through the first precipitation operation. The exposures were accumulated with this meager shielding in position.

Wrist film badges as well as body film badges were worn by the operating personnel. The percentage of permissible exposure received by the wrists was about ⅓ that received by the body. In neither the case of the body nor the wrist badge was the beta exposure significant.

From the above discussion it is apparent that the body gamma exposure is the controlling factor. In order to reduce the body exposure, it is necessary to separate out the daughters of the U^{232}, if only for a short while. Some work by Kircher and others at LASL indicated that ion exchange columns would accomplish the necessary cleanup. A heavily shielded drybox was designed and constructed for this job, which can be operated with a minimum of actual hand operations. It was designed to handle two lots of U^{233} feed material which started out at 2 r/hr each. With an operating time of 100 min/week, the shielding was designed to allow the operator 0.10 rem/week. This ion exchange procedure is an addition to the procedures used during 1956 and 1957. As yet this box has not gone into operation. It is expected that one passage through the ion exchange column will reduce the gamma emission of each batch by a factor of ⅒th to ⅓rd of the original level. All material will pass through the ion exchange column procedure before it is fed into the peroxide precipitation line where a large number of actual hand operations are performed. It is expected that the use of this additional step will appreciably reduce the personnel exposure.

In addition to the chemical processing, some limited experience has been gained in casting and machining the metal. At LASL the casting and machining of metallic components is done in the same drybox line in which Pu^{239} is cast and machined. Since the permissible air concentration for Pu^{239} is much less than that for U^{233}, no additional

restrictions were necessary, as far as airborne activity was concerned. During a 7-week period about 14 kg U^{233} metal was cast and machined. The average body exposure per week for the five persons who cast, machined, and nickel coated the metal was about 0.7 rem. For these operations the wrist exposures were about the same percent of permissible exposure as the body exposures. During this period, five exposures to personnel exceeded 0.3 rem/wk. Although more material has been cast and machined, it did not result in significant exposures.

In the past, metallic buttons of U^{233} feed material have been made and stored for 6 months or more before a casting was made. If U^{233} metal production were to become a full-time job, more remote control machining would be necessary, additional shielding in the dryboxes where the machining is done would have to be installed, the exposure would have to be spread over more personnel, and all work, from the ion exchange step to the final machining and nickel coating, would have to be done as rapidily as possible and with as few and as short delays as possible.

Radiation Hazards in Recycled Thorium Fuels

SAMUEL ZWICKLER
Brookhaven National Laboratory, Upton, New York

As nuclear fuels are recycled or irradiated for long periods of time, nonfissionable isotopes of the fuel material are built up. Since these isotopes are not chemically separable from fissionable and fertile material, they will dilute the purified fuel and may create radiation hazards in their handling. Solid fuels in particular will be affected, since existing techniques of fuel manufacture and fuel reentry require direct handling.

The purpose of this report is to evaluate the radiation hazards that will exist at high burn-ups.

U^{232} is produced from Th^{232} through an $(n,2n)$ reaction. U^{232} decays by α-emission to Th^{228}. After chemical separation, U^{232} contaminates U^{233}, and its daughter Th^{228} contaminates Th^{232}. The decay daughters of Th^{228}, Pb^{212} with a 0.238-Mev γ and Tl^{208} with a 2.62-Mev γ, present radiation problems both in reprocessed Th^{232} and in U^{233}.

In Figures 1 and 2 the contaminations of separated U^{233} and recovered Th^{232} are plotted as functions of irradiation time and flux. The plots have been prepared on the basis of an assumed $Th(n,2n)$ cross section of 1 mb. The actual cross section for this reaction will depend on the location of the fuel in the reactor. However, the contamination will be directly proportional to the true cross section expressed in mb.

U^{232} must be present to the extent of 3×10^4 ppm before any spontaneous fission problem is encountered; consequently, it is neglected. Com-

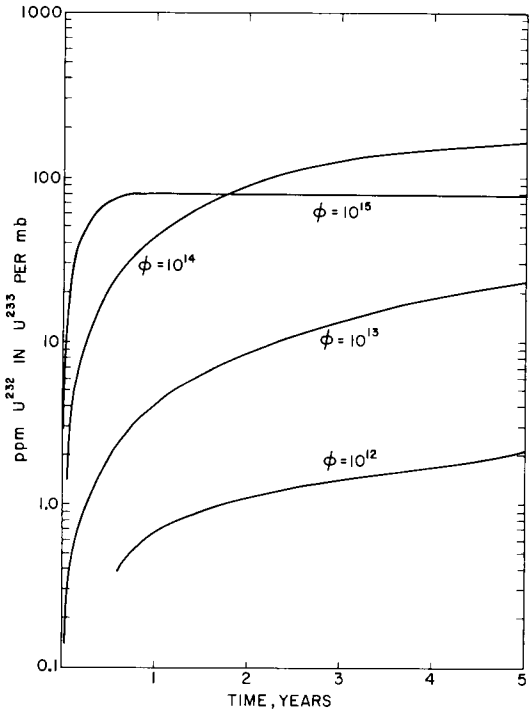

Figure 1. Concentration of U^{232} in U^{233} (ppm) per $\sigma_{Th^{232}}(n,2n)$ mb on irradiation of Th^{232} and after 110 days of cooling, plotted as a function of thermal flux and irradiation time.

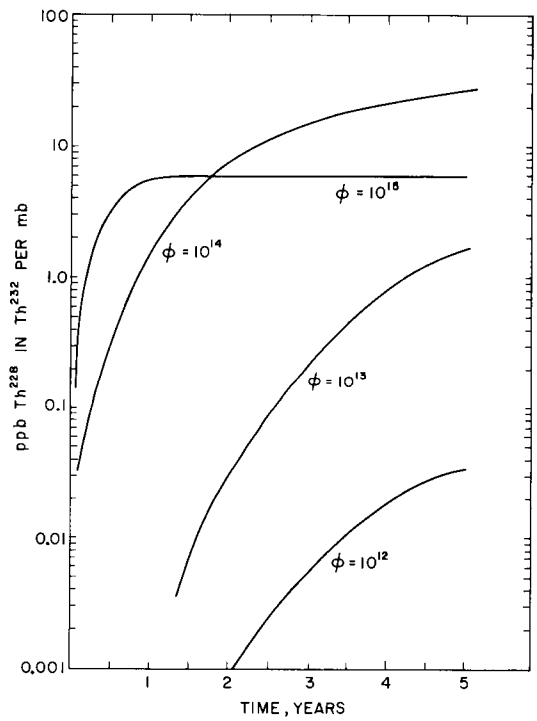

Figure 2. Concentration of Th^{228} in separated Th^{232}(ppb) per $\sigma_{Th^{232}}(n,2n)$ mb on irradiation of Th^{232} and after 110 days of cooling, plotted as a function of thermal flux and irradiation time.

pared to the gamma radiation problem, the (α,n) problem is also considered negligible.

The radiation hazard in U^{233} will increase with time as freshly separated uranium containing U^{232} decays. During the first year of decay, the rad/hr at the surface of a 1-kg sphere of uranium will be approximated by $(0.04+0.01T)$ rad/hr/ppm U^{232}, where T is in days.

Separated U^{233} fuels present a hazard which increases with cooling time because of the build-up of daughters of relatively long half-lived Th^{228}. Thorium, which contains its maximum amount of Th^{228} at the start of the cooling period, will decrease in activity upon reaching equilibrium with its daughters after 30 days.

At separation time the radiation at the surface of a 1-kg sphere of thorium will be 0.5 rad/hr/ppm Th^{228}. After 30 days of cooling, at equilibrium, the activity level will be 700 rad/hr/ppm Th^{228} initially present. The activity level then decreases with the half-life of Th^{228}.

