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PHASE I REPORT . . .

**DEVELOPMENT OF
TECHNIQUES
for
POWER PRODUCTION
FROM
MIXED FISSION
PRODUCTS**

CONTRACT AT(30-1)2605
UNITED STATES
ATOMIC ENERGY COMMISSION

GENERAL INSTRUMENT CORP. -- THERMOELECTRIC DIVISION

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UC-23, Isotopes-Industrial Technology
A.E.C. Research and Development Report

THE THERMOELECTRIC DIVISION
OF THE
GENERAL INSTRUMENT CORPORATION

PHASE I REPORT OF
"DEVELOPMENT TECHNIQUES FOR POWER
PRODUCTION FROM MIXED FISSION PRODUCTS"

Prepared and Edited by

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Approved by

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PHASE I REPORT OF "DEVELOPMENT TECHNIQUES FOR POWER
PRODUCTION FROM MIXED FISSION PRODUCTS"

ABSTRACT

PREPARED AND EDITED

BY

D. L. EATON

This report describes the Phase I investigation into the various processes for the fixation of Mixed Fission Products as solids in order to determine the extent they could be utilized as heat sources for thermoelectric generators. Generators of up to ten watts can be designed and built with "state-of-art" thermoelectric materials and Mixed Fission Products soon to be available from the Idaho Falls calcination pilot plant. Mixed Fission Products from other processes and plants to be "on stream" in this decade will be capable of fueling practical generators into the kilowatt range using thermoelectric materials available in the same time period. A survey of the literature was made and the various national laboratories were contacted regarding current research and development efforts on waste fixation processes. The results of the survey are presented in this report along with brief descriptions of the most promising fixation processes. Studies showed that a wide range of power densities (from 0.002 to 0.2 watts per cubic centimeter) will be available from calcined fission product wasted.

An experimental program for the consolidation of low density, Idaho Chemical Processing Plant alumina type wastes is reviewed. Preliminary results indicate that densification factors of three to four are readily obtainable for such wastes. Bulk densities of 0.8 g/cc were increased to 2.9 g/cc by selective use of fluxes and cold compacting techniques. This means that power densities of up to .001 w/cc will be possible from waste materials in the Idaho Chemical Processing Plant tanks.

An experimental program for the evaluation of the high temperature life characteristics of bismuth telluride alloys is discussed. A program for the optimization of thermoelectric convertor design utilizing the diffuse heat from a Mixed Fission Product source is described, derivation of pertinent equations are presented and results of the study are discussed in this report.

Conceptual designs for thermoelectric generators utilizing diffuse fission product heat sources are described. Problem areas regarding the use of Mixed Fission Products in conceptual thermoelectric conversion device designs are discussed, with particular emphasis being placed on underwater applications.

In view of these recent technological developments regarding the power reactor program and waste disposal utilization of calcined wastes such as the Idaho Chemical Processing Plant high level waste stream now appears very attractive. With power densities of 0.0002 watts per cubic centimeter available now, and increases by factors of 50 to 1000 likely within the near future, thermoelectric power generators of 3 to 300 watts are within the realm of present day design and fabrication techniques. Higher power levels, up to kilowatts will be available with the inevitable increase in thermoelectric material efficiency.

FOREWORD

This is the final report of work performed during Phase I of Atomic Energy Commission Contract AT(30-1) 2605. This report covers results of progress made during the period of June 28th, 1960 through January 1st, 1961. This work was carried on under the auspices of the Aircraft Reactor Branch of the Atomic Energy Commission.

I. INTRODUCTION

Mixed Fission Products have been proposed for various purposes since the beginning of the "Atomic Age". To date none of these has been particularly successful for a variety of technical and economic reasons. Technological developments, however, now make possible the use of mixed fission products as heat sources for thermoelectric power generators.

As envisioned, the program for the development of a mixed fission product fueled thermoelectric generator would consist of three separate phases of work. They are:

Phase I - The investigation of the availability and physical, chemical and nuclear characteristics of various types of calcined nuclear wastes. The goal of this phase of the work is to determine the feasibility and extent to which such mixed fission products could be used in the conversion of waste heat to useful power via a thermoelectric convertor.

Phase II. - The development and evolution of technology and designs required to fabricate an electrically heated prototype of a mixed fission product fueled generator. The goal this phase of the program is twofold. One, to fabricate a proof of principle device in the 3 to 5 watt power range and two, to develop the necessary technique for the safe handling, fabrication and encapsulation of a mixed fission product heat source.

Phase III - The fabrication of a mixed fission product fueled generator for underwater applications. The goal of this portion of the program would be the "hot" demonstration of the ability to safely fuel and check out a thermoelectric generator containing a radioactive fission product heat source.

It is the purpose of this report to review Phase I of AT(30-1) 2605, the feasibility and parameter study of Mixed Fission Product thermoelectric generators.

The most important factor in the current proposed use of mixed fission products is their availability. Due to the large Atomic Energy Commission program aimed towards the concentration and fixation, in solid form, of the radioactive wastes from uranium and plutonium recovery processes, there will soon be large quantities of calcined M. F. P. available. Large scale development efforts leading to the accomplishment of this goal are currently being carried on at many Atomic Energy Commission installations. These include Oak Ridge National Laboratory, Hanford National Laboratory, National Reactor Test Station, Brookhaven National Laboratory, Argonne National Laboratory and others. Indeed, a complete pilot plant calcining facility has been constructed at the National Reactor Test Station and "hot" operations yielding mixed fission products at the rate of hundreds of watts (thermal) per day should begin sometime during the next year.

