LEGAL NOTICE

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

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

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

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

**IONIUM (THORIUM-230) FOR RADIOISOTOPE PREPARATION
(STATUS REPORT)**

by

E. A. Coppinger and C. A. Rohrmann

December 15, 1959

This document is
PUBLICLY RELEASABLE
Hugh Kinsner *H. Kinsner*
Authorizing Official
Date 10/4/06

PROGRAMMING OPERATION
HANFORD LABORATORIES OPERATION

LEGAL NOTICE

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

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

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

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

NOTICE

This report was prepared for use within General Electric Company in the course of work under Atomic Energy Commission Contract AT (45-1) -1350, and any views or opinions expressed in the report are those of the author only. This report is subject to revision upon collection of additional data.

DISCLAIMER

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

DISCLAIMER

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

TABLE OF CONTENTS

	<u>Page No.</u>
INTRODUCTION	4
OBJECTIVES	4
CONCLUSIONS	5
RECOMMENDATIONS	5
DISCUSSION	5
Fission Products	6
Reactor By-Products	7
Irradiation of Special Materials for Isotope Production	8
Less Conventional Isotope Production Schemes	8
"Value" of Thorium-228	14
Work Done by Others	15
Other Uses	16
Ionium (Thorium-230) Occurrence	17
The Uranium Industry and Processes in the United States	19
Ores and Ionium "Enrichment"	19
Processes	20
Favorable Processes	22
Processes Which are Less Attractive for Th-230 Recovery	23
Unknown Processes	24
Status and Results of Uranium Ore Mill Samples	25
Thorium-230 Irradiation to Produce U-232	26
Nuclide Buildup	27
Uranium-232 Production Program	31
Proposed Research and Development Program	34
Utilization of the "St. Louis" Residues	36

100 63. 9

-4-

IONIUM (THORIUM-230) FOR RADIOISOTOPE PREPARATION

INTRODUCTION

For many years effort has been directed toward the development of means for the practical utilization of the heat evolved from the radioactive decay of certain fission and irradiation products. Fission products, in view of their availability in the plentiful, high-level wastes resulting from the processing of irradiated, nuclear reactor fuels have been most intensively studied for applications where their heat of decay might be converted into useful energy such as electricity for the operation of certain devices in place of chemical batteries.⁽¹⁾ In addition other materials having desired radioactive properties may be produced by neutron bombardment of readily available elements.⁽²⁾

A general review of a chart of the nuclides discloses a large number of candidate radioactive isotopes. However, when certain requirements such as half-life, type and energy of radiation, availability of target material and feasibility of the nuclear manufacturing process are taken into consideration the choice of elements rapidly shrinks to a relatively small number. However, in this small number of candidate materials there are some which have outstanding characteristics and yet have received less attention than others. Uranium-232 and its daughter thorium-228 are examples.

This report reviews the general prospects of several radioisotopes, points out the special properties of U-232 and Th-228, discusses the target material, ionium (thorium-230) and protactinium from the standpoints of availability and chemical separations processes required for the preparation of U-232 and Th-228.

OBJECTIVES

By study of analytical data and process technology the objectives of this effort are:

- (1) To review the properties of various radioisotopes for comparison with uranium-232 and thorium-228 and to propose uses for these latter two.
- (2) To evaluate in a preliminary way the possibility of routine recovery of thorium which is rich in thorium-230 from uranium milling process waste streams.
- (3) To outline a potential scheme for irradiation of thorium-230-thorium-232 mixtures for protactinium-231 and eventually uranium-232 production from which thorium-228 would be recovered.

(1) "Radioisotope Power Sources for Space Vehicles" by R. S. Rochlin, General Electric Company, General Engineering Laboratory Report No. 58GL243, dated August 14, 1958.

(2) "Radioisotopes as Power Sources - A Preliminary Investigation" by J. P. Neissel, V. V. Verbinski, H. D. Briggs, General Electric Company, General Engineering Laboratory Report No. 59GL13 dated January 20, 1959.

- (4) To outline a proposed research and development program for early recovery of sufficient thorium-230 for experimental production of gram scale quantities of protactinium-231 and significant amounts of uranium-232 and thorium-228.

CONCLUSIONS

Study of uranium ore milling processes in the United States and analytical results on these process streams support the conclusion that substantial quantities of material rich in thorium-230 are available and may be recoverable at reasonable cost. Furthermore, the thorium-230 which may be recovered, although highly contaminated with thorium-232, is of sufficient concentration and has nuclear properties that such thorium mixtures can be used without processes of isotopic separation for direct irradiation to produce material from which protactinium can be separated by chemical means. This element (Pa-231) can then be irradiated to produce uranium-232 from which pure thorium-228 can be "milked" at intervals of six months to one year.

Although thorium-228 and uranium-232 also have high gamma activity, the high heat generating rates of these potent alpha emitters make them especially suitable for primary consideration as heat sources for small thermoelectric generators. The exceptionally high alpha activity of these isotopes also suggests their use in special neutron sources which should be cheaper than equivalent radium-beryllium sources and may have sufficiently high neutron generating rates to put such devices in competition with some of the smaller research reactors and experimental neutron producers.

Although the analytical investigation is not represented as comprehensive, work done on mill process streams including one very large operator has indicated that about 20% of the U.S. milling capacity routinely ~~contains~~ ^{process selection} contains thorium with a thorium-230 content of about 2.5% to 5.5%. These are regarded as highly encouraging results.

RECOMMENDATIONS

It is recommended that research and development be continued to assure the economical and early recovery of sufficient rich thorium-230 material for experimental irradiation to produce grams of protactinium-231 and subsequently uranium-232 and thorium-228 for chemical process and target fabrication development and for the determination of physical and nuclear properties, irradiation yields, activities, etc. Such work is recommended in order to provide support for a proposed continuing, future, plant scale irradiation and production program which will involve an addition to inventory of one to four kilograms of thorium-230 per month.

DISCUSSION

For some time there has been an interest in the use of the heat evolved by the decay of radioisotopes for the production of power to replace, in special cases, that available from batteries. Such applications are particularly appealing in those situations where dependable power is needed only in small quantities for the operation of instruments, data recorders, radio transmitters, or other sensing and signaling devices. The use is specific for space satellites, navigation markers, and generally for any automatic instrumentation in unmanned, remote

locations, such as in the oceans or in the Arctic areas or in space. It is also conceivable that certain radioactive heat sources may be sufficiently energetic to be considered for use for propulsion in outer space in place of nuclear reactors. In other words, in place of sending complex massive reactors into space for propulsion and power, certain high energy radioactive materials produced in a variety of earth-bound reactors may constitute entirely adequate alternatives.

Isotopes must have certain properties in order to be usable:

- (1) Their activity and energy of the radiations must be sufficient to provide the required amount of power.
- (2) Their half-lives must be long enough to provide the power for the necessary length of time between visits for maintenance or for the duration of the need (satellite life).
- (3) They must be practically procurable.
- (4) For uses where mass is an important factor, such as in space satellites, they must have high heat generation rate per unit of mass (including containment and shielding, if such are required). Gases such as Krypton-85 thus have significant disadvantages.