To estimate the magnitude of the radiation problem with both uranium and thorium, an irradiation time of 27 months at a flux of 10^{14} n/cm^2-sec was chosen. It is assumed that this irradiation, which is more than 7×10^{21} nvt, is somewhat greater than will be achieved in practice. The maximum activity of a 1-kg sphere of thorium will be 7 rad/hr-mb at the surface. The activity at the surface of a 1-kg sphere of U^{233} will be 360 rad/hr-mb after one year's cooling. Obviously, heavily shielded, remotely operated facilities will be required for fabricating U^{233} fuel elements. The shielding necessary for U^{233} is estimated to be about 4 ft of concrete. For thorium, a concrete shield 1.5 to 2 ft thick would be required.

Therefore, for the case of recycled thorium and U^{233}, the handling problem for highly decontaminated fuel seems to be extremely difficult. It is probably worthwhile to intensify efforts on schemes for putting these fuels into forms that can be handled remotely.

Radiation Experience in Handling Thorium at Fernald

R.C. Heatherton
National Lead Company, Mount Healthy Station, Cincinnati, Ohio

This paper presents information, observations, and data pertinent to occupational exposure to external radiation from thorium and to air-borne radioactivity in processing thorium nitrate to produce metal reactor fuel elements. No difficulty was experienced in controlling external radiation exposures to levels well below the recommended maximum permissible, but there was considerable difficulty with the control of air-borne radioactivity. Recommended maximum allowable concentrations were exceeded throughout the latter part of the operating period.

INTRODUCTION

The Fernald experience covered approximately two years, from January 1954 through December 1955. During this time the thorium plant at Fernald was operated for both production and process development, and major process changes were made in the fluoride manufacturing and metal remelting steps. With the exception of the modified process whereby thorium oxide was converted to thorium fluoride by hydrofluorination, all operations in the production of thorium metal were accomplished in a single building $\approx$160 ft long and 100 ft wide. The building center height was $\approx$40 ft dropping off to 20 ft at eaves on either side. Conversion of thorium ingots to rods was done off-site; however, the rods were returned to the same building for machining into fuel slugs. In the original process, a modification of the Ames method, thorium fluoride was precipitated from thorium nitrate solution with 70% hydrofluoric acid, and, after reduction to a metal derby, remelting and casting into ingots was done in an induction-type furnace. The wet fluoride precipitation method was later replaced by the previously mentioned hydrofluorination method, and arc melting was substituted for induction melting. This latter process is described in detail in TID 7521.[1]

Conventional detection methods were used for radiation survey and personnel monitoring with film badges for beta and gamma radiation. Similarly, the air-borne activity was measured by collection of particulate on filter paper and analysis by radioactive count. For the purpose of presenting this information, the entire operating period can be divided into four periods as follows:

1. Start-up	Jan. '54 – Mar. '54	Modified Ames: wet fluoride precipitation and induction melting.
2. Change-over	Apr. '54 – Mar. '55	Oxalate-oxide-ThF_4 hydrofluorination and arc melting.
3. Peak production	Mar. '55 – Oct. '55	Same as 2.
4. Reduced production	Nov. '55 – Dec. '55	Same as 2.

Throughout the four periods there were no serious problems with external radiation. On a few occasions film badges worn by operating personnel indicated doses above the maximum permissible of 300 mr gamma radiation per week; however, on a 13-week or yearly basis all exposures were well below permissible level. Quarterly exposures ranged from 15 to 30% of the maximum permissible quarterly dose. The highest received by any individual in any quarter was 1600 mr. The highest exposures were received in the third calendar quarter of 1955 when the plant average was 1100 mr for the 13-week period.

The highest sources of exposure to external radiation were the dezincing condenser, inner surfaces of the induction furnace, and parts of the remelting furnace where there was condensation of the decay products. These sources gave radiation readings of about 80 mr at the surface. Radiation readings for other surfaces and materials ranged downward to $<$1 mr. Although there were a number of places where exposures of 7½ mr/hr could be obtained, it was possible to control personnel

exposure through rotation and use of time limits in higher radiation areas.

AIR-BORNE ACTIVITY

During the start-up period there was no serious problem with air-borne radioactivity. General air samples were usually below the accepted maximum allowable concentration of 70 dis/min/m^3 of air in use at Fernald. Breathing zone samples in general were from 70 to 200 dis/min/m^3. Occasional breathing zone samples were on the order of 10^3 dis/min/m^3. During the change-over period these concentrations went up by about an order of magnitude. Where the concentration had been, on numerous occasions, <10 dis/min/m^3 in the general air during the first period, at no time during the second period were these low levels attained. During this time attempts were made to correct the sources of air-borne contamination. However, since the process was in the developmental stage and a number of other problems were present, production continued with the expectation that the difficulties would be overcome.

After installation of the arc melting was completed in March 1955, the plant began its peak production period. Again there was a significant rise in the air-borne contamination, and it was during this period that the highest air-borne levels were measured. Breathing zone samples were generally in the 10^3 to 10^5-dis/min/m^3 range. Some of the inherent problems in design became apparent, as well as difficulty with operating units above their expected capacity. In the wet operation one of the causes of high contamination was the deterioration of equipment due to corrosion by the hydrous HF and nitric acid present at the start-up period. Correction of the bad conditions could not keep pace with equipment failure.

In October 1955 it was decided that the operation would be shut down in order to permit correction of the more serious problems and a thorough plant cleanup. The plant was then restarted in November at a 30% reduction in the production rate. In this period there was a slight lowering of the air contamination; however, it was concluded that the plant could not continue to operate even at the reduced rate without endangering operating personnel. An engineering study of the requirements for desired control completed at this time indicated that an expenditure of about $250,000 would be necessary, a large part of which would be for ventilating equipment, including an additional air supply to meet the requirements of additional exhausts. It was decided that the thorium needs were not sufficient to justify such an expenditure, and the operations were shut down in December.

CONCLUSIONS

Although the measured air-borne radioactivity in the thorium operations was high, it was not very different from that first encountered in uranium production, and control of the hazards in the process has progressed to a satisfactory level at this date. In spite of the high air-borne activity levels, it is concluded that a plant could be designed and operated for production of natural thorium metal with sufficient control to prevent exposure of personnel above recommended maximum permissible levels. This would require careful attention to adequate ventilation for the various sources. Such operations as arc melting, sawing, arc welding, and metal breakout would require complete, or nearly complete, enclosure; however, similar operations have been done with uranium metal without hampering production. It is believed that segments of the operation, such as the wet operation or arc melting, should be put into individual buildings, or physically separated from other parts of the process.

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Session VIII

GENERAL SESSION

SUMMARIES of SPECIAL SESSIONS

Basic Physics

W.C. Redman
Argonne National Laboratory, Lemont, Illinois

This written summary draws primarily upon those data and opinions presented at the basic physics session but not recorded elsewhere in the proceedings of the conference. The emphasis was on the word "basic," and material for discussion was selected on the basis of its pertinence to the design of reactor systems containing Th or U^{233}. Much of the session revolved about the status of our knowledge regarding certain neutron parameters required for reactor physics design. The interrelation and importance of several of the specific items discussed is revealed by the two-group age-diffusion criticality equation,

$$k_{\text{eff}} = \frac{\eta f p \varepsilon e^{-\tau B^2}}{1+L^2B^2}.$$

Comments on most of these parameters are summarized below.

ηf

Knowledge of the thermal absorption cross sections of Th and U^{233} is required to evaluate the thermal utilization (f), plus the fission cross section and neutrons per fission for η. The status of existing measurements of these quantities was reviewed.