The reasons for this large program of concentration and solid fixation of long life radioisotopes appear to be twofold. Concentration in a solid form will reduce many elements of storage cost. Fixation, furthermore, will reduce the potential hazards markedly and permit the introduction of "accountability" procedures to radioactive wastes. Continuing plutonium production and the initiation of military and industrial power reactors makes these problems of ever increasing concern. The McKinney report of 1956 predicted conservatively that power producing reactors installed by 1975 would annually yield radioisotopes creating more than 50 megawatts of thermal energy. (1) Even though the amount of radioisotopes will decrease with time due to decay, continued production from old and newly installed reactors will more than offset this decrease, causing enormous annual storage and heat problems.

The increasing number of nuclear power reactors is also a contributing factor in the design and enhanced characteristics of the proposed utilization of Mixed Fission Products. Power reactors have higher uranium "burn up" than plutonium production and test reactors. Thus, radioactive waste streams from uranium and plutonium recovery processing of power reactor fuel elements will have energy densities that are orders of magnitude higher than those from other sources. This increased energy density will also be present in the solid fixed waste arising from these streams. Energy density, as described later, has a vital influence on the design, economics and utility of mixed fission product heat sources for electric power generators.

The last major factor leading to the current proposed use of mixed fission products is the recent revival in thermoelectricity. Although discovered by Seebeck in 1832, it has remained for modern understanding of the solid-state to make useful efficiencies possible. As demonstrated by recent Atomic Energy Commission developed devices, radio-isotopes provide ideal heat sources for thermoelectric generators. Mixed fission products, however, would not serve as a useful heat source for the type of thermoelectric generator designs demonstrated to date. The Thermoelectric Division of the General Instrument Corporation has recently evolved a design concept to make use of the diffuse heat from mixed fission products. Further analytical efforts, detailed later, verify this. It appears probable that mixed fission product thermoelectric generators can be built for terrestrial use up to the kilowatt level and still be of reasonable size (less than 6 feet in diameter). Specific sizes will be determined on analysis of the mission requirements.

II. INVESTIGATION OF MIXED FISSION PRODUCT WASTES

A. Criteria for Evaluation of Mixed Fission Product Wastes

At the beginning of the program certain criteria were set up upon which the evaluation of the various waste fixation processes and their respective products were based.

The first and most important factor for the evaluation of mixed fission products as heat sources in thermoelectric conversion devices is power density. Power density can best be defined as the thermal energy liberated per unit volume, or as the product of specific power (thermal watts unit wt.) of the mixed fission products times the density of the waste. The specific power of the waste fission products is dependent upon a number of factors. They are the source of waste products, 'burn-up' of fissile material, reactor life, chemical re-processing cycle, age of wastes and waste disposal methods employed. The density of the wastes is dependent on the chemical composition of the waste solution, the type fixation process employed and the degree of consolidation obtained by other processes such as cold compacting or casting into solid form.

There are two areas where power density affects the design of thermoelectric power conversion devices. First, the higher the power density of the heat source, the hotter it can become without incurring excessive extraneous heat shunt losses. This results in greater power output, since the power output is directly proportional to the temperature differential between the hot and cold junctions of the thermoelements. Secondly, the volume and cost of heat source encapsulation, as well as shielding, is exponentially related to power density.

Another important factor in the utilization of such wastes is their stability. In essence, this means the ability of property of the Mixed Fission Products materials to resist changes in their chemical or physical composition due to external or internal factors. This includes solubility in various solvents, radiation degradation, thermal decomposition, etc. A high degree of stability means a greater degree of safety regarding the ultimate use of mixed fission products. It may also mean that higher hot junction temperatures and, therefore, greater thermoelectric conversion efficiency can be obtained due to increased allowable center line temperatures resulting from greater inherent thermal stabilities. Such factors regarding the stability of the products of the various fixation processes may spell the difference between their success and failure in various applications.

Of vital importance regarding the use of Mixed Fission Products are the physical, chemical and nuclear characteristics of the calcined wastes. Of specific interest are the melting point, thermal conductivity, specific heat, chemical activity, vapor pressure, particle size, chemical composition., gamma spectrum and dose rates of the calcined waste products. These properties are of particular importance in the design of the heat source in order to determine thermal gradients, center line temperatures, possible internal pressure buildups, shielding requirements and methods of containment. Since knowledge of these fundamental properties is a prerequisite for the design of the heat source and the thermoelectric generator, one of the major efforts of this program was the accumulation of data regarding the physical characteristics of the mixed waste products.

Also of important consideration regarding the utilization of mixed fission products is the physical form of available calcined isotope wastes. It is of particular importance regarding the handling, consolidation and encapsulation of

these materials. From the present survey, it is apparent a wide variety of forms ranging from that of a fine powder with insulating properties to that of a cast solid within a stainless steel container may be available. Of course it is obvious that the latter case is much more desirable from the standpoint of both handling and power density and, if possible, one should strive to obtain mixed fission products in this form.