At first the task of selecting candidate radioisotopes from the hundreds which are known would appear to be a formidable one; however, with a certain few reasonable criteria the list narrows readily to just a few choices. (2) Apart from availability, half-life is perhaps the most significant criterion, followed by the type of emission. Those isotopes which have most of their energy in gamma emission are of little interest because to recovery energy from these, the gamma photons must be absorbed. This can be done only in the heavy shielding materials in which the heat is generated and dispersed. Beta and alpha energy in contrast is converted into heat by self-absorption and absorption in any thin layer of adjacent mass. If for the half-life a minimum figure of about one year is chosen, the list of candidate materials is further limited. In addition, if we assume that a practical process must be at hand for preparation of reasonably pure isotopes and target materials, an additional important reduction in numbers of candidate materials is achieved. This requirement eliminates those which would need to be isotopically separated, since economical isotope separations processes for most elements have yet to be developed.

Fission Products

At first review, the potentials of certain fission products which can probably be obtained in required quantities appear attractive. But there are only a few of these which because of half-lives, fission yield (availability) and type and energy of activity (beta or gamma) can be considered. None of these include alpha emitters. Among fission products the following may be regarded as candidate materials:

TABLE I

Element	Half-Life	Type of Radiation	Fission Yield, % (From U-235)	Heat Potential KW/Kg (from Pure Isotopes)
Cs-Ba-137	26.6 years	Gamma / Beta	5.9	0.46
Sr-Y-90	28 years	Beta	5.9	0.78
Pm-147	2.6 years	Beta	2.6	0.40
Ce-Pr-144	285 days	Gamma / Beta	6.1	21.5
Kr-85	10.3 years	Beta / Gamma	0.3	0.54
Ru-Rh-106	1 year	Beta / Gamma	0.38*	25.6

*Effective yield depends on exposure level.

There are deficiencies in some characteristics of each of these. With the exception of Pm-147, all of these as recovered from waste streams are highly contaminated with stable as well as less desirable radioactive isotopes of each element. Therefore without an isotope separations process, the heat potential of practically obtainable materials will be substantially less than that shown above. For cerium oxide recoverable as a fission product, the heat potential would be about 4 KW/Kg instead of the 21.5 figure shown because of the presence of stable Ce-140 and Ce-142. Ruthenium-106 is diluted with stable Ru-101, Ru-102, and Ru-104 along with radioactive Ru-103. Cesium has a low heat potential with its energy largely gamma. Strontium-90, which would also contain stable strontium-88 has, in addition, objectionable biological properties. Because of the probable presence of gamma emitting Sr-89, Sr-90 as recovered cannot be assumed to be a pure beta emitter, but for certain applications it may still be satisfactory. Promethium among candidate beta emitters has about the smallest heat potential; however, in aged waste, should exist as the only pure beta emitter; this may be a distinct advantage in some applications. Cerium, although prominent as a heat source, has an unfavorably short half-life for some applications; but among the candidate fission products it probably has considerable potential.

Reactor By-Products

Radioisotopes may also be recovered as by-products of reactor operations in which conventional materials are converted to active isotopes. Also, intermediate elements may be produced which on further irradiation may be converted to active isotopes. However, either of these processes is likely to produce only a few, if any, candidate materials. Sodium-24 is produced in sodium cooled reactors, but its half-life is so short that it cannot be considered for these applications. Similarly, polonium-210 would be produced in any reactor containing bismuth. Polonium-210 with a half-life of 138 days may be satisfactory in some applications. Its very high heat potential of 141 watts per gram and ease of preparation as the pure isotope tends to overshadow its half-life deficiency. The extremely high and advantageous alpha emitting activity also introduces toxicity problems. Among the intermediate materials, neptunium-237 is produced

in all uranium reactors and may be separated and converted to plutonium-238 which has a long half-life (90 years) and a heat potential of 0.54 watts per gram. Its unfavorable biological properties (like Po-210), unimpressive heat potential and probable high cost are perhaps significant drawbacks for widespread application.

In addition, some mention may be made of the higher isotopes, such as curium-242, etc., which exist in all plutonium containing reactors. Although the heat potential of Cm-242 is high (120 watts per gram), its half life is only 163 days. The principal problem with such a material is, however, its extreme rarity - probably only a few tenths of a milligram per ton of uranium exposed under Hanford conditions. With power reactors under high exposure conditions using plutonium as a fuel different figures would apply but practical amounts of such material are not expected to be available for many years. The other curium isotopes have less heat potential and are even less available. However, the low gamma radiation from Cm-242 and Pu-238 are distinctive and advantageous features of these materials and therefore favor their consideration.

Irradiation of Special Materials for Isotope Production

Another class of radioisotopes comprise those which can be produced by intentional irradiation of other materials. Although here the field is broader for the selection of isotopes of most desirable properties, the selection in most cases becomes involved with isotopic separation of either the target material or the product, if the most desirable materials are to be obtained with high power potential and at reasonable neutron economy. This factor reduces an impressive number down to a very few likely candidate materials, since the technology for practical isotope separation processes is not available for most elements.

The isotopes shown in Table II are representative of potentially desirable ones; however, most would involve isotope separations processes for preparation of either or both the target material and the product.

Some rare earth candidates have been left out of this table because of high neutron absorbing cross sections in them and their neighboring isotopes which minimize the possibilities for their practical preparation and recovery.*

If suitable isotope separations processes could be realized, silver-110, antimony-125, and thallium-204 would all be of interest. Except for possible biological properties the others in the table show little advantage over the fission product candidates of Table I.

Less Conventional Isotope Production Schemes

Among all the radioisotopes, those producible by the irradiation of naturally occurring radioactive elements have perhaps the most interesting possibilities but have been studied in least detail. These are uranium-232, thorium-228, and actinium-227. The target materials, thorium-230, protactinium-231, and radium-226 are rare but existing and recoverable from world uranium ore processing operations. In the case of thorium-230, particularly, hundreds of kilograms per year are now discarded in uranium milling wastes. Table III lists such materials.

*Europium-154 and 155 are typical of these.

TABLE II

<u>Product</u>	<u>Half-Life</u>	<u>Target Element</u>	<u>Type of Radiation</u>	<u>Heat Potential KW/Kg</u>
Silver-110	253 days	Silver-109	Gamma + Beta	78.7
Zinc-65*	245 days	Zinc-64	Gamma + Beta	24.5
Cobalt-60*	5.2 years	Cobalt-59	Gamma + Beta	17.7
Cesium-134*	2.1 years	Cesium-133	Gamma + Beta	13.9
Antimony-125	2.0 years	Tin-124	Gamma + Beta	4.6
Thallium-204	3.6 years	Thallium-203	Beta	0.71
Promethium-147**	2.6 years	Neodymium-146	Beta	0.40
Tritium	12.3 years	Lithium-6	Beta	0.34
Thulium-171	1.9 years	Thulium-169 Erbium-170	Beta + Gamma	0.21

*Isotopes with most of their energy from gamma activity are probably not satisfactory because of the difficulty in effectively absorbing gammas to produce heat.