Measurements of the capture of thermal neutrons by Th^{232} lead to a weighted average value of 7.43 ± 0.22 barns. The present "best values" for U^{233} thermal neutron absorption and fission are 588 ± 7 and 532 ± 6, respectively. Combining these with the present accepted value of ν for U^{235} and a value of ν_{23}/ν_{25} based on a recent determination[1] of the relative number of prompt neutrons from U^{233} and U^{235} fission and delayed fractions[2] of 0.0026 and 0.0064, respectively, yields a value of

$$\eta_{23} = \nu(\sigma_f/\sigma_a) = 2.46 \times 1.020 \times (532/588) = 2.27 .$$

The thermal η for U^{233} has also been determined[3] by comparison of aqueous solutions of U^{233} and U^{235}. The original analysis yielded a value of $\eta_{23} = 2.31 \pm 0.03$ based on $\eta_{25} = 2.08$. This value was found to be insensitive to temperature from 25° to 100°C. This comparison was made for water reflected systems, and a recent re-evaluation to consider the effect of epicadmium absorption and fission resulted in no change in the value of η_{23}. Analysis of unreflected systems of U^{233} and U^{235} solutions yielded a slightly higher value. However, an assumption was made that the leakage was the same in each case. This measurement will be repeated with boron added to the U^{233} solution to match the core absorption and hence leakage of the U^{235} system.

ENERGY DEPENDENCE OF η

The energy dependence of η_{23} near thermal energies has been investigated by direct measurement[4] relative to U^{235} as a standard and by calculation from the measured variation in fission and total cross section of U^{233}. Both methods showed that η_{23} is constant from 0.01 to 1.0 ev. Above 1 ev, data from crystal spectrometer and fast chopper measurements show a pronounced energy dependence for η_{23}, and the fluctuations do not coincide with the resonance peaks. The Eisenbud-Wigner type of treatment has been successful in fitting the fast chopper and crystal spectrometer data for the fission cross section of U^{233}.

The following values for η_{23} at higher energies have recently been reported:[5] 2.25 at 30 kev, 2.43 at 140 kev, 2.45 at 250 kev, and 2.60 at 900 kev. The last value is consistent with a value of 2.65 for $(\eta-\alpha)_{23}$, established by comparison with U^{235} in the Topsy and Jezebel assemblies at Los Alamos.

p AND RESONANCE INTEGRAL FOR THORIUM

A recent determination[6] for the resonance integral of thorium is 96 ± 6 barns. This is in good

agreement with the value calculated from known and assumed resonance parameters. One such calculation resulted in 67 barns for the first seven resonances, 25 for the contribution of higher unresolved levels, and 3 for the $1/v$ contribution, for a total of 95 barns. A second calculation resulted in the same total based on 79 for the first 18 resonances, 13 for higher, and 3 for the $1/v$ part. This is to be compared (or contrasted) with an earlier measurement[7] of 67 ± 5 barns. Both the experimental values have the $1/v$ portion subtracted.

These values for the infinitely diluted samples are of less importance in reactor design than a knowledge of the effect of clustering the resonance absorber. Consequently, there have been several recent determinations of the effective resonance integral of thorium as a function of the surface to mass ratio.

A simple theoretical form[8]

$$(RI)_{\text{eff}} = A\left(1 + \frac{M}{8\sigma_p} C \frac{S}{M}\right)$$

for the effective resonance integral, which takes into account the effect of Doppler broadening and corrects for the possibility that a neutron which enters the lump escapes with collision, was used to compare the several sets of experimental values. Actually a twofold check on such data is possible, one involving the shape of the S/M dependence and the second the scaling factor between similar measurements on metal and oxide samples. Three recent measurements [9-11] on various samples of uranium, thorium, and their oxides all agree with the shape expected theoretically. A fourth determination[12] does not appear consistent on either the shape or scaling basis and so a systematic error is suspected.

The factor of 0.6, required for the second term in the simple theoretical model to give good agreement with the earlier experimental observations, is not needed for agreement with the more recent results. However, a consistent value for the magnitude of the effective resonance integral still is lacking in the measurements reported on thorium.

ε

There is no significant bonus to be expected from the fast fission of thorium, in contrast to the situation existing in a reactor containing U^{238}. This is a consequence of the higher threshold and lower fission cross section for Th^{232}, and the lower value of ε has been confirmed by recent BNL measurements in lattice cells.

τ

Measurements of the neutron age in both light and heavy water systems containing moderate quantities of thorium and ThO_2, respectively, are reported in summary papers included in these proceedings. At present there do not exist sufficient experimental data to decide whether the ages for systems containing thorium are in complete agreement with theoretical predictions.

REACTIVITY EFFECTS

Several items related to both short and long-term reactivity effects were mentioned in the discussions. The first is the low yield of delayed neutrons in U^{233} fission,[2] about 40% of that for U^{235}, and the associated problems in reactor control due to the reduced margin between delayed and prompt critical.

The second major item of concern was the effect of Pa^{233}. The long half-life and high capture cross section of this intermediate product in the production of U^{233} present a serious problem for the achievement of good neutron economy in a thorium reactor. Particularly in a maximum performance reactor, burn-up of Pa^{233} represents a significant twofold loss of both useful neutrons and potential U^{233} atoms. For the 27-day half-life Pa^{233}, a thermal capture cross section of approximately 65 barns was reported, but there exists very strong epithermal capture as well.

GENERAL COMMENTS

The physics of U^{233}-Th reactor systems does not seem to involve any gross uncertainties, in spite of the fact that most of the measurements made to date have not had the impetus of need for any purpose other than general knowledge.

In the past the only systems containing U^{233} or thorium which have been operated were thermal criticals with U^{233} solutions (ORNL), fast criticals with U^{233} cores (LASL), and a $U^{235}O_2$-ThO_2-H_2O boiling reactor experiment (ANL). At pres-

ent both light and heavy water criticals involving enriched uranium and thorium are under way (B&W and ANL), as well as the analytical design of a variety of systems. Future plans which will yield basic physics information include zoned criticals involving a U^{233}-aluminum alloy (BNL), thoria-urania light water exponentials and possibly criticals (ANL), and the refueling of the MTR with U^{233}.

Because of reduced radiation damage and chemical compatibility with water, thoria fuel elements are attractive for a long fuel cycle. Consequently, there will be the need for precise physics design work to provide a high initial conversion ratio so that reactivity effects will not limit the useful life of the fuel elements. The higher absorption cross section of thorium argues for systems less heterogeneous than existing in present U^{238} reactors. The epithermal region of operation appears promising on the basis of present knowledge.

The real problems in thorium-U^{233} reactor systems do not seem to be physics problems, but rather those related to chemical processing, fuel refabrication, and economics.

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Thorium Crudes to Fuel Grade Thorium

O.R. Magoteaux
National Lead Company, Cincinnati, Ohio

A production process for the preparation of both thorium oxide and thorium metal has been put into practice. The oxide is an intermediate product having a purity acceptable for further processing into metal.

Ample thorium ores are available, principally in the form of monazite. Thorite-type materials occur in the United States, and, although large-scale production from them is not yet under way, these deposits are expected to add significantly to our usable thorium reserves. By-product thorium from uranium mixing may become of some importance; some sources are currently under development. Present commercial production capacity for thorium materials is of the order of one million lb ThO_2 annually. Solvent extraction of sludges was used to produce material of low uranium and rare earth content. Some quantities of arc-melted thorium metal are now available at Fernald in the form of ingots which can be hot-rolled into sheets or extruded into rods as desired. Machining operations have been developed to process these further into solid fuel elements.