Regardless of all the factors previously mentioned, the ultimate utilization of any product depends on the availability of a given product, mixed fission products being no exception. At the present time there exists no process which is on stream and producing calcined mixed fission products. However, the Idaho Chemical Processing Plants' fluidized bed waste calcination pilot plant is in being, and should be on stream sometime in 1962. This plant is capable of calcining from forty to sixty gallons of waste fluids per hour. This results in a possible energy yield of 40 watts per hour from the solid calcined wastes. Within the next five years several other Atomic Energy Commission national laboratories may be producing calcined waste fission products of even greater potential value, if current research (described later) is continued at its present rate. These new sources of mixed fission products offers power densities of ten to one thousand fold that of present Idaho Chemical Processing Plant - Mixed Fission Products power densities. If the reactor program continues to expand at rates predicted by McKinney, Culler and Lane (1,2,3,) there will be ever increasing amounts of mixed fission products available for use as heat sources. In fact it is predicted that by the year 2000 there will be 376,000 megacuries of total mixed fission product activity.(2).

B. Description of Mixed Fission Products Fixation Processes

During the course of the investigation of various processes for the fixation of mixed fission products as a solid, several things became apparent about the government waste

research program as a whole. One, motivated by the vast problems anticipated concerning future disposal and control of high level activity wastes from our power reactor program, the U.S. Atomic Energy Commission is presently sponsoring major programs in almost all of its national laboratories leading to the fixation and disposal of reactor wastes. The basic philosophy of the major effort in this vast program is concentration, containment and accountability. Two, basically all the processes can be subdivided into two categories, either those involving concentration and containment or dilution and fixation of the mixed fission products in some stable medium.

Since power density was of utmost concern regarding the utilization of these waste fission products, major emphasis was placed on those processes aimed at concentrating present wastes into relatively inert solid forms. Primary research and development centers of such processes are Oak Ridge, Argonne, Brookhaven, Hanford and Idaho Falls. The principal processes for the concentration and fixation of mixed fission products currently under development are.

1. Fluidized Bed Calcination
2. Radiant Heat Spray Calcination
3. "Pot" Calcination
4. Ball Kiln Calcination

There are numerous other investigators studying methods incorporating mixed fission products in ceramic, glass or mica structures (7,8,9) or developing schemes for the chemical separation of specific isotopes in crude form (90-95% purity). (10,11,12,13) The latter, methods for crude separation of specific radionuclides, have a large potential merit for utilization in thermoelectric conversion devices. The techniques were briefly investigated and will be discussed in some detail in this report.

The products of the reactions are granular solids, primarily aluminum oxide of one form or another.

Following promising test work at Argonne, The Phillips Petroleum Company undertook the development and adaptation of the process for large scale concentration and calcination of "hot" reactor wastes. As a result, today there exists a multimillion dollar engineering test facility at the National Reactor Testing Station at Idaho Falls, Idaho. This facility, after necessary checkout experiments, will be ready to go on stream sometime in 1962 and is capable of turning out calcined mixed fission products at the rate of 50 pounds per hour.

This facility, as designed, is an experimental test (15) facility which should be extremely versatile and capable of handling a variety of feed solutions. The test facility consists of a series of heavily shielded hot cells housing the basic components of the fluidized bed process. The basic components of this facility consist of a fluidized bed calciner and its auxiliaries, an off-gas treating system and a solids storage unit. They are designed to process aluminum nitrate type wastes which have undergone a 200 day decay period after discharge from the reactor. In practice, however, they will first be used to process about 1,000,000 gallons of existing waste solutions.

The design basis for this facility as outlined in the Fluor Corporation, Title I, design report (14) is as follows:

Feed Solution

1. Rate	60 gph for 300 days per year.
2. Age	200 days out of reactor for design of process facilities, 200 years out of reactor for design of solids storage
3. Fission Products	Fission product distribution assumed to be same as given in PTR-86 for MTR-type fuel elements with allowance made for radioactive decay.

1. Fluidized Bed Calcination Process (Figure 1)

At the National Reactor Testing Station in Idaho there is a chemical processing plant (I.C.P.P.) for the recovery of fissionable material from irradiated enriched uranium fuels. At the present time high level activity wastes, principally from Materials Testing Reactor type fuel elements and other low 'burn-up' research reactors, are stored in the form of acidic aluminum nitrate solutions in underground stainless steel tanks at a cost of \$2.40 to \$2.62 per gallon (5). Following the basic interests of the Atomic Energy Commission the Phillips Petroleum Company is working on a program aimed at the reduction and fixation of existing and future waste products by a fluidized bed calcination process. The development of the fluidized bed calcination process was influenced by earlier work: carried out by the Argonne National Laboratory (6) in relation to the conversion of simulated and spiked waste solutions to the oxide form by a fluidized bed calciner.

Briefly, the process consists of the conversion of nitrate and about 1% fission products, to their respective oxide compounds. Primary chemical reactions taking place during this thermal decomposition are. (14)

Minor constituents in the feed undergo conversion as follows:

Fission Product Nitrates $\xrightarrow{\Delta}$ FP oxides (100% conversion assumed)

	Quantity of fission products, their specific heat liberation and activity have been increased proportionately to be consistent with the criterion of 25 Btu (Hr.)-(Lb) heat liberation of solids produced from 200 day waste.		
4. Specific Activity	1400 curies gal. as calculated from the assumed fission product composition.		
5. Heat Liberation	21.5 Btu Hr.-Gal. (Consistent with assumed fission product composition of feed liquid).		
6. Specific Gravity	1.32 at 20°C.		
7. Composition	<u>Component</u>	<u>Molarity</u>	<u>Wt%</u>
	Al(NO ₃) ₃	1.80	29.05
	NaNO ₃	0.01	0.06
	Hg(NO ₃) ₂	0.01	0.25
	HNO ₃	1.84	8.78
	H ₂ O		61.86

Calcination Section

1. Calciner Diameter	Direct ratio scale-up from Phillips pilot plant rate of 100 ml min. in 6" Sch. 40 pipe calciner.
2. Fluidizing Air Rate	2.24 ft. sec. superficial velocity in calciner.
3. Calcination Temperature	400°C. (Additional heat transfer surface provided in calciner heater to permit 40 gph feed rate at 500°C.).
4. Fission Product Volatility	None except for ruthenium at 400°C. calcination temperature. 99% of ruthenium in calciner assumed to leave in off-gas.