**Also available as a fission product (see Table I).

TABLE III

<u>Element</u>	<u>Half-Life</u>	<u>Target Element</u>	<u>Type of Radiation</u>	<u>Heat Potential KW/Kg</u>
Thorium-228*	1.9 years	Radium-226	Alpha, Beta, Gamma	165 **
Polonium-210	138 days	Bismuth	Alpha, Gamma	141.
Actinium-227	22 years	Radium-226	Alpha, Beta, Gamma	14.3**
Uranium-232	74 years	Protactinium-231 or Thorium-230	Alpha, Beta, Gamma	4.4**
Plutonium-238	90 years	Neptunium-237	Alpha, beta , Gamma	0.54

*As discussed later, this isotope may be more practically recovered in applicable amounts as the daughter from stored U-232.

**In contrast with some tabulations of heat generation potential, these figures include the heat from the whole decay chain of each isotope (Table IV) rather than the heat evolved, for example, from the one step alpha decay of Th-228 to Ra-224.

Although Po-210 and Pu-238 are not produced from naturally occurring radioactive target materials, they are included in this table for comparison purposes. Compared with fission products, the half-lives of isotopes produced from materials, as shown in Table III, are long and the heat potentials are impressive. Their high heat production results from decay chains of many short lived alpha emitting daughter products. The target materials are in the waste from all uranium ore processing operations. Protactinium and radium exist in uranium ores, each to the extent of about 0.3 gram per short ton of contained uranium. Thorium-230 (also called ionium) is found in a concentration of about sixteen grams per short ton of contained uranium.

If all of the protactinium were recovered from U.S., Canadian, and African uranium ore processes, about eight kilograms should be available annually. A nearly equal amount of radium may also be available. Similarly, about five hundred kilograms of thorium-230 would be available. In addition, there exists stockpiles of waste generated in earlier processing of ores which might provide additional sources. The thorium-230 would be contaminated with large and varying amounts of thorium-232. In this application for thorium-230 an isotope separations process would not be required, if the quantity of thorium-232 in the uranium ore was low enough.* The half-lives and cross-sections of the irradiation products from these isotopes and the intermediate protactinium-231 and 233 which would be formed permit application of chemical methods alone for the eventual preparation of pure uranium-232. Furthermore, overall neutron economy could be high because the uranium-233, which would be formed from the Th-232, may also be recovered and used as valuable by-product fissionable material. If the U-232 content was high enough in this by-product it could also be used as a source of Th-228.

The three target elements of interest exist in nature as the radioactive daughters of uranium-238 and uranium-235. For their recovery, special processing facilities would therefore have to be provided - most probably at the uranium ore processing plant. They are very active alpha emitters and for naturally occurring materials have relatively short half-lives. Their biological properties put them in a class as hazardous as plutonium.

Although U-232 has a relatively long half-life, its high heat generation is due almost entirely to the rapid and energetic decay of its daughter products (see Table IV). It is therefore feasible to consider creating a stockpile of U-232 and to reprocess it routinely or as necessary to obtain required amounts of pure Th-228, instead of using the less active but longer half-lived U-232 as the heat source. The use of radium as a source of Th-228 may also be considered, but the routine recovery of the milligram quantities of radium from uranium mill wastes for this purpose does not appear to be practical as a long range activity. However, for filling any immediate need for milligram quantities of Th-228, production via irradiation of radium may be a justified effort. Similarly the recovery of protactinium may be a justified effort to achieve early production of small amounts of uranium-232.

The decay chain in Table IV accounts for the high heat potential of U-232 (and Th-228). Where radioisotopes, such as Pm-147, Ce-Pr-144, Sr-Y-90, Po-210, and Pu-239 have only one or two significant steps in their decay, Th-228 has seven with most of these including high energy alpha emissions.

*And this need not be low by ordinary standards. A substantial supply of a mixture of Th-230 and Th-232 containing as little as 5 to 10% of the total thorium as Th-230 would be regarded as a rich source. References to sources richer than about 30% Th-230 have not been found.

TABLE IV
RADIOACTIVE DECAY OF URANIUM-232 (AND THORIUM-228)

<u>Element</u>	<u>Half-Life</u>	<u>Emission</u>
U-232	7 ⁴ years	Alpha, Gamma
Th-228	1.9 years	Alpha, Gamma
Ra-224	3.6 ⁴ days	Alpha, Gamma
Em-220	52 seconds	Alpha
Po-216	0.16 second	Alpha
Pb-212	10.6 hours	Beta, Gamma
Bi-212 (decays via both beta and alpha)	60.5 minutes	Alpha, Beta, Gamma
Po-212	0.3 microseconds	Alpha
Tl-208	3.1 minutes	Beta, Gamma
Pb-208	Stable	--

Since the heat potential shown on Table III is the maximum attainable for both the element and its daughters the comparisons are not representative of the instantaneous situation. In the case of U-232, the heat generation rate increases as the daughter products grow in to a maximum at about 10 years from the date of purification. The heat generation rate then decreases as shown in Figure 1. U-232 is initially then only slightly better than Pu-238 as a heat producer but in three years U-232 has attained about 80% of its maximum heat generating capacity. Thus, it exhibits the unusually prominent property of showing an increasing heat generating rate for a long period.* This property is quite in contrast with the usual fission and irradiation product candidates which have a strongly decreasing heat potential, as is to be expected with short half-life materials. Whether or not advantage can be taken of this property has not been investigated. However, except for special applications, it emphasizes that to obtain full advantage of U-232 will apparently require the utilization of this element as a source of Th-228 which has the spectacular heat generating properties as shown in Table III and Figure 2. U-232, therefore, has features which make it especially attractive in comparison with other heat producers. It may be made from naturally occurring elements without need for an isotope separations process. It has a long half-life. It has an initial heat producing potential equivalent to some materials which are receiving consideration. It is a source of a most energetic heat producer, Th-228.

*Calculations as plotted on Figure 1 show that U-232 also has an unusually uniform heat generating rate for a long period; after five years of ageing and for twenty years thereafter the heat generation is in a range within $\pm 10\%$ of the rate at five years.

FIGURE 1

POWER BUILDUP AND DECAY IN U-232

WATTS / GRAM U-232

1.0

0.1

0

5

10

15

20

25

30

35

BD-7050-001 (3-59)

TIME SINCE SEPARATION, YEARS

604

11

10

FIGURE 2

POWER BUILDUP AND DECAY IN TH-228

WATTS / GRAM TH-228

-14-

The actual anticipated prices of fission products such as Sr-90, Ce-144 and Pm-147 recovered in mega-curie quantities have not been disclosed in unclassified reports. However, prices have been estimated for use in this document. Willard F. Libby has estimated an eventual "rock bottom" price of \$0.30 per curie for Cs-137.⁽³⁾ A. D. Little, Inc., has developed a curve showing the price of Cesium-137 as a function of the level of production. These prices vary from about \$0.65/curie at an annual production rate of 1 megacurie to about \$0.15/curie at an annual production rate of 100 megacuries.⁽⁴⁾ It seems reasonable to assume that depreciation charges and operating costs should be roughly the same for recovering a given fission product from a given amount of radioactive waste. On this premise, the ratio of Cs-137 price per curie to Sr-90, Ce-144, or Pm-147 price per curie should be similar to the ratio of the curies of Cs-137 to the curies of Sr-90, Ce-144, or Pm-147 present in the waste. This latter ratio can be approximated from ratios of the fission yields and half-lives. Using the fission yields and half-lives shown in Table I and using \$0.30/curie as the price for Cs-137 in megacurie amounts, the eventual prices of Sr-90, Ce-144, and Pm-147 in megacurie quantities are estimated to be \$0.30/curie, \$0.01/curie and \$0.07/curie, respectively. Heat sources of Sr-90, Ce-144 and Pm-147 capable of delivering a minimum of 100 watts of electricity at 10% conversion efficiency (thermal to electrical) over a two year period would cost as shown in Table V. From these figures the equivalent "value" of Th-228 per gram is calculated and illustrated in Table V. These "values" of course do not reflect differences in costs for source fabrication, shielding, etc.