Other methods of preparation of the metal have been developed. One method investigated at the Bureau of Mines is the reduction of halides (principally $ThCl_4$) to sponge metal, followed by arc melting. The Metallex process, developed at ORNL, involves the reduction of $ThCl_4$ by sodium amalgam to a powder which can be directly extruded to thorium rod. A third process, successfully piloted at Horizons, Inc., produces a crystalline thorium readily adaptable to cold consolidation and arc melting, and to warm extrusion to billets approaching 100% theoretical density. A fourth process, tried at NLO on a pilot scale, produces thorium powder by the reduction of thorium oxide with calcium. The powder can be hydraulically pressed into rods and, from all indications, can be arc-melted into ingots.

The present cost of thorium metal is in the neighborhood of $20 per pound. Other processes being developed show promise of reducing this somewhat, although it is not yet certain how much.

The quality of the product, either oxide or metal, depends on the type of process used in production. Thorium oxide and some metallics seem to be the largest impurities, with iron, nickel, and aluminum being worth mentioning. Acceptable levels of these impurities have not yet been defined. Rare earth contents generally are less than 100 ppm in the products or have not yet been determined.

Further development work is needed to improve the production process with respect to process yields, and development of some of the alternate processes under investigation should be completed.

Fuel Preparation and Radiation Experience – Solid Fuels

J. SCHUMAR
Argonne National Laboratory, Lemont, Illinois

The following general comments can be made regarding solid thorium and thorium-uranium fuels. Thorium binary alloy systems have been thoroughly investigated and the data ably compiled at Battelle. The systems Th-C, Th-Bi, Th-Pb, Th-Zr, and Th-Mg have recently been revised. Th-Ce, Th-Pu, and Th-U have recently been determined. Further work on water corrosion resistant alloys should be continued with Th-Zr holding some promise. The metallurgical and physical properties of thorium have been carefully studied and reported. Effects of small amounts of impurities and effects of oxygen, nitrogen, and carbon on properties have been well observed. Pure thorium has been irradiated to 1.5% burn-up of metal atoms with little change. Pure thorium has been successfully clad with aluminum and zirconium by extrusion, roll cladding, etc. Zirconium cladding of pure thorium is much more favorable than cladding with aluminum. Zirconium and thorium are more compatible and form an alloy system with better properties. Al-Th alloys form brittle intermetallic compounds.

Alloys of uranium and thorium have been and are under investigation. Alloys of up to 5.5% U^{235} in thorium have been irradiated up to 4% burn-up of total atoms with excellent results. These have been irradiated in the MTR in the temperature range 50° to 200°C. Alloys of uranium and thorium up to 28% U are being prepared for irradiation to several percent burn-up at temperatures up to 800°C or higher. Th alloys containing 10% U^{235} have been irradiated by A.I. to 0.35% burn-up of total atoms up to 1250°F with volume increases of the order of 5% (calculated). Although the diameter of a ⅜-in. pin increased 0.003 to 0.005 in., these uranium-thorium materials remained relatively ductile after irradiation and appeared to be far superior to any uranium alloys previously tested.

Powder metallurgy of thorium and uranium-thorium alloys has also been investigated. Powders of thorium have been produced by the hydraulic process and by the calcium reduction of ThO_2.

Cold pressing of thorium powder to densities 95% of theoretical can be performed at pressures of 75 tons/in.^{2}. Sintering of powders in the 1200° to 1600°C range was studied. Generally speaking, higher densities were obtained with higher sintering temperatures. Hot pressing was also studied and, by control of the type of powder used, pressure, and temperature, densities of 11.5 g/cc were obtained. Aluminum canning of thorium by hot pressing has been successfully accomplished.

ThO_2 and ThO_2-UO_2 bodies have been studied with compositions of UO_2 in ThO_2 as high as 75%. ThO_2-UO_2 with UO_2 up to 30 wt % has been fired in air. Conventional methods of pressing powders and sintering were used. Irradiation studies at temperatures up to the melting point and 0.42 atom % burn-up have been made on 10% UO_2 ThO_2 bodies. Some 6.36 wt % UO_2 ThO_2 bodies have been irradiated to 1% burn-up at MTR temperatures with good results. Dimensional changes due to irradiation have surpassed the best metallic fuel.

Babcock & Wilcox is planning to use UO_2-ThO_2 bodies in the Consolidated Edison project. The objective is to obtain high density and close tolerances without grinding by using commercially available powders. High temperature loop tests in the MTR to study stainless clad UO_2-ThO_2 fuel elements are being initiated.

ThO_2-UO_2 bodies reinforced with Nb, Mo, and Zr metal fibers show thermal shock resistance and thermal conductivity properties far superior to those of pure ThO_2.

Methods of fabricating ThO_2 bodies have been thoroughly studied at Oak Ridge. Slip casting techniques were the least successful. Studies on calcining ThO_2 at various temperatures for use in the Homogeneous Reactor indicated that ThO_2 calcined at 1800°C results in the best slurries.

Several conclusions resulting from the session can be made:

1) No work has been done on incorporating U^{233} into fuel. Facilities are lacking.
2) It is not necessary to have a U^{233} facility to study uranium-thorium bearing materials.
3) No work is under way on U-Th-graphite bodies as possible fuel material.

Fuel Preparation and Radiation Experience – Fluid Fuels

R.N. Lyon
Oak Ridge National Laboratory, Oak Ridge, Tennessee

Fluid fuels may be of three forms: solutions, slurries, and fluidized beds. Fluidized beds have not been thoroughly investigated, although minor studies have been carried out at Brookhaven, ORNL, and other installations.

Fluid fuels consist of two components, the fuel element or compound and the fluid vehicle. In water or D_2O and in liquid Bi or Pb-Bi a slurry is required to provide sufficient Th concentration for reasonable conversion. In fused fluoride mixtures, however, a true solution can be used.

The present large-scale ThO_2 production method at ORNL consists of calcination of thorium oxalate in an oxidizing atmosphere. The method by which the oxalate is formed has a direct influence on the form of the oxide after calcination, since the oxide resulting from calcination retains, in relic form, the shape of the original oxalate crystal. Crystallites of oxide form within the relic oxalate structure, and the degree to which they approach the original oxalate crystal in size depends on the temperature at which the calcination occurs. Thus, if oxalate particles of a particular uniform size are produced, the resulting oxide particles will shrink, but will be comparably uniform in size.

Since the optimum size of thorium oxide particles appears to lie between one so small that the surface forces strongly influence the mechanical behavior of the slurry and one so large that abrasion becomes prohibitive, it is essential that the particle size of the oxalate be controlled with unusual care.

Small-scale precipitation of the oxalate by the addition of 1 *M* oxalic acid to 1 *M* $Th(NO_3)_4$ with agitation at 10°C produces oxalate in the desired 1 to 2-μ range.

Further refinement of the oxalate size is produced by digestion for several hours before filtration. This permits the finer crystals to grow until the resulting size distribution is more uniform than could be obtained with the original precipitate by common mechanical methods of size separation.

Jet precipitation for producing oxalate was at first believed to offer an important method for large-scale production, but it has been found to produce a mixture of small and large size fractions which on calcination results in serious sintering and clinker formation.

A new precipitation method is now being developed which involves the gradual introduction of oxalic acid to a recirculating solution of $Th(NO_3)_4$. It is believed that following the initial strike to produce seed crystals of thorium oxalate, recirculation of the seed crystals through the precipitation region will cause them to grow uniformly to the desired size. Following the digestion period, calcination is carried out first in an electric furnace to about 650°C. The material is then transferred to a gas-fired furnace where it is subjected to 1600°C for 4 hr. The final high temperature produces ThO_2 crystallites within the relic oxalate structure which approach the relic structure in size, and the resulting particles are much less susceptible to degradation than particles calcined at lower temperatures.