Off-Gas Section

1. General Ruthenium Behavior	No allowance has been made anywhere in the design for possible plating out of ruthenium on equipment or piping.
2. Ruthenium Adsorber Efficiency	99.9% ruthenium is removed by the adsorbers after repeated cycles of on-stream and regeneration operation. Residual ruthenium remaining on adsorbers after regeneration assumed to be negligible with respect to adsorber performance in subsequent cycles.

3. Solids Ruthenium Content	1 per cent of total in calciner feed.	
4. Maximum Solids Temperature	Limited to 400°C. to prevent possible volatilization of fission product.	
5. Thermal Conductivity of Solids	$K = 1.39 \times 10^{-4} + .07 \text{ Btu/(Hr)}$
(Ft. ²) (°F./Ft.)	
6. Fission Product Composition	Fission product nitrates assumed to be completely calcined to equivalent oxides	
7. Particle Size Distribution	<u>Tyler Mesh</u>	<u>Weight Fraction</u>
	14	0.190
	14-20	.274
	20-28	.277
	28-35	.191
	35-60	.063
	60-100	.003
	-100	.002
		1.000
8. Solids Temperature	Determined from assumption that all radioactive emanation energy is liberated within and absorbed by the stored solids.	

Operationally the process (as illustrated in Figure 1) can be best described in the following manner:

The highly active feed solution of mixed fission products and other inert materials is sprayed into a heated bed (350-500°C) of fluidized alumina particles where the water is vaporized off and the nitrate compounds are thermally decomposed to volatile nitrogen oxides; leaving behind the cation portion of the nitrate compounds incorporated in granular alumina particles. As the bed builds up, the excess particles overflow into a take-off duct and are blown into cooled, solid storage bins. The fluidizing medium is preheated, fresh air. The necessary heat for the fluidized bed calcination of the solutions is supplied by an oil fired NaK heat exchanger immersed in the bed of alumina particles. The contaminated off gases, transport and fluidizing air are decontaminated by dry cyclone separation, water scrubbing and filtration before they are rejected to the atmosphere through a stack.

FLUIDIZED BED CALCINATION PROCESS

The process and equipment just described have all been thoroughly tested and successfully operated on a smaller, "cold" scale for a sufficient length of time to demonstrate the feasibility of this project. The properties of the calcination products from this process will be discussed in a later section of the report.

But for such uncontrollable factors as labor relation problems and the steel strike, this test facility would have been operational in 1960. At the present time, the equipment has been completely installed, and is now being checked out. The process will be "dry run" within the year and anticipated processing of (hot) reactor wastes is planned to start sometime in 1962. Utilizing an existing sampling station and Idaho Chemical Processing Plant hot cells, it would be possible to start source fabrications using Idaho Chemical Processing Plant wastes as soon as the facility goes on stream.

2. Radiant Spray Calcination Process (Figure 2)

While a considerable amount of effort has been spent on the development of fluidized bed calcination techniques just discussed, several other promising techniques have been developed simultaneously by other investigators. Notable among these has been the radiant spray calcination process.

Initially the work started at Oak Ridge (17) with the spray calcination of uranyl nitrate. Gauvin, (18) of the Pulp and Paper Research Institute of Canada also developed a similar process for the pyrolysis of sulfite liquors. Since then Allemann and Johnson (19) of Hanford have adapted these basic methods to the radiant heat-spray calcination of simulated Purex IWW feed solutions.

Basically the chemistry of the process is very similar to that of the fluidized bed process described; in fact the same general reactions occur (see equation below), the only difference being the specific products of the reaction which are characteristic of the starting feed materials. In the case of Purex IWW waste solutions, the main products of the thermal decomposition are iron oxide, aluminum oxide and sodium nitrate.

Where M is any cation such as Fe^{+3} , Al^{+3} , Na^{+1} etc. and X equals the valence of the cation, in the case of Purex IWW waste solutions, the main products of thermal decomposition are as noted above.

The process equipment as described by Allemann (19) for radiant heat spray calcination of simulated reactor wastes consists essentially of -

1. a feed make-up auxiliary system
2. radiant spray reactor
3. off gas clean up system
4. auxiliary pot kiln

Schematically the apparatus is shown in Figure 2. The atomized feed solution is introduced at the top of the pre-heated column by a pneumatic nozzle. As the droplets containing the fission products fall down the column, the water is flashvaporized off, then the particles are dried and finally calcined to oxide compounds. Subsequently, the solidified particles may either be withdrawn for packaging or be melted down to form a dense clinker. The off gases are condensed, neutralized and filtered being before being released. The experimental spray column is heated between 800 and 850°C by a rather novel method; by passing a low voltage, -high

RADIANT HEAT SPRAY CALCINATION PROCESS

C
P
U

current through the column, the column, itself is used as a resistance heater. A number of different simulated feed solutions have been successfully calcined in this manner and their properties will be reported in a subsequent section of this report.