TABLE V
"Value" of Th-228 (as a Heat Source)

Isotope	Initial KW/Source	Initial Units/Source	Unit Price \$/Unit	Cost/Source, \$
Ce-144	5.9	873,000 Curies	0.01/Curie	8730
Sr-90	1.05	191,000 Curies	0.30/Curie	57300
Pm-147	1.7	3,900,000 Curies	0.07/Curie	273,000
Th-228	2.1	12.7 g.	687/g. 4510/g. 21500/g.	8730 57300 273,000

Although this study has not attempted, up to this time, to estimate the cost of producing Th-228, the figures of Table V indicate a very high "value" for this material, and therefore based on what is known about the cost of irradiation, separation, and special fuel fabrication, costs less than those indicated for value appear attainable.

(3) "Price of Isotopes Drops With Use", Chemical and Engineering News, May 20, 1957, p. 19.

(4) "Radiation: A Tool for Industry", by A. D. Little, Inc., January, 1959.

In summary, there are fission products and irradiation products which may find particular and important use as power generating sources. These include cerium-144, promethium-147, strontium-90, polonium-210, plutonium-238, uranium-232, and thorium-228, as likely candidates. Until isotope separation processes are applied to other elements this list is not expected to grow. Of these materials, the possibilities of uranium-232 and thorium-228 have been least explored. Intensive consideration of these materials is justified because of their high heat generating potential and the expected availability of materials needed for their preparation. The intense radioactivity and heat generating capacity of these materials which encourages their application also necessitates the development of special new technology in target element fabrication and chemical processing. The problems involved here should be recognized as severe but not insurmountable. The unique and potentially useful properties of these materials are believed to be sufficiently attractive to justify the required efforts directed at the resolution of the anticipated recovery, fabrication, and processing problems.

Work Done by Others

A large part of the work done on Th-230 and protactinium recovery over the last fifteen years still remains reported in the classified areas. We expect, however, that work done with U.S. uranium milling residues would be reported as unclassified information since the milling industry in our country has developed greatly only in the last few years, since about 1953. Only eight mills were in operation in 1952. In 1948 domestic production U_3O_8 amounted to only 110 tons. There are now twenty-three mills. No references to work on Th-230 in mill process streams in the United States has been reported. The AEC sponsored work on Th-230 recovery from an accumulation of residues from the now abandoned Mallinckrodt ore plant in St. Louis, Missouri, have been noted. Some of this work was done at the Argonne National Laboratory. Peppard et al.⁽⁵⁾ reported on these efforts which involved the recovery of about sixty grams of Th-230 in a mixture in which Th-230 comprised 11% of the thorium. Recovery campaigns were also conducted by Mallinckrodt from 1954 to 1956 from which several hundred grams of Th-230 were recovered and the basis for a plant design were scoped.⁽⁶⁾

Work on the recovery of about two grams of protactinium was reported by L. L. Katzin.⁽⁷⁾ Salutsky⁽⁸⁾ also reported work on Pa-231 separation from uranium ore processing residues. Similar British work was reported by Goble.^{(9)*}

(5) Peppard, D.F. et al, "Studies of the Solvent Extraction Behavior of the Transition Elements, II Isolation of Gram Quantities of Th-230 (Ionium) from a Pitchblende Residue", J. American Chemical Society 75, 45 76-78, 1953.

(6) MCW-1427, Topical Report "Ionium Recovery Plant Design Report" by R. M. Edwards, R. H. Fariss and R. G. Werkema, 4/15/59 (Unclassified).

(7) L. I. Katzin, "Analysis of Ore Residues for Ionium and Protactinium", J. American Chemical Society 72 4815 (1950).

(8) M. L. Salutsky, et al "Separation of Protactinium from Uranium Residues" J. Inorganic Nuclear Chemistry 3 289-295 (1956) (Mound Laboratory).

(9) A. G. Goble et al "The Extraction of Protactinium from Refinery Residues" Progress in Nuclear Energy Service III Process Chemistry Vol. 2 page 86.

*More recently the British have reported the recovery of about 100 grams of protactinium at a cost of \$2800/gram. "Applied Atomics", December 8, 1959 Page 14.

Work reported from the Mound Laboratory indicates that the material (Th-230) probably came from the Argonne or Mallinckrodt campaigns. The extraction of milligram quantities of thorium with a Th-230 content of about 28% from a Canadian pitchblende residue was reported by Van Cleave.⁽¹⁰⁾ The British work on Th-230 recovery is covered by Carswell.⁽¹¹⁾ French work is discussed by Bouissieres.⁽¹²⁾

The American work, particularly that reported by Mallinckrodt investigations, is probably the most extensive and has produced the most material, but probably less than a kilogram of Th-230. The disposition of this material has not been disclosed. No work has been reported on Th-230 (or Pa-231) recovery from current U.S. uranium ore milling operations.

Other Uses

Although the potential use of thorium-228 and uranium-232 as heat sources has been emphasized here in comparison with competitive materials, a different more specific use for these elements may be considered. The potent alpha emitting characteristics establish these materials as candidate neutron sources when in contact with elements such as beryllium. The activity of such sources depends directly on the alpha particle concentration and the energy of these emissions; in both factors thorium-228 has significant advantages. Based on the neutrons produced from alpha energies of other elements,⁽¹³⁾ gram quantities of thorium-228 should with beryllium be capable of producing sources of more than 10^{10} neutrons per second over the 1.9 year half-life of this element. Milligrams of Th-228 should therefore be equivalent to grams of radium in neutron sources. Such sources should be of great interest in academic and industrial research and should not only be competitive with other sources such as Ra-Be and Po-Be as experimental neutron producers but also may find widespread application in place of the low flux research reactors which have fluxes in the range of 10^7 to 10^{10} neutrons per second per square centimeter. Initially for demonstration purposes at an early date, it even may be practical to produce Th-228 in milligram quantities via the irradiation of a few grams of radium rather than to obtain it by way of the route from Th-230 to Pa-231 to U-232 and then from the U-232. Via the Th-230 route milligram amounts of Th-228 may be available about 1 year after the beginning of experimental irradiation of Th-230.

In the course of producing gram quantities of thorium-228 by irradiation of thorium-230 to yield the necessary uranium-232 from which the thorium-228 can be "milked", large amounts, kilograms, of protactinium-231 would be recovered and processed as the intermediate product. Although this isotope (Pa-231) occurs in all uranium ores in about the same concentration as does radium, no significant uses for this material have been developed. Whether because of its rarity or as

(10) A. B. Van Cleave and A. P. Baerg "Canadian J. Tech. 34 425 (1957).

(11) D. J. Carswell and J. M. Fletcher, "The Recovery of Thorium-230", Progress in Nuclear Energy Service III Process Chemistry Vol. 2 page 80.