The Houdry Company is developing a method of making small spherical oxide particles. A $Th(OH)_4$ sol is made and then converted to a gel. The gel is spray-dried, and the resulting spheres when calcined form dense solid oxide spheres. ThO_2 spheres of less than 5 μ have been produced by this technique, currently being studied in slurries at Oak Ridge.

Larger spheres are also being studied to determine their possible use in fluidized beds.

Although direct flame firing of $Th(NO_3)_4$ would appear to be the most straightforward method of obtaining ThO_2, the method has yet to produce particles of the integrity and uniformity of particle size obtained from the oxalate.

Thorium formate is an alternative intermediate for the production of the oxide. In producing the formate a temperature of about 90°C must be maintained, and difficulty is caused by the fact that the reaction is exothermic, which tends to cause boiling off of the formic acid. Formic acid must be added to decompose the nitric acid as well as to combine with the thorium. The precipitate is more easily filtered and washed than the 10°C precipitated oxalate discussed above. In excess formic acid it dissolves, and when in solution it decomposes to form finely divided $Th(OH)_4$ in the presence of platinum or platinum salts.

During Session V it was concluded that at present the oxalate method gives the greatest promise for particle size control, and that direct flame firing of the nitrate and the Houdry sphere production offer important alternatives.

Molybdenum trioxide has been found to be a very effective catalyst for recombination of both H_2-O_2 mixtures and D_2-O_2 mixtures formed by the radiolytic decomposition of slurries. A high temperature, high pressure hydrogen treatment after deposition of the molybdenum oxide on the ThO_2 greatly improves the recombining ability of the catalyst.

In the absence of molybdenum or other added catalysts, the *G* value for ThO_2 slurries has been found at ORNL to be 0.5 molecules H_2 per 100 ev. All fission products with the possible exception of Cs have been found to be adsorbed essentially quantitatively on the solid phase where they are not appreciably removed by HNO_3 digestion. It has been found at Westinghouse, however, that pretreatment of the solid with minor amounts of aluminum oxide gives almost quantitative removal of fission products with nitric acid, and at ORNL that treatment with lead oxide after fission makes the fission products available for removal by nitric acid.

In irradiation studies for periods up to 2500 hr at expected blanket fluxes, fission has not been found to produce detectable changes in the slurry properties. Uranium can either be adsorbed in ThO_2 or coprecipitated with the Th as tetravalent uranium oxide. The latter is presumed to permit formation of ThO_2 containing uranium within the crystal lattice.

Liquid metal slurries studied at Brookhaven involve either bismuth or lead-bismuth eutectic as the vehicle. They include either particles of intermetallic compounds or ionic or nonmetallic compounds. Of the latter, ThO_2 is the most obvious candidate, but ThO_2 is not wet by bismuth or lead-bismuth alloys. It is believed that wetting of ThO_2 can be achieved by the addition to the melt of small amounts of Th, Ca, or Mg, but little work has yet been done on ThO_2 liquid metal slurries, since most of the effort at Brookhaven has been directed toward slurries of intermetallic compounds. Intermetallic compounds available are Th_3Bi_4, $ThBi_2$, and $ThPb_3$, of which $ThBi_2$ appears to be the most suitable from the standpoint of flow properties and thermal neutron utilization.

Preparation of $ThBi_2$ slurries can be carried out in several ways. Perhaps the simplest method is to add the powder to molten Bi at 500°C. The Bi_2 forms rapidly by an exfoliation from the Th particle surface. Chips of Th can be used in place of the powder, but rapid exfoliation appears to occur only at points on the surface which have small radii of curvature, and as a result formation of $ThBi_2$ from chips is much slower than with powder. An interesting phenomenon is the evolution of a gas, as yet unidentified, during the Th-Bi formation. Continued soaking of the $ThBi_2$ particles results in a growth to about 50-μ particles which have good slurry properties.

Electrodeposition of thorium from a molten salt mixture into a liquid bismuth electrode will also produce $ThBi_2$ particles. Careful control of conditions is not required, but it is necessary to stir the system to force the thorium beneath the Bi surface. Unfortunately, the stirring also forces molten salt into the liquid metal and as a result slurries made by this method are not satisfactory, since the salt makes the slurry unsuitable and its removal is extremely difficult.

Quenching of the melt produces $ThBi_2$ flakes which form a highly viscous slurry, but continued heating causes thickening of the flakes and ultimately leads to a satisfactory slurry. Temperature cycling appears to hasten the improvement of the slurry.

If the melt, instead of being quenched, is allowed to cool slowly while subjected to high frequency sound, a satisfactory slurry is also obtained. To date the ultrasonic method has been applied only on a small scale.

Continued thermal cycling causes continued particle growth to about 100 to 200 μ, but tellu-

rium is found to inhibit growth up to about 800°C.

Pa formed by neutron absorption in the thorium is largely retained by the solid, but 20 to 25% of the U is found in the liquid. Higher temperatures increase the proportion of U in the liquid.

In general, caking and plugging does not occur on smooth metal walls. However, walls which have become roughened appear to offer a purchase for the particles, and a cake develops from that point. Complete plugging of pipes with roughened walls has been experienced on several occasions.

In the production of a satisfactory fused fluoride mix, particular attention is paid to removal of oxygen and oxygen containing compounds. Although most oxides are reasonably soluble in molten fluorides, it is possible to precipitate UO_2, ThO_2, and possibly fission product oxides if oxygen is available. The purification of the crude melt is carried out by alternately bubbling HF and H_2 through the mixture.

Containment materials for handling fused fluorides are usually nickel base alloys. The ARE was constructed of Inconel, but more recently it has been found that an alloy containing 15 Mo and only 7 Cr was superior. Although pure nickel is very resistant to fused salts in isothermal systems, it tends to migrate from the hot zone to the cold zone in a nonisothermal circulating system.

If unalloyed nickel is available at the heated portion, the fugacity of the nickel in the melt is high enough to permit formation of nickel crystals in the cooler sections. Alloying the nickel reduces its fugacity in the melt, and it is removed at the cold end only by alloying with the metal at that point.

The other constituents of the alloy behave similarly, with the result that the inner surface of the tube at each point reaches a particular composition corresponding to the temperature at that point.

Further mass transfer is then sharply limited by the low diffusion rates of the alloy constituents in the metal wall. The alloy currently being used consists of nickel with 15 Mo and 7 Cr. This alloy is stronger than Inconel and contains less Cr. Chromium has about 8 times the solubility of nickel. Iron incidentally has about twice the solubility of chromium.

$$Cr + 2UF_4 \rightleftarrows CrF_2 + 2UF_3 .$$

Irradiation studies, including examination of the ARE after operation, have shown no evidence of damage to the salt and no evidence of radiation-accelerated corrosion. It should be pointed out, however, that no experiments have been made to high burn-up.

Xe and other gases appear to follow Henry's law, but the noble gases have increasing solubility with increasing temperature. It is believed that Xe and other fission product gases will not form bubbles within the mix under expected conditions, while the solubility is low enough to permit adequate stripping of the Xe.

Rare earth solubilities are probably adequate.

While all the possibilities for fluid fuels are not being actively pursued, it appears that impressive strides are being made along the lines of greatest promise.

Chemical Reprocessing

F.R. Bruce
Oak Ridge National Laboratory, Oak Ridge, Tennessee

INTRODUCTION

When discussing the chemical reprocessing methods employed for reactors using the thorium-U^{233} cycle, it is convenient to divide the reactors into four categories: nonaqueous fluid fuel reactors, aqueous fluid fuel reactors, thorium-uranium alloy fuel reactors, and ThO_2-UO_2 fuel reactors. In general, reprocessing development of fluid fuel reactors is conducted as an integral part of the reactor system development, and is centered at the site responsible for the reactor. Studies applicable to the reprocessing of thorium-uranium alloy fuel reactors are being carried out at many sites, with pyrometallurgical studies being centered at North American Aviation. Investigations of ThO_2-UO_2 reprocessing methods are being conducted at many sites, but the Oak Ridge National Laboratory has the primary responsibility.