Initial experiment at Hanford were performed on 3" diameter, 3' long column. Since then a larger apparatus, 8" in diameter and 10' long, has been constructed, and is now being used to obtain engineering data concerning the process. This latter system has a capacity of about one gallon per hour and is capable of being used with radioisotopes tracers for the study of process variables.

This calcination and fixation process has been developed to its highest degree by the Hanford Laboratories who at the present time are evaluating it along with "pot" and fluidized bed calcination techniques. Hanford felt that no matter which process was selected, it was a distinct possibility that any of these processes could be scaled up, a pilot plant constructed and be put into production by 1965 or 1966. (20) The Hanford IWW wastes calcined by any of the proposed methods would offer a tenfold increase in power density over Idaho Chemical Processing Plant process wastes.

3. 'Pot' Calcination (Figure 3)

Another developmental fixation process which appears very attractive at this time is the "Pot" calcination techniques originated by the Oak Ridge National Laboratories and now being developed by both Oak Ridge and Hanford. The calcination reactions are similar to those already described. Liquid and slurry wastes are thermally decomposed into solid fission product oxides and 'off-gases' of nitric and nitrous oxides and steam.

In essence the process is a very simple one. In fact its simplicity is one of the things that makes it so attractive as a processing technique for the fixation of "hot" reactor wastes. Processing of wastes by this method involves the following process equipment:

- a) A feed make-up and metering system
- b) A furnace and stainless steel "pot"
- c) An off gas decontamination system
- d) An auxiliary welding system

The process as illustrated in Figure 3 involves the metering of feed solutions into a heated stainless steel retort. As the solution is heated up to operational temperatures (800-900 C) it is first concentrated to a heavy sludge, then the sludge is dried and finally it is thermally decomposed or calcined. This process is repeated until the pot is filled. The feed metering system is then disconnected and the pot is sealed by welding a lid on it. The pots are then removed and stored in appropriately shielded storage areas. This process is particularly adept at handling a great variety of feed solutions of varying specific activities. In addition, it reflects to the greatest extent the optimum waste management philosophies of the Atomic Energy Commission.

Initially, studies of this process were carried out on a very small scale by Oak Ridge National Laboratory. Since then the experimental process equipment has been modified and elaborated on by Oak Ridge until today it consists of a 8 inch diameter retort, seven feet long, housed in a low level shielded hot cell. It is the opinion of J. Blomeke (21) that this size will closely approximate full scale pilot plant equipment planned for initiation of construction at National Reactor Testing Station pilot plant facility in 1962. As previously mentioned, the Hanford Laboratory has also been very active in the development of this process.

6.1. 21

POT CALCINATION PROCESS

4. Ball Kiln Calcination (Figure 4)

In addition to the three processes already described, there is a fourth direct fixation process for calcination and concentration of reactor wastes which has been under development for the past five years at Brookhaven National Laboratory (22). This is a rotary ball kiln process which is depicted in Figure 4. Oak Ridge National Laboratory, working in conjunction with Dr. Hatch at Brookhaven National Laboratory, has developed this method to the point where the process is now planned to be scaled up for pilot plant operation along with the pot calcination process at the National Reactor Testing Station in the very near future.

The process chemistry is similar to all those previously described. However, the manner in which the waste solutions are converted to solid oxides differs from the others in that the reaction takes place in a rotary ball calciner. As the solution is evaporated, dried and calcined; it is also ground into a powder of uniform characteristics. The exact particle size and composition depends on the average dwell time in the calciner and the temperature which the material attains. The process equipment will consist of a feed handling system, the rotary calciner, gas decontamination facilities and "hot" material storage bins or containers.

5. Ceramic Fixation Processes

In addition to the processes for the direct fixation of mixed fission products as calcined oxides, just discussed, there are numerous other processes being investigated which attempt to solve the long term waste storage problem by incorporating the mixed fission products in various mineral, glass or ceramic structures. In the incorporation of Mixed Fission Products into ceramic structures, it is hoped that a highly stable structure will be

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BALL KILN CALCINER

FIGURE 4

achieved which will require the minimum amount of surveillance and maximum degree of stability.

To mention briefly but a few of the fixation methods being investigated: the Russian's (23), the British (24) and Brookhaven National Laboratory (28) have studied the absorption and fixation of radioisotopes, on montmorillonite type clays. The Canadians (7), have looked extensively at the incorporation of Mixed Fission Products in nepheline syenite glasses and Hanford has investigated the formation of glassy products from IWW wastes. The use of synthetic mica to incorporate fission products into a stable structure is being studied by the French (25) and John Hopkins University (26). Massachusetts Institute of Technology (27) is studying the feasibility of incorporation aluminum bearing fission wastes into ceramic type glazes.

While there is much research being carried on regarding processes for the incorporation of Mixed Fission Products into synthetic mineral, glass or mica structures, they are of little or no interest with regards to their utilization as heat sources for thermoelectric convertors because they further dilute an already diffuse heat source.

6. Crude Isotope Separation

Another technique proposed to help the waste disposal dilemma is the separation and recovery of the long life fission products. However, as Moore and Burns (32) have so aptly pointed out, this will only help the thermal problem in the storage of Mixed Fission Products and not assist in the storage problem itself. To reduce such large volumes of wastes to drinking water tolerances for low level dispersal is economically unfeasible since chemical decontamination factors of 10^6 would be required. Such processes do, however, offer the promise of readily available, high power density heat sources at comparatively low costs. Because of the potential importance of crude separation processes, they will be discussed in more detail.