(12) G. Bouissier et al "The Recovery of Radium and Protactinium as By-Products in the Treatment of Uranothorinite Ores" Progress in Nuclear Energy" page 101.

(13) AECD-3645 - "Reactor Handbook" Vol. I page 2 Table 1.1.1 and Table 1.1.2.

a result, the chemistry and chemical technology of this element has not been developed to the degree of that for radium. It is conceivable that with substantial quantities of this, heretofore rare element, at hand study may be greatly encouraged with the potential for development of important but as yet unknown applications. Similarly for Th-230 there may be considerable interest in this unique isotope once it is learned that substantial amounts are available. In addition with continued emphasis on the health aspects of uranium milling and attendant waste disposal problems some mills may find it attractive to recover thorium-230 for disposal to those who may have use for it. Also from the standpoint of conserving this depleting and now wasted resource, some may regard recovery as justified for reserve for some future but at present indefinite use.

Since the properties of thorium-228 make it especially distinctive for use either as a heat or alpha source, it is the intent here to consider the prospects for its manufacture rather than the possibilities for these two applications which appear to be sufficiently established (exclusive of classified uses which may also exist).

Ionium (Thorium-230) Occurrence

Of the radioactive elements which exist in nature, uranium is the only one which has a decay chain in which other radioactive elements remain as equilibrium daughter products in significant amounts.* Thorium-230 is by far the most prominent of these. Plutonium and neptunium do not exist in significant amounts in nature, therefore their decay chains are of no interest here. Thorium-232, although common, has such a long half-life and such short-lived daughters (including thorium-228) that it can not be considered as a source for significant amounts of decay products.

The equilibrium concentrations of the relatively long-lived elements** (half-lives in excess of one year) which are produced in the three "natural" decay chains are shown as follows: (14)

Uranium-238 Daughters (equilibrium concentrations, grams/ton of U-238, and half lives)

Uranium-234	50 grams/ton	250,000 years
Thorium-230	16 grams/ton	80,000 years
Radium-226	0.32 grams/ton	1,620 years
Lead-210	0.0045 grams/ton	22 years

*By significant amounts is meant, "grams per ton".

**Those elements with half-lives less than one year are present in much smaller and negligible amounts.

(14) Progress in Nuclear Energy Series III, Process Chemistry, Vol. 2, Editor: Bruce, Fletcher, and Hyman page 77 "Recovery of Radioactive By-Products from Uranium and Thorium Ores".

Uranium-235 Daughters (equilibrium concentrations, grams/ton of associated U-238, and half-lives)

Protactinium-231	0.31	34,000 years
Actinium-227	0.0002	22 years

Thorium-232 Daughters (equilibrium concentrations, grams/ton of Th-232, and half-lives)

Radium-228	0.00043	6.7 years
Thorium-228	0.00012	1.9 years

From an inspection of the above data it is obvious that from the availability standpoint alone thorium-230 is the most logical and perhaps the only element among these which can be considered for practical applications. Furthermore, since the only source of Th-230 is uranium ore it is probable that it could be recovered cheaply from uranium ore milling waste streams with no costs for mining, processing, or plant write-off up to ~~the point at which it might be recovered by chemical means.~~ the point at which it might be recovered by chemical means. The actual cost of recovery therefore can be expected to be minimum. This is in contrast with the recovery program developed for extraction of Th-230 from the "St. Louis" stockpile of thousands of tons of residues (containing about 5 grams of Th-230 per ton on a dry basis) accumulated from World War II processing of Belgian Congo ore. (S) In this case the operating cost exclusive of plant write-off was estimated to be \$51/gram. With plant write-off this figure may be about \$235/gram*. These figures should not be taken as a basis for concluding that the St. Louis residues are not an attractive source of suitable Th-230. This residue which we conclude from the unclassified report amounts to several thousand tons on a dry basis contains not only about 5 grams of Th-230 per ton but also about 13.5 pounds of uranium per dry ton (about 0.8% U₃O₈). In the area of classified reports there are conflicting data as to the magnitude and composition of these residues. The uranium content thus puts this material in the class of very high grade uranium ores. It may be reasonable then to consider shipping this material to a uranium mill (known to process material of high Th-230 quality) where both the uranium and Th-230 may be most economically recovered. The recovery work done to date utilized a nitric acid dissolution process on this material. The feasibility of recovery via the sulfuric leach process common to the usual uranium ore milling industry would have to be established along with the technique of Th-230 recovery in such processes. With the attractive uranium content, shipment of such processing may be economically favorable even though the residue is highly alkaline and would thus involve high consumption of acid. The recovery of at least 10 Kg of the Th-230 known to exist in this material as 8 to 12% of the total thorium is indeed an appealing possibility.

(15) ~~WPA 2427, 24/15/59, "Thorium Recovery Plant Design Report"~~.

*Although this study has not progressed to the point of defining a process to be used at a mill, we believe that an ion exchange system for such recovery could be installed and operated with a five year write-off of investment such that a selling price in the range of \$7 to \$20 per gram would yield a satisfactory profit. The \$235 assumes no profit, but includes plant write-off (3 years), operating cost and credit for co-recovered uranium; no costs for residue handling delivery and waste removal are included.

At the present time analytical data is essentially non-existent on the Th-230 content of U.S. uranium ore milling process streams. Results have, however, been obtained on a few samples which have been requested. There is information, yet to be substantiated, that there is available a "one shot" residue having a concentration about eight hundred times that of the residues on which most of the earlier research and development work has been done. A review of the milling processes lends encouragement to the expectation that similar residues are being routinely produced by others; and also that somewhere ores which have a suitably low extractable thorium (Th-232) content are being processed and probably the mill operator is totally unaware of this striking situation!

The Uranium Industry and Processes in the United States

Ores and Th-230 "Enrichment"

For Th-230 recovery to be practical it is obvious that ores low (and extremely low) in extractable thorium-232 must be consumed in the mill. Although uranium ores low in thorium are the common ores in U.S. deposits (carnotite, autunite, etc.) references to the actual thorium content have not been uncovered. There is the possibility that such data do not even exist. In anticipation of this situation, samples of ores and feed liquors of several mills have been requested.