NONAQUEOUS FLUID FUEL REACTORS

Liquid Metal Fuel Reactor

The reprocessing of this reactor has been studied at Brookhaven National Laboratory. Molten salt extraction is favored for removal of fission and corrosion product poisons from the Liquid Metal Fuel Reactor (LMFR). The poisons are divided into three categories according to their behavior in the processing cycle: gaseous fission products, molten-salt-extractable fission products, and non-extractable fission products.

In-pile loop studies have shown that iodine, xenon, and bromine were expelled from the uranium-bismuth fuel.

Salt-extractable fission products are removed from the fuel by countercurrent salt extraction with the sodium chloride – potassium chloride – magnesium chloride eutectic. Removal of fission products, primarily of groups IA, IIA, IIIA, and the rare earths, proceeds by formation of molten-salt-extractable chlorides and is enhanced by the addition af small amounts of bismuth chloride to the eutectic. The chemistry of the process has been verified by in-pile loop experiments.

Non-salt-extractable fission product removal is being investigated by American Smelting and Refining under subcontract to Brookhaven National Laboratory. The preferred method involves their removal from the bismuth-uranium alloy by molten zinc extraction. Zirconium requires special treatment and is removed from the fuel solution by formation of zirconium carbide at 900° to 1000°C.

Blanket processing of the LMFR, being studied at BNL, has not received as much attention as core processing; however, the same principles should apply equally well.

Some of the problems associated with LMFR processing are as follows. It has been observed that I^{135} reacts with the alkali and alkaline earth fission product metals to form low solubility iodides which are expelled from the fuel and absorb on nonwetted reactor surfaces. Xe^{135} has also been observed to collect on core surfaces, particularly graphite. The full significance and methods of alleviating these phenomena remain to be determined. Continuous extraction of the bismuth-uranium alloy – molten chloride system remains to be demonstrated, and the engineering feasibility of the entire process verified.

Molten Salt Reactor

There are two possibilities for reprocessing the LiF-BeF-UF_4-ThF_4 core and blanket fluids of the molten salt reactor. The first is fluoride volatilization of the uranium as uranium hexafluoride. Uranium is converted to the volatile hexafluoride by passing fluorine gas through the molten salt, and is subsequently purified by an absorption-desorption cycle employing sodium fluoride as a solid phase. Alternatively, uranium hexafluoride may be purified by fractional distillation. A pilot plant which

uses the volatilization and sodium fluoride absorption principle is in operation at ORNL, and has recovered about 20 kg uranium from NaF-Zr-UF_4 spent fuel from the Aircraft Reactor Experiment. The disadvantage of this process is that fission product and corrosion product poisons remain with the fuel carrier, which is constituted from Li^7, and the value of this material which would be sent to waste annually from a 650-Mw reactor would be 2.5 million dollars. Therefore, methods are being investigated for removing poisons from the fuel without otherwise substantially changing it.

Partial freezing of the fuel results in concentration of the rare earths, which are the main poisons, by a factor of 2 to 4 in the liquid. In another approach, addition of calcium oxide to the molten fuel results in separation of the rare earths as the insoluble oxides. The corrosion products – iron, nickel, chromium, and molybdenum – may be removed from the fuel by hydrogen reduction to the metallic state.

Molten salt reactor processing by removal of the uranium as uranium hexafluoride is not an economically optimum method, and the major reprocessing problem is further development of the alternative schemes for fission and corrosion product removal, which have only recently been undertaken.

AQUEOUS HOMOGENEOUS REACTOR PROCESSING

Thermal Breeder Reactor

The aqueous Thermal Breeder Reactor employs a solution of uranyl sulfate in heavy water as fuel in a central core, and a blanket slurry of thorium oxide in heavy water. In the core solution all the important fission product and corrosion product poisons, except cesium and niobium, are insoluble under reactor operating conditions. The insolubles are removed from the core by passage of the solution through a hydroclone which concentrates the solids in an underflow receiver. In the case of a 500-Mw reactor, 10,000 l/day of fuel would be fed to the hydroclone, and the insolubles concentrated in about 100 l. This solution, also containing uranium and soluble fission and corrosion products, would be combined with an equal volume of ThO_2 slurry from the blanket and sent to an evaporator for D_2O recovery. The solids would then be dissolved in HNO_3-HF and processed by Thorex solvent extraction. The U^{233} product would be converted to the sulfate and returned as fuel to the core of the reactor. The thorium product would be converted to ThO_2 and returned to the blanket. The core processing method will soon be demonstrated in the chemical plant associated with the HRT.

The major problem associated with homogeneous reactor chemical processing is the development of a thorium oxide processing method more economical than Thorex. In preliminary studies it has been found that 3 *M* nitric acid containing hydrogen peroxide may be used to remove uranium without significantly altering the thorium oxide. Similarly, addition of lead oxide to the slurry blanket makes it possible to remove much of the uranium, fission products, and corrosion products by dissolution of the lead oxide after irradiation without changing the thorium oxide. In addition, sodium carbonate fusion of the thorium oxide makes it possible to remove 60% of the uranium by water leaching.

Pennsylvania Advanced Reactor

The reprocessing of the Pennsylvania Advanced Reactor which employs a slurry fuel of ThO_2-UO_2 is essentially the same as that of the TBR blanket. A modified Thorex process eliminating thorium and uranium partitioning may be used, or new methods which permit removal of corrosion products and fission products without altering the slurry would be applicable.

THORIUM-URANIUM ALLOY FUEL

Fuels which employ thorium and uranium in the metallic state are amenable to low decontamination processing by pyrometallurgical methods, or they may be processed by Thorex. Pyrometallurgical processes should involve low capital costs and have high capacity and small waste volumes. They will, however, require remote fabrication of the fuel elements, since the recovered products are only partially separated from fission products. This may not be a serious disadvantage, since thorium and uranium are inherently radioactive from U^{232} decay and may require remote handling. Three types of volatility processes are under development: direct volatilization, salt bed processing, and fused salt electrolysis.

The direct volatilization process separates the thorium and uranium from iodine, xenon, krypton, cesium, and some of the rare earths, but leaves the fuel contaminated with zirconium, molybdenum, and ruthenium. This method is relatively simple but gives low decontamination.

In the salt bed process the molten thorium-uranium alloy is contacted with the salt which extracts the fission and corrosion product impurities. Iodine, xenon, krypton, strontium, cesium, and rare earths are removed. It is moderately effective for fission product removal, but suffers from the fact that some thorium is lost to the salt phase.

The fused salt electrolysis processing method removes essentially all the fission product contaminants except zirconium. While it provides the highest decontamination of the three pyrometallurgical processing methods, it is relatively complicated because of the several steps required.

Pyrometallurgical processing is of particular interest for thorium-uranium processing since it may be more economical than solvent extraction, and the recovered products from any processing method will require remote refabrication because of the activity resulting from the U^{232} decay chain. The major problem in the case of pyrometallurgical processing is demonstration of the techniques on an engineering scale with acceptably low product losses in all the waste streams. Successful exploitation of pyrometallurgical processing techniques also requires solution of a companion problem: development of methods for remote fabrication of fuel elements.