As a result of the Atomic Energy Commission's radioisotope programs, today, there exists a vast amount of experience regarding separation and recovery of radionuclides. Major centers of research regarding the development of separation processes have been the national laboratories, in particular Oak Ridge National Laboratory, Hanford and Idaho Chemical Processing Plant. A number of schemes for the bulk separation of fission products elements have been developed and proven out on a pilot plant scale. Fortunately, emphasis has been placed on the long-lived fission product elements which are potentially good heat source materials. Of current interest as heat sources for thermoelectric convertors are cerium-144 strontium-90, cesium 137, promethium-147 and the actinide rare earths. It is not however, within the scope of this report to discuss in detail these processes, but merely to point out their significance.

Until recently, emphasis regarding the use of radioisotopes as heat source materials have been towards space-power applications. These applications required pure radioisotopes in order to obtain maximum power densities and minimize weight. Past experience has shown that specifications for such heat sources were difficult, if not impossible to meet. Purities of 90 to 95 percent were not acceptable.

However, terrestrial applications of radioisotopes in thermoelectric convertors do not necessarily impose such purity restrictions. The main requirements for their use in these applications are availability and power density. It has been adequately demonstrated by Hittman (33) and others (34,35) that Sr-90, Ce-144 and Pm-147 have adequate power densities for use as thermoelectric heat sources. Therefore, the main problem regarding the use of separated radionuclides is their availability.

In the past, the availability of separated isotopes from Oak Ridge's fission-product pilot plant (F-3-P) facility has been somewhat limited. Recent technological developments permitted the Hanford Laboratories (10,30) to alleviate the availability problem regarding large scale use of separated radioisotopes. Utilizing unused Purex "head end" processing equipment and newly developed double sulfate and peroxy-acetate separation processes, they have demonstrated the capability of supplying Sr-90, Ce-144 and Pm-147 with purities of at least 90 percent in megacurie quantities. A flow sheet for this separation scheme is shown in Figure 5.(10) Basically, the process for the separation of these radionuclides is as follows:

Strontium and the rare earths are separated from the bulk of the waste materials as double sulfate precipitates. The rare earths are separated from the strontium by digestion and precipitation as the oxalates. Cerium is then separated from the trivalent rare earths by precipitation from a hydrogen peroxide acetate buffered solution. Highly purified promethium is isolated from the other trivalent rare earths by EDTA ion-exchange chromatography.

C. Characteristics of Calcined Mixed Fission Products Wastes

1. Composition of Mixed Fission Products Feeds and Calcined Products

The composition of the calcined Mixed Fission Products depends primarily upon starting feed materials and secondarily on the type and conditions of the calcination process employed. Feed materials of course are dependent on the type of fuel element reprocessed and on the recovery processes utilized. Typical compositions of starting feed materials are shown in Table I.

CRUDE RADIOISOTOPE RECOVERY FLOW SHEET

TABLE I

TYPICAL COMPOSITIONS OF REACTOR FUEL ELEMENT PROCESSING WASTES

TYPE FUEL ELEMENT WASTE	MOLAR CONCENTRATION									
	H	Al	Fe	Cr	Ni	Zr	Hg	NO ₃	SO ₄	Na
<u>Aluminum</u>										
a) (MTR) (acid)	0.6-1.3	1.6	0.005	-	-	-	0.01	5.5-6.5	-	0.1
b) (MTR-neut)	0.1	1.6	0.001	-	-	-	0.01	7.0	-	0.1
<u>Stainless Steel</u>										
<u>Zirconium</u>										
	0.8-2.0	0.8	-	-	-	0.5	-	2.3-3.5	-	-
<u>Purex 1WW</u>										
a) acid	0.5-2.2	0.1	0.5-0.6	0.02	0.01	-	-	0.5-3.0	1.0-2.6	1.0-2.5
b) neut.	-	0.1	0.5	0.01	0.006	-	-	7.5	0.5	7.5
c) HCHO killed	0.5	0.1	0.75	0.04	0.020	-	-	0.95	1.0	0.5

During the process of calcination, the feed materials are primarily decomposed to the oxide or sulfate compounds. Typical examples of calcined product compositions are:

a) Idaho Chemical Processing Plant - Fluidized Bed Calcine Product

Alpha alumina (Al_2O_3)	- - - - -	-12%
Amorphous "	- - - - -	-Approx. 86%
Nitrates	- - - - -	-0.97 millimoles/g
Residual Impurities of HgO		

b) Oak Ridge National Laboratory - Pot Calcination

Fe_2O_3	20.6%
NiO	0.4%
Cr_2O_3	0.4%
Al_2O_3	2.6%
Na_2SO_4	66.0%
CaSO_4	7.0%
CaO	2.9%

The exact composition of any specific calcined Mixed Fission Product cannot be predicted with any degree of accuracy due to the wide variations in starting feed materials. However, thermochemical studies indicate that only residual amounts of nitrates will remain after calcination and that in the case of wastes arising from aluminum clad reactor elements the calcination product will be composed mainly of oxides. A mixture of oxides and sulfates will result from "Purex" and stainless steel clad fuel element wastes.

2. Chemical Stability

By fixation of Mixed Fission Products as relatively stable solids, one decreases the hazards associated with liquid storage of high level wastes in that the mobility of the

fission products is decreased. However, no process for the fixation of radioactive wastes has yielded products so stable that they are completely inert to all environmental conditions.

In general, the products of the various fixation processes are quite stable with respect to dry air. Air-borne contamination is minimized by the "in process" vaporization of the more volatile radionuclides and incorporation of the remaining radioactive constituents into solid forms during calcination.