Because of the short half-life of Th-230 with reference to geologic time one would not expect to find altered minerals in which Th-230 existed in forms separate from the parent uranium. In a million years any segregated Th-230 would be diminished by a factor of about 5,000 by its own radioactive decay. Therefore we would not expect to find any Th-230 in the common thorium ores except in conjunction with any uranium which may be present. It is assumed that all uranium ores are at secular equilibrium and that they should contain, therefore, sixteen grams of Th-230 per short ton of uranium. If we assume that for a satisfactory product the Th-230 content may need to be only 10% Th-230 (and 90% Th-232), the maximum amount of Th-232 should therefore be 9×16 or 144 grams/ton of uranium. If we assume that the ore contains 0.2% uranium, then one ton of ore should contain not more than 0.288 grams or 0.32 ppm of extractable Th-232. Moeller⁽¹⁶⁾ lists thorium as comprising 0.0011% of the earth's crust, or 11 parts per million. This is then about thirty-four times the amount of extractable thorium desired in uranium ore suitable for Th-230 recovery! It may therefore be concluded that there are few rocks of any kind which one would expect to contain so little of this element. This fact and the existence of several rich thorium ores such as monazite may be the reason for thorium not being reported in the routine analysis of low-thorium uranium ores. For elements which may normally occur together, such as uranium and thorium in minerals such as uranothorianite, one would expect even higher concentrations of thorium in all uranium ores than is found in the average crust of the earth. From the standpoint of these physical data the prospects for the recovery of high concentrations (even 10%) of Th-230 are indeed dismal. However, there are factors which may be expected to favor recovery of

(16) Therald Moeller, "Inorganic Chemistry" (1952) page 32.

reasonably high concentrations of Th-230. Thorium minerals such as monazite (a phosphate), thorite (a silicate), and thorianite (an oxide) are not easily dissolved; furthermore, these minerals are not expected to be associated with ionium even though it is an isotope of thorium. Thorium-230 should exist only in the crystal structure of the uranium mineral. Uranium in minerals is generally readily dissolved even in dilute sulfuric acid and for some minerals also in sodium carbonate. By contrast thorium minerals such as monazite require boiling concentrated sulfuric acid for dissolution. Conveniently this reagent (dilute sulfuric acid) is used with all U.S. ores which are low in lime. Such ores comprise about 70% of the feed to U.S. mills. With Th-230 as well as protactinium and radium atoms uniformly dispersed throughout the uranium constituent lattice of the ore, when the uranium is dissolved in the dilute sulfuric acid, Th-230 would be expected to go into solution also. Separate thorium minerals such as monazite or thorite, on the other hand, would not be expected to dissolve so readily. Thereby a sort of isotopic separation or enrichment may be obtainable which favors the achievement of acceptable Th-230 concentrations. This, it is believed is a factor which may account for the fact that Th-230 compositions have been obtained in the range of 5 to 30% from several uranium ores.⁽¹⁷⁾ In addition we conclude that these reported high Th-230 concentrations (high isotopic ratio of Th-230/Th-232) were found by analysis of material derived from selected mineral specimens, very rich ores or ore concentrates in which the normal Th-232 content of the accompanying rock or gangue would be minimized. Certainly at the start the U.S. demands were met by importation of unaltered concentrates which were far richer than those being processed today, where, so far as we know no U.S. mill utilizes (other than ore selection or blending) any beneficiation process to yield an ore concentrate as feed to the leaching process. Low and preferably very low thorium contents must therefore be emphasized in review of ores most promising as sources of Th-230.

If a normal mill process is found to be a prospective source of material encouragingly high in Th-230, say about 1% or more in the Th-230-Th-232 mixture, there are some approaches which could be taken by the mill operator in an effort to improve the isotopic ratio, yield, and process simplification. In certain parts of the milling process the sulfuric acid concentration or other conditions may possibly be changed to minimize dissolution of thorium-232 minerals without adversely influencing the overall uranium recovery. Selection of preferred ores or sections of an ore body for special Th-230 recovery campaigns may also be feasible.

Processes

Next to the type of uranium ores being processed the variety of uranium ore milling processes utilized in the United States also permits some selection or gradation of the feasibility of Th-230 recovery to be made (along with residual thorium also). Two major process classifications exist (1) those based on sulfuric acid for uranium dissolution and (2) those based on alkaline carbonate for uranium removal. The latter type of process would be regarded as the least likely source of Th-230 because of the expectation of minimum solubilization of the Th-230 and the belief that any particulate Th-230 which may result would therefore leave the process with the mass of insoluble residue

(17) ANL-4405, ANL-4411, and Canadian Journal of Technology Vol. 34 (1957) page 425.

or gangue.* In the sulfuric acid processes the leach solutions which would be expected to contain the solubilized Th-230 along with the uranium are treated in a variety of ways by the different mills with variations in processes within mills to accommodate different types of ore. From an Th-230 recovery standpoint these processes can be further broken down into two classes, one favorable and one less attractive. The favorable process utilizes a step for clean separation of insoluble solids from the leach liquid. The less attractive ones carry on further treatment of the leach solution for uranium recovery in the presence of the gangue. The favorable processes treat the clarified leach liquor by either solvent extraction or ion exchange methods. In these steps different solvents and ion exchange resins are used. By detailed knowledge of the physical chemistry of these processes the most reasonable routes for the passage of Th-230 through the process can be anticipated. At this stage, precise analytical data are required to establish the route, yield and potential recovery techniques. Samples from specific processing steps in certain mills have been obtained. Analyses are, however, incomplete.

It should be understood that the possibility exists for Th-230 recovery from any uranium milling process. However, there are clear economic and process factors which make one milling operation more attractive than another. The following tables list all U.S. mills and their processes as reported in current unclassified literature (or private communications) arranged with regard to our evaluation as to their economic or process feasibility for Th-230 recovery. (18)

*This conclusion may, however, be premature, since a soluble thorium carbonate complex is known to exist under certain conditions. A single analysis of leach solution should be made before this type of ore process is completely dismissed from consideration as a source of Th-230.

(18) U.S. Atomic Energy Commission, Twenty-Fifth Semi-Annual Report to Congress, July-December, 1958 "Atomic Industrial Progress and Second World Conference" pages 6 and 7.

Favorable Processes

Plants which provide clarified leach solution to solvent extraction and ion exchange systems.

Plants Utilizing Liquid-Liquid Solvent Extraction

<u>Operator</u>	<u>Solvent Process</u>	<u>Location</u>	<u>Tons Ore/Day</u>
Climax Uranium Company	Dapex*	Grand Junction, Colorado	330
Gunnison Mining Company	Amex***	Gunnison, Colorado	200
Kerr-McGee Oil Industries**	Dapex	Shiprock, New Mexico	-
Union Carbide Nuclear Company	Dapex	Rifle, Colorado	1,000
Susquehanna-Western, Inc.**	Amex	Riverton, Wyoming	724
Lakeview Mining Company	Amex	Lakeview, Oregon	210
Kermac Nuclear Fuels Corp.	Amex	Ambrosia Lake, (Grants) New Mexico	3,300
Texas-Zinc Minerals Corp.	Amex	Mexican Hat, Utah	1,000
Vanadium Corp. of America		Durango, Colorado	750
Vitro Uranium Company	Amex	Salt Lake City, Utah	600

*Di(2 ethyl-hexyl)phosphoric acid is the solvent, (2DEHPA).

**These mills operate two different processes. Susquehanna-Western formerly Fremont Minerals, Inc.

***Highly branched secondary amine is the solvent ("Amine 9D-178 or Amberlite LA-1").

Plants Utilizing Ion Exchange*

<u>Operator</u>	<u>Location</u>	<u>Tons Ore/Day</u>
Dawn Mining Company	Ford, Washington	525
Kerr-McGee Oil Industries**	Shiprock, New Mexico	300
Lucky Mac Uranium Company	Fremont County, Wyoming	1,000
Union Carbide Nuclear Company	Uravan, Colorado	<u>1,000</u>
Total for Solvent Extraction and Ion Exchange Processes based on Clarified Feed Liquors		10,939***

*The anion exchange resin is a strong base quaternary amine, Dowex 1, Permutit SK or Amberlite IRA-400.