ThO_2-UO_2 FUEL REPROCESSING

Only aqueous processing via the Thorex route has been seriously considered for the fuels employing thorium oxide – uranium oxide mixtures. However, the radioactivity inherent in the thorium-uranium cycle makes it impossible to realize the major advantage of high decontamination obtained in the Thorex process, and it would be desirable to develop for this class of fuels new inexpensive reprocessing methods equivalent to pyrometallurgical processing.

Clad Removal

Stainless steel and zircaloy cladding may be used for thoria-urania fuels. Two methods of exposing core material for dissolution exist. The fuel may be chopped to make the core accessible for dissolution, or the clad may be removed chemically. In the case of stainless steel jackets the clad would be removed by dissolution in 4 *M* sulfuric acid, while zirconium cladding would be removed by ammonium fluoride dissolution. The feasibility of chopping and leaching techniques on an engineering scale remains to be demonstrated, while the losses of thorium and uranium during the chemical dejacketing steps are uncertain.

Core Material Dissolution

Thorium oxide – uranium oxide core material is readily dissolved in boiling 13 *M* nitric acid containing 0.04 *M* sodium fluoride catalyst. Dissolving studies with simulated Consolidated Edison core material, 96% ThO_2 – 4% UO_2, calcined at 1700°C, showed that 98% dissolution occurred in 5.3 hr. The dissolvent used for ThO_2-UO_2 is identical with that used in the Thorex process, and the resulting solution is suitable for introduction to the feed adjustment step of the Thorex process.

THOREX PROCESSING

The Thorex process has been developed at Oak Ridge National Laboratory, Savannah River, and Knolls Atomic Power Laboratory. A 200-kg/day pilot plant has been in operation for three years at ORNL. The flow sheet now employed consists of thorium dissolution and feed adjustment prior to solvent extraction. Thorium and uranium are coextracted into tributyl phosphate, while fission products and protactinium remain in the aqueous phase. The products are then stripped from the solvent with water and sent to a second solvent extraction cycle. In the second cycle thorium and uranium are again extracted into tributyl phosphate in the first step; next thorium is preferentially stripped with dilute acid in a second tower; and finally the uranium is stripped with water in a third tower. The uranium goes to a third cycle for final separation from fission products. The Thorex flow sheets developed at Savannah River and KAPL differ from this in that they would employ a head-end MnO_2 precipitation to achieve additional separation of the products from protactinium, ruthenium, and zirconium-niobium. It is thought that MnO_2 head-end scavenging offers more advantages in the Thorex process than in

the Purex process. Mixer-settlers would be used as a contacting device rather than pulse columns. In recent work at Savannah River, the very promising possibility of substituting di-*n*-amyl-*n*-amyl phosphonate for TBP has been investigated. In laboratory studies this solvent gave 10-fold greater equilibrium separation of thorium from zirconium than did tributyl phosphate.

The Thorex process with two cycles of solvent extraction for both thorium and uranium yielded products which met specifications. In these runs the gross gamma decontamination factors were 4×10^4 and 5×10^7 for thorium and uranium, respectively. While the uranium product met specifications for direct handling, the thorium product exceeded the specifications by a factor of 200, with the major contaminant in both products being ruthenium.

Thorium and uranium losses were 1.59% and 0.26%, respectively. During the short-cooled processing runs, many operational problems were encountered. Normal plant operation required access to many areas which became excessively radioactive during the short-cooled processing. For example, a solvent extraction column pump interface element which required only light shielding during the long-cooled runs read 200,000 r/hr during the short-cooled processing runs. In addition, the cell and vessel off-gas systems proved inadequate for handling the extremely high levels of irradiation attendant to the short-cooled processing. None of these difficulties indicates lack of Thorex flow sheet capability for short-cooled processing, but they show that the Thorex pilot plant in its present form is not satisfactory for handling extremely high activity levels. Modifications to the plant are now being made to permit handling these levels of irradiation.

Major problems remaining in the Thorex program are increasing the separation of thorium and ruthenium obtainable in the process and decreasing thorium losses. By processing extremely short-cooled thorium, the thorium product would be essentially free of the U^{232} decay chain, and the flow sheet should be demonstrated with thorium cooled significantly less than 30 days.

SEPARATION OF U^{233} FROM U^{232} DECAY CHAIN

In laboratory studies it has been demonstrated that the third uranium cycle separates uranium from thorium by a factor of 10^3, therefore the product immediately after processing should be free of U^{232} decay chain activity. However, after standing, the activity in the uranium builds up, and it may be necessary to remove it before direct handling.

At Los Alamos shielded glove box equipment has been set up to accomplish this purification. The Thorex product is evaporated to dryness and taken into solution with 0.05 *M* nitric acid, and Th^{228} is removed by passing the solution containing 250 g U^{233} through a cation exchange bed containing 200 ml AG-50 (Analytical Grade Dowex-50) cation exchange resin. In a typical run the activity level of a batch was reduced from 2 r/hr to 30 mr/hr. Preliminary observations on the behavior of the U^{232} decay chain during metal reduction suggest that all the members except Th^{228} are volatilized. On melting uranium in a calcium oxide lined crucible, good decontamination from the decay chain was obtained.

Experiments at ORNL have shown that a chloride anion exchange step yields 50- to 75-fold decontamination of the U^{233} from thorium and radium, while a thorium fluoride scavenging precipitation yields 3- to 4-fold separation.

CONVERSION OF URANYL NITRATE TO METAL

The uranyl nitrate Thorex product is purified by one or more precipitations of uranium peroxide from a solution which contains citrate and malonic acid to complex iron, and Versene to complex thorium. The uranium peroxide is decomposed to UO_3, and this is converted to U_3O_8 by calcination at 900°C. The U_3O_8 is reduced with hydrogen to UO_2, and this is hydrofluorinated with greater than 98.5% yield to UF_4. The uranium tetrafluoride is reduced by calcium, with an iodine booster, to uranium metal in an iron pot having a calcium oxide or magnesium oxide liner.

SUMMARY

Many satisfactory methods for reprocessing thorium bearing fuels exist or are being developed. An important future problem will be the development of remote refabrication methods.

Fuel Recycle and Handling

E.D. Arnold
Oak Ridge National Laboratory, Oak Ridge, Tennessee

The problems associated with recycle and handling of thorium and U^{233} can be divided into several categories: reactor irradiation, activity of recovered irradiated thorium and U^{233}, handling of thorium and U^{233} after processing, and allowable or workable specifications for recovered products. Separate papers on each of the above categories were given. The major problems in handling these materials are due to the external gamma hazard from U^{232}-Th^{228} daughters or the internal hazard due to alpha contamination of air. The problem of spontaneous fission or α-n reactions, although present, appears secondary to the others.

REACTOR IRRADIATION

The formation of U^{232} in the thorium-U^{233} system can be shown by the following scheme:

$$Th^{232} \xrightarrow{n,2n} Th^{231} \xrightarrow{\beta} Pa^{231} \xrightarrow{n,\gamma} Pa^{232} \xrightarrow{\beta} U^{232} .$$

Thus the formation rate of U^{233} will be proportional to the cross section of Th^{232} for the $n,2n$ reaction. The value of this cross section depends upon how much fuel a thorium element "sees," since only neutrons in excess of 6.37 Mev can cause $n,2n$ reactions. The apparent pile cross section is thus a function of the fast/thermal flux ratio for any given reactor.

If we wish to achieve a low value for $\sigma(n,2n)$, we must "separate" the fast and thermal flux. However, to do so we pay the price of lower production rates for U^{233} and low power operation. High U^{232} content is associated with high U^{233} production.