The thermal stability of calcined materials is good up to original calcination temperatures. Beyond these temperatures residual nitrates and other products of thermal decomposition may be driven off. It is for this reason that low centerline source temperatures are desirable and that leakproof encapsulation is necessary.

Calcined solids of aluminum type wastes are fairly insoluble in water, while Purex and stainless steel type wastes with high sulfate contents are very soluble. However, none of the products of any of the calcination or glass fixation processes satisfy standard health physics requirements regarding ground water dispersal. Solubilities of cesium and strontium range from 0.04% to 11%, respectively, for M.F.P. incorporated in the best glasses and calcined IWW Purex wastes (39). Chemically speaking, the calcined products are soluble in both acids and bases. The degree of solubility depends on the chemical composition of the calcined waste being tested.

At the present time the radiation stability of calcined Mixed Fission Products is unknown. However, it is believed that any residual nitrates remaining after calcination will be decomposed to gaseous nitrogen compounds and oxygen by the intense radiation fields

present in massive quantities of Mixed Fission Products (41). This problem might be alleviated if "getter" materials can be incorporated into the heat source design.

Because of the solubilities and possible gas evolution exhibited by calcined Mixed Fission Products, containment will always be a requirement. However, by decreasing the chemical activity of the original waste solutions and converting them to a solid, use of cheaper storage container materials is possible. In addition catastrophic hazards associated with sabotage, fire, explosion or other natural phenomena such as earthquakes are greatly reduced by the immobilization of the fission products as solids.

3. Physical Properties

The information available at the present time regarding the physical properties of the calcined products from the various fixation processes is quite meager. Generally speaking only melting points, densities and thermal conductivities were available. Data which were available at the time this report was written are presented in Table II. The values for the various properties vary considerably, as do the feed materials and conditions of calcination. Melting points can be correlated to starting feed materials and calcination temperatures. Density, thermal conductivity and particle size are related to the calcination process employed, feed materials used and calcination temperature attained. A wide range of densities and particle sizes or cake porosity is not uncommon for any of these experimental processes at this time. Figure 6 illustrates this point by showing the variation in particle size produced by the various calcination processes. Number one (1) in Figure 6 is Idaho Chemical Processing Plant calcined, Materials Testing Reactor type aluminum waste, Number two (2)

TABLE II

PHYSICAL PROPERTIES OF MIXED FISSION PRODUCTS CALCINED WASTES

Process Description	Calcination Temp (°C)	M.P. (°C)	Density (g/cc)	Thermal Conductivity Btu/hr/ft/°F	Particle Size (Mesh)
I.C.P.P.) Fluidized Bed (Aluminum type waste)	400°-500°	1800	0.6-0.9	0.08-0.30	-28 + 35 37% -35 + 60 58% -60 + 100 5%
(HW)-Fluidized Bed (Purex 1WW)		800°-1000°	1.1-1.3	0.08-0.15	-20 + 100 80% -100 5%
(HW)-Spray Calcine	850°				
a) (Purex 1WW)	"	800°-1000°	0.8-0.9	.05-0.13	avg. 25 microns
b) (TBP - 25)	655°	800°	0.1	.03	
c) (item b - melted)		800°	2.17		Dense glass
ORNL "Pot" Calcine (Purex 1WW)	900°	800°-1000°	1.0-3.0	0.2-2.4	Solid cake, consistency varies
HW Pot Calcine (Purex 1WW)	850°--900°	800°-1000°	2.0-3.0	0.18-0.65	Same as above

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is a simulated Purex waste processed by the Hanford spray calciner (the darker color is due to the high iron content) and Number three (3) in Figure 6 shows the variation in different type pot calcined products (notice the variations in porosity).

While the data obtained regarding physical properties was inadequate for specific heat source designs it did furnish a basis for the conceptual design and parameter studies.

4. Nuclear Characteristics

Knowledge of the nuclear characteristics of the calcined fission product wastes is just as essential in their utilization as heat sources for thermoelectric convertors as it is in design of storage facilities for their containment. The nuclear properties of the various calcined fission product wastes are dependent upon the fission fragment yields during irradiation and the fractions of the individual nuclides present at any time after irradiation. Once fission fragment yields have been calculated, gamma and beta energy spectrums, activities, shielding requirements and heat generation values may be obtained.

Figure 7, taken from the Fluor Design Report (14), illustrates typical total activities resulting from Materials Testing Reactor aluminum process wastes at various times out of the reactor. The total gross activity for Mixed Fission Products is the summation of the specific activities of individual radionuclides, as can be seen from Figure 7. Similar curves must be calculated for any different type Mixed Fission Product contemplated for use as a heat source material. For comparison, activities of approximately 180,000 curies per pound of calcined oxides can be expected from fuels having hypothetical burn-ups of and 10,000 MWD/TU at a 33 MW/T power level. These fuel burn-ups

SPECIFIC ACTIVITY FOR ICPP CALCINED WASTES

correspond to anticipated future power reactor fuels.

Assuming the same hypothetical type fuels, burn-ups and a cooling off period of two years; a comparison was made of the power densities available as a function of time. This comparison is made in Figure 8. The topmost curve represents the energy densities available from future power reactor fuel processed into Mixed Fission Product calcined wastes. The lower dotted line corresponds to power densities obtainable from present day fluidized bed calcined Idaho Chemical Processing Plant aluminum type reactor wastes prior to any densification steps.

It is obvious that there will be a wide range of energy densities available within the near future. Some of the higher powered Mixed Fission Products wastes may even approach the specific power of separated, crude radioisotopes such as Sr-90.