**Two different processes are operated in this mill.

***This is slightly over one-half of the total U.S. ore milling capacity (or about 22 tons of uranium per day and represents from these "preferred" processes a present discard or potential for recovery of 352 grams of Th-230 per day. At 330 operating days per year this amounts to 116 kilograms per year.

Processes Which are Less Attractive for Th-230 Recovery

Plants Utilizing "Resin in Pulp" Type Ion Exchange Process

Anaconda Company**	Grants, New Mexico
Federal Uranium Corporation	Gas Hills District, Wyoming
Mines Development Company (a)	Edgement, South Dakota
Rare Metals Corporation	Tuba City, Arizona
Trace Elements Corporation	Maybell, Colorado
Uranium Reduction Company	Moab, Utah
Western Nuclear Corporation	Split Rock, Wyoming

A mill operated for U.S. Government, Monticello, Utah to be abandoned 1/1/60.**

**Two different processes are operated in these mills.

from four plants reported to be using Dapex with the filtration step. However, from the replies we learn that none of these are using Dapex as described in reference (19); one is using Amex; one uses the filtration step after RIP ion exchange treatment. One indicated that the filtration step could be re-started at anytime, if economically justified.

Status and Results of Uranium Ore Mill Samples

The composition of the ore or more particularly the ore mill leach solution with respect to both thorium-232 and thorium-230 content is the most important information obtained in this study. The information was unavailable and had to be obtained by our own efforts including the development of special analytical techniques. The milling processes are fairly well publicized at least to the extent necessary for selection of the most attractive processes from the standpoint of economical Th-230 recovery. The fact that five to ten years ago, before the establishment of the present spectacular uranium milling industry in the United States, Th-230 materials from ores (probably concentrates) obtained outside the United States containing greater than 10% Th-230 content were noted and processed, (5,11) encouraged expectations for similar disclosures among the present day processors. Samples were received from ten such mills. In requesting samples mills representative of major uranium areas and particularly some mills in remote locations which may be involved in the processing of special types of ores were contacted.

The survey of the ore milling industry and the procurement of samples has not been as extensive as would be most desirable. This review was not aimed at a comprehensive evaluation principally because it was merely desired to determine the existence of high Th-230 materials in large scale milling operations in order to assess the potential for recovery. Considerably more analytical work is necessary to provide a comprehensive review of only the U.S. industry. However, in this present limited evaluation fully 20% of the U.S. industry (represented by mills) appears to be a source of thorium concentrates containing from about 2.5 to 5.5% Th-230. This is regarded as a highly encouraging situation. Some of the mills which analyses show to be unacceptable because of high Th-232 content may as their ore receipts change become acceptable sources. These encouraging preliminary results plus the possibilities of the "St. Louis Airport" residues support the belief that large scale routine recovery of "high analysis" Th-230 by economical processes is a distinct possibility.

If as a result of this report there develops sufficient interest in the unique possibilities of recovered Th-230 as a starting material for heat sources, alpha-neutron sources, conservation, or for public health reasons to support further efforts, a more extensive analytical program would be proposed as an essential part of an expanded study.

This is not meant to imply that the PRTR would be used for such irradiations. PRTR conditions were used only because they are unclassified. The cross sections in Table VII were used with the exception that the (n, γ) reaction of Th-233 was neglected because of the short half-life of Th-233. In the case of Th-230-Th-232, the target elements were assumed to be 75 weight percent (about 50 volume percent) thorium oxide pellets in aluminum. In the case of Pa-231, the target elements were assumed to be 10 weight percent protactinium (as the oxide) in aluminum. In both cases the target elements were assumed to be solid cylinders 1.4 inches in diameter.

Uranium-232 Production Program

Protactinium-231 and U-232 can be produced by conventional irradiation of Th-230-Th-232 or Pa-231 in the form of solid target elements or by the less conventional irradiation of these elements in the form of solutions. In such liquid systems, the target solution can be irradiated for short periods of time, continuously or intermittently removed from the reactor, processed in a close-coupled separations plant either immediately or after a short-cooling period, and returned to the reactor.

Each system has its advantages and disadvantages. The technology of solid element irradiation is well developed while solution irradiation in Hanford production reactors would require development of a new technology. Solid-element irradiation will require remote fabrication of fuel elements and a shielded reactor-charging method because of the buildup of Th-228, Th-229, and Th-234 in recycled Th-230 and because of the presence of Pa-233 in Pa-231. Liquid systems would not have target fabrication problems. Desired production could be attained and specific amounts of U-232 obtained sooner with a liquid system. Such production advantages are not as great as might be thought when first considering the possibility of short cooling times, since, in order to obtain high purity U-232 from Pa-231 produced from Th-230, a long cooling time (about 200 to 300 days) would be required to allow short-lived Pa-233 to decay. A liquid system would allow more efficient utilization of the target materials, Th-230 and Pa-231, by removing the desirable materials before they can be transformed to other nuclides or fissioned. However, this means that the target material must be processed oftener. Also, the liquid system (essentially "poison" columns) could possibly be lost from the reactor by accidental leakage. The enriched uranium columns added to support the liquid system would then cause a difficult control problem.

Initial comparisons of the two schemes, has led to the conclusion that advantages of the less-conventional liquid system at the proposed scale of operation do not justify the research and development effort required. This conclusion is based on (a) comparisons which indicate production gains of less than a factor of two for the liquid system, and (b) the premise that a smaller scale of development effort is needed for remote fabrication and shielded reactor-charging of solid elements. Some experience in these fields is already available. Therefore, in this document, solid target elements are used for production estimates.

To show the results of an irradiation program, a 5 to 10 year program incorporating the steps shown in Figure 2 has been assumed. In the assumed program the Th-230-Th-232 target material is collected and charged every three months. The reactor residence time is six months (an irradiation time of 136 days at 75% operating efficiency). After discharge, these elements are cooled

for three months (maximum) for fission product decay and partial decay of Pa-233. They are then processed to recover and separate the Th-230-Th-232 mixture, the Pa-231 produced, (along with residual Pa-233) and the U-232-U-233 mixture produced. The recovered Th-230-Th-232 mixture is remotely refabricated and recycled to the reactor along with a quarterly charge of virgin Th-230. Processing and refabrication are assumed to take three months. Some time during the quarter the elements are processed and fabricated on a campaign basis. Such scheduling flexibility allows the processing plant (say the Hot Semiworks) periods of time for decontamination, maintenance, and processing of other materials. Thus, Th-230 is outside the reactor for six months per cycle.

Six months after Th-230 is discharged from the reactor the recovered U-232-U-233 mixture is available for storage to allow Th-228 to grow in. At discharge, there is about 0.5 g. of Pa-233 present per g. of Pa-231. After separation from fission products and other nuclides, the Pa-231-Pa-233 mixture is held for additional Pa-233 decay to provide a total cooling time of 10 months after reactor discharge. The additional cooling is provided to decrease the heat generation in Pa-231 during handling, the radioactivity of Pa-231 target elements, and the amount of U-233 in U-232 produced from subsequent Pa-231 irradiation. After cooling, Pa-231 is reprocessed to remove and recover pure U-233. Allowing one month for reprocessing the Pa-231 and fabricating the target elements, the elapsed time between charging the Th-230 targets and charging the Pa-231 produced is 17 months.