ACTIVITY OF IRRADIATED THORIUM AND U^{233}

The radiation intensities in recycled thorium are high enough to alter the handling procedures during recycle. The major sources for the high gamma activity are Bi^{212} and Tl^{208} – decay daughters of Th^{228}. Th^{228} is a natural decay product of Th^{232} and therefore it, as well as the decay daughters, is found in nature. However, additional Th^{228} is produced by the decay of U^{232} – an isotope produced through the $n,2n$ reaction on Th^{232}. This build-up scheme, as well as the decay scheme indicating the characteristics of the decay daughters, is shown in Figure 1.

The gamma intensity at the surface of a kilogram sphere of thorium can be given by

$$I = 0.5 \text{ rad/hr/ppm } Th^{228} .$$

The radiation intensities in U^{233} are much higher than those in any other fuel handled to date. These intensities are also due to the gamma-rays of Bi^{212} and Tl^{208} – decay daughters of U^{232} which will follow U^{233} after processing (see Figure 1).

The radiation intensity at the surface of a kilogram sphere of U^{233} can be given by

$$I = (0.04 + 0.01T) \text{ rad/hr/ppm } U^{232}$$

where T = days since final separation.

The other activity problems in U^{233} and Th^{232} are due to α,α-n reactions, and spontaneous fission in the case of U^{233} and α for Th^{232}.

PRESENT HANDLING TECHNIQUES FOR THORIUM

To date no recycled thorium has been handled beyond chemical reprocessing. However, large quantities of natural thorium have been handled at the Fernald site. There the external hazard was below tolerance, but air contamination was a major problem. The average radiation exposure during all phases of conversion and fabrication was 18% of tolerance (based on 300 mr/40-hr wk), i.e., 54 mr/wk. With the new standards for

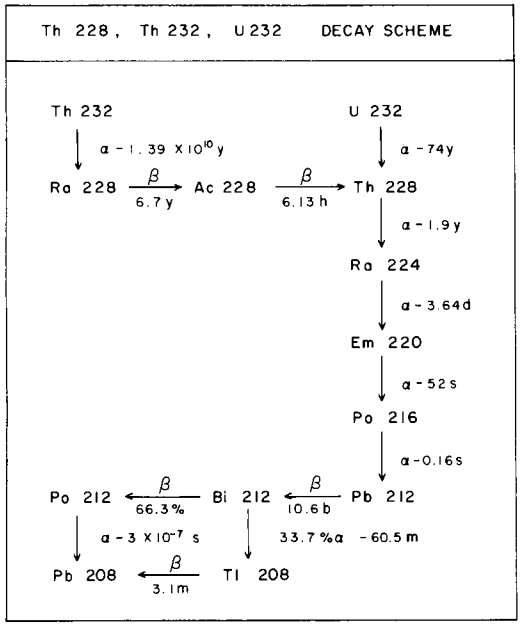

Figure 1.

radiation protection, thorium having a gamma activity in excess of twice that of natural thorium could not be handled by the same techniques.

On the other hand, the air contamination appeared to be a major problem. In many cases during peak operation the air contamination was above tolerance. The worst areas for air contamination were the wet processing area, the blending and charging area, and the arc-melter. In order to lower the air contamination levels, it may be necessary to place the major operations in separate buildings and improve the air ventilation system.

PRESENT HANDLING TECHNIQUES FOR U^{233}

The experience in handling U^{233} at Los Alamos has indicated that dry box techniques must be used for all steps between uranyl nitrate and finished U^{233} metal.

Experience with the chemical processing line has indicated an average exposure of $\approx$ 5 rem/man after working 32 kg. The U^{233} had been aged at least six weeks prior to working and had not been cleaned of Th^{228} by ion exchange.

There will be some additional radiation exposure due to the α-n reaction on fluorine in the UF_4 product following hydrofluorination, but this radiation level is minor compared to the gamma level.

In the metal area, exposures of 0.7 rem/man-wk average have been acquired. If ion exchange cleanup is used prior to chemical conversion, it should be possible to triple the throughput for the same personnel exposure.

In all previous cases Los Alamos has been handling U^{233} containing an average of 20 ppm U^{232}. Future or power reactor U^{233} fuels may contain 100 to 150 ppm U^{232}, and then it will be necessary to use increased shielding for dry boxes, shorter time schedules, and more rotation of personnel from other areas.

The time schedule for the manufacture of MTR fuel elements using U^{233} must be 14 days if the U^{232} content is 30 to 40 ppm and complete cleanup by ion exchange prior to metal reduction is assumed. If fuels containing higher U^{232} contents are processed, then it will be necessary to shorten the time schedules accordingly or go to remote or semiremote fabrication.

SPECIFICATIONS FOR THORIUM AND U^{233}

The Thorex process is capable of high decontamination factors from fission products and protactinium such that the FP+Pa gamma activity is less than 17% of the total gamma activity for recycled thorium and less than 30% of the total gamma activity in recovered U^{233} aged 30 days. Specifications are written for infinitely recycled thorium so that thorium having an activity 1.4 times that of natural thorium can be handled directly, and thorium having an activity 5.0 times that of natural thorium can be handled semiremotely with only distance shielding. Semiremote fabrication will allow irradiation levels to 5000 g/t and infinite recycle. For all cases of recycle the Th^{228} chain activity is increased by a factor of 3 over that for one cycle. If higher g/t levels are economically necessary, then additional light shielding will be required. If very high g/t levels (15,000 to 30,000 g/t) are required, then it may be necessary to refabricate thorium elements remotely.

Another alternative which may be used is to fabricate fresh fuel elements each cycle and hold back the recycled thorium for a period of 7 years between each cycle. [At 15,000 g/t and 6 mb $\sigma(n,2n)$, 7 years will reduce the total Th^{228} activity

to less than twice that for natural thorium.] This is a costly item in terms of additional inventory, but the additional cost of inventory may be less than the additional cost for remote fabrication over direct fabrication.

Air-tight enclosures will be necessary for thorium refabrication because the air contamination limit must be less than 10 $\mu g/m^3$. However, thorium oxide pellets are at present being manufactured and canned by equipment operated in air-tight enclosures.

CONCLUSIONS AND RECYCLE SUMMARY

The conclusions of this session can be summarized as follows:

1) The $n,2n$ cross section for power reactor fuel elements will probably be several mb, since optimum irradiation and heat transfer properties are necessary for economic reactor operation.

2) If aqueous processes are used, then short decay (20 to 30 days) and early shipping of reactor fuel are necessary.

3) Aqueous processing can limit fission product levels to a minor fraction of the total activity in both U^{233} and thorium. If fission product levels are low, then decontamination of a remote or semiremote facility is easy and direct maintenance of equipment is achievable.

4) Some conversion steps for thorium can be accomplished directly, while others will require dry box facilities. U^{233} conversion will require dry box facilities.

5) Refabrication of U^{233} must be done in dry box facilities, at least until the U^{233} is contained and is no longer an alpha hazard. Refabrication of thorium will require air-tight enclosures or better ventilation equipment.

6) A judicious selection of schedules, personnel rotation, and containment will be necessary for both thorium and U^{233} handling. Thorium may be a bigger problem than U^{233} since it is the bulk constituent.

7) In the case of thorium, several avenues are open for its recycle: a) aqueous processing plus semiremote enclosed fabrication with direct maintenance of fabrication equipment, b) use of fluid fuel reactors, c) aqueous processing plus 7-yr hold-up of thorium between cycles and direct fabrication of natural thorium each cycle, and d) pyroprocessing plus remote fabrication and remote maintenance of fabrication equipment.

8) Recycle data for thorium and U^{233} are available but have not been correlated or collected into one report.

9) Further study of remote or semiremote handling techniques is justified. This study will be necessary before any final selection of the best combination of steps for the recycle of thorium and U^{233} can be made. A study of the use of oxide vs metal fuel elements should be made. Such a study should include both the use in nuclear reactors and the requirements for recycle and refabrication.