The reactor residence time for the Pa-231 target elements is one year (an irradiation time of 9 months at 75% operating efficiency). After discharge these elements are cooled for three months and then processed to recover both the Pa-231 and U-232. The recovered Pa-231 is remotely refabricated and recycled to the reactor with Pa-231 recovered from the Th-230 irradiation. Processing and fabrication is assumed to take three months with scheduling similar to that employed for Th-230. Thus, the Pa-231 is outside the reactor for 6 months. Six months after irradiated Pa-231 is discharged from the reactor, the recovered U-232 product is available for use or for storage to allow Th-228 to grow in.

Thorium-230 and Pa-231 losses during processing and fabrication are assumed to be two percent per cycle. Uranium-232 losses are assumed to be 0.5%.

On the assumption that recovery, irradiation and processing of Th-230 on a substantial and prolonged scale of operation is justified, the bases and essential production steps are summarized below. In view of the favorable preliminary analytical results (page 26), it appears that about four kilograms of Th-230 per month may be available from U.S. mills. One kilogram per month has been used in this study as the basis for the calculations for an initial program. With evidence indicating the substantially greater potential availability from only the domestic sources a factor of four can be applied to the figures on the following page.

Bases:

1. 12 Kg of Th-230 (10% Th-230, 90% Th-232) delivered from uranium ore mills every year beginning January 1, 1961. (1 Kg per month)
2. Duration of program - five to ten years minimum.

3. Pa-231 recovered first along with U-232 and Th-230 for recycling.
4. Product will be fairly pure form of U-232 from irradiation of Pa-231 but will contain some of U-233 and U-234.
5. U-232 produced will be stored and processed every six to twelve months for the recovery of pure Th-228.

Steps:

1. Manufacture of target elements or reactor feed material.
2. Irradiation and ageing.
3. Chemical separation and recovery of Pa-231, U-232 and Th-230.
4. Manufacture of Pa-231 target material and preparation of recycled Th-230.
5. Irradiation of Pa-231 and recycled Th-230 and ageing.
6. Chemical separation of U-232 for storage and Pa-231 for recycle.
7. Ageing and chemical separation of Th-228 from U-232.

Using the program and bases described above and in Figure 3 the results of an irradiation program five years and ten years after the first kilogram of Th-230 becomes available are shown below:

	<u>5 Years</u>	<u>10 Years</u>
Th-230 inventory, Kg	53.8	93.9
Pa-231 inventory, Kg	3.8	10.7
U-232 Available		
From Th-230-Th-232 irradiation, g	180	740
From Pa-231 irradiation, g	200	2670
Th-228 Produced		
Total Recovered (after five years accumulation), g	2.7	-
Total Recovered (Intermittent recovery every 6 months), g	3.4	69
Pure U-233 Recovered, g	~60	~250

There is more U-232 produced than is shown as available at the end of the 5-year or 10-year program. It is somewhere in the "pipeline", either in the reactor or cooling basin.

As mentioned earlier the U-232 produced from the Th-230-Th-232 is highly diluted with U-233 and U-234 while the U-232 produced from Pa-231 will be only slightly diluted. The amount of dilution will depend on irradiation and cooling times. Anticipated product compositions for the assumed program

desired.

Research and development programs devised to promote the objectives of an initial effort would be related to three areas of interest.

1. Work directed at the analysis and recovery in the near future of a substantial quantity of suitable Th-230 for study purposes.
2. Work related to the development of economical and practical routine, large scale recovery processes for Th-230 for application in U.S. ore mills.
3. Work related to process development for the long range, large scale, routine production of U-232 and Th-228 via irradiation of Th-230.

In view of such interests the following research and development program should be planned:

1. Complete the analytical work to uncover the most likely sources of Th-230 for both short and long range activities.
2. Appraise the quality, quantity and economics of Th-230 recovery from the standpoint of achieving a five to ten year program on the scale of at least 12 Kg Th-230 per year.
3. Recover on an experimental basis a few hundred grams of Th-230 from the most promising mill residues in our own laboratory facilities.
4. Prepare target material.
5. Conduct irradiation of a few hundred grams of Th-230.
6. Recover several grams of pure Pa-231 from the irradiated Th-230 along with the U-234, U-233, U-232 by-product mixture.
7. Irradiate Pa-231 and recycle Th-230.
8. Recover grams of U-232.
9. Recover milligrams of Th-228.
10. As an alternate evaluate the irradiation of grams of radium for the recovery of milligrams of Th-228.
11. The analytical program should also be extended to provide sufficient data to evaluate the possibilities of Pa-231 recovery from uranium ore milling process streams.

It is intended that the details of the above program include studies of physics constants, target element fabrication, reactor loading alternates, thermal conductivity investigations of target elements, chemical processing, and economics. In addition one would expect to have at hand an evaluation of the magnitude and value of anticipated uses in order to clearly justify the proposed program and an advanced program for large scale, routine production.

It is also conceivable that other and more extensive research and development programs could result, if interest in Th-230, Pa-231, U-232 and Th-228 develops. Some programs could be proposed in the following areas:

1. Conduct a more comprehensive program of analysis of essentially all suitable U.S. and Canadian uranium ores and milling processes for the Th-230-Th-232 ratio and the Pa-231 content. (Including the extension of the study to the "carbonate leaching" processes.
2. Study process and economic feasibility of recovery for attractive sources uncovered in one above (Th-230 and Pa-231).
3. Determine the extent to which Th-230 (and Pa-231) is involved in the health aspects of the existing U.S. uranium ore milling industry.
4. Study possible uses for Th-230, Pa-231, U-232 and Th-228.
5. Establish the technology and economics of the recovery of the uranium and Th-230 values of the "St. Louis Airport" residues in an existing U.S. uranium ore mill (sulfuric acid or carbonate leach process).

Utilization of the "St. Louis" Residues

Although the to date analytical efforts should not be regarded as comprehensive especially with reference to specific ores in custom mills, the operations which have been surveyed as a result of this present work have indicated substantial sources of Th-230; however, the "St. Louis" or "Mallinckrodt World War II" residue⁽¹⁵⁾ still appears to be the source in which Th-230 exists in greatest concentration (8 to 12% of total thorium). As mentioned on page 18 the uranium content of this material justifies consideration of the development of a process applicable to sulfuric acid dissolution as practiced in uranium ore mills, in order to recover both uranium and thorium. The uranium content (2.7 pounds per gram of Th-230)⁽¹⁵⁾ may be sufficiently high to bear the cost of chemicals as well as shipping. Under such circumstances the thorium (Th-230) could "go along for the ride" and be recovered at very low cost. The objective here would be to conduct such recovery in a mill known to process an ore which normally would yield thorium of high Th-230 content. The Lakeview Mining Company plant at Lakeview, Oregon, based on our analysis of their leach liquor, would be the most logical point for conducting such a recovery program. Other mills by selection of very low thorium content ores (such as Vitro or Kermac) may also be considered. However, the comparatively small scale operations at Lakeview Mining and the fact that their ore appears to yield leach liquors containing thorium of highest Th-230 content favors a recovery program at this mill. Initiation of such a recovery campaign requires the additional research and development work anticipated ~~above~~.

above,

Chas. G. Rohrman
C. A. Rohrman

Date 12/15/59

E. A. Copinger
E. A. Copinger

Date 12-15-59