D . Discussion

Each of the fixation processes currently under study and described within this report has certain inherent advantages and disadvantages. However, it was not the intended purpose of this study to discuss these except from the viewpoint of whether or not they increase or decrease the end product's desirability as a heat source material in a thermoelectric generator.

From this standpoint, of the four principle direct calcination processes investigated, the "pot" calcination approach is the most desirable. It offers the following advantages over the other methods:

COMPARATIVE POWER DENSITY vs. TIME

1. Containment

The material is calcined within its own container and can be used without further processing or encapsulation as a thermoelectric heat source. This minimizes handling and provides a permanent storage vessel without any increased processing costs.

2. Higher Densities

The evaporation of waste solutions in this manner results in the formation of a solid cake; with certain feeds, densities of 2 to 3 g/cc are achievable as compared to less than one gram per cubic centimeter for ball mill, spray and fluidized bed calcination process.

3. Increased Thermoconductivity

Higher densities means increased thermal conduction of available heat; subsequently, centerline temperatures are lowered.

4. Versatility

The process itself is extremely versatile. It is capable of handling a variety of waste feed solutions and different size cylinders. This is extremely important; in that, knowing the specific power density of the calcined feed, one can select various geometric container configurations for specific missions without any further modifications to process equipment or procedures.

5. Economy

The fact that the process provides a sealed source minimizes the potential users costs. Costs may be reduced to that of providing a portion of the container cost.

While the "pot" calcination method for the fixation of Mixed Fission Products provides a more desirable end product, its availability is another matter. Current plans for "hot" pilot plant studies of the pot calcination method indicate it will be at least 1963 or 1964 before "hot" calcined wastes from such a process could be obtained. Even then, the output capacity may be somewhat limited. From the viewpoint of availability, the Idaho Chemical Processing Plant's fluidized bed calcination process is the

most attractive of those discussed. At this time the pilot plant facility is complete, cold-run tests will be completed within the year and then the facility will go on stream. Output capacity of this process is estimated at forty to fifty pounds per hour of calcined solids which corresponds to more than 40 watts (thermal) per hour. Utilization of Idaho Chemical Processing Plant calcined Mixed Fission Products is possible therefore at least two years ahead of any other process.

Ceramic incorporation processes for the fixation of fission products wastes are of little or no interest regarding the utilization of Mixed Fission Products. They all have the tendency to grossly dilute an already diffuse heat source and increase processing costs without ever achieving stable structures which require no further containment for terrestrial environments.

Crude separation processes for specific radioisotopes are of great interest regarding their use as potential heat source material and in the long run may well be the most economic way of accomplishing a given task.

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III. CERAMIC STUDIES OF SIMULATED IDAHO CHEMICAL PROCESSING PLANT WASTES

A. Objectives of Program

In consideration of the utilization of calcined fission product waste in thermoelectric power devices, there arises the problem of densifying the calcined waste. As described earlier, a high power density leads to more efficient heat source. As part of this Phase 1 feasibility study, we have conducted a brief investigation of various means of increasing the density of a simulated, non-radioactive aluminum oxide-type waste as supplied by the Idaho Chemical Pilot Plant. We hoped to determine the ultimate density which might be attained. As a result of this brief investigation, densities were increased by a factor three over as received materials. By the selective use of ceramic fluxes, densities of 2.9 g/cc or 59 per cent effective density (theoretical density of simulated Idaho Chemical Processing Plant waste only) were achieved.

The limitation of time has dictated that this investigation be one of a preliminary nature and that the experimentation with various techniques was necessarily somewhat superficial. Likewise, some techniques requiring specialized equipment could not be investigated in this phase due to the lack of time necessary for obtaining such equipment.

B. Description of Calcined Idaho Chemical Processing Plant Simulated Wastes

The Idaho Chemical Processing Plant simulated fission product materials used in this study program has the following characteristics:

Alpha Alumina Content	12%
Amphorous Alumina Content	88%
Residual Impurities	NO ₃ , NaOH, HgO
Particle Density	3.26 g/cc
Bulk Density	1.095 g/cc
Particle Size Distribution	-20 +28 0.6%
(Mesh)	-28 +35 36.7%
	-35 +60 57.6%
	-60 +100 5.1%

Maximum Calcination Temp. 500°C.

The actual calcined product will closely approximate the above characteristics with the exception that it will be extremely radioactive and will have to be handled remotely in a hot cell. This must be kept in mind in future developments of methods for consolidating the simulated wastes, since any process developed will ultimately have to be adapted to hot cell working conditions.

C. EXPERIMENTAL PROGRAM

At the onset of this Phase of the program an outline of the intended program was made to serve as a guide during the investigation. That outline is shown below and, in general, it was followed as far as time and equipment limitation permitted.

I. Cold Compaction of "As Received" Material

- A. Determine effect of compacting pressure vs. density
- B. Study the effects of binders, plasticizers and lubricants on density
- C. Determine effects of calcining and sintering on density

II. Particle Size Optimization Effects of Calcined Wastes

- A. Determine optimum particle size for maximum density
- B. Study combined effect of particle size and
 - 1) compacting pressure vs. density
 - 2) binder, plasticizers and lubricants vs. density
 - 3) calcining and sintering vs. density

III. Investigation of Slip Casting Techniques

- A. As a method of fabricating dense bodies
- B. As a means of densifying as received materials for other consolidation methods.

D. RESULTS

1) Cold compaction of "As Received" Materials

Early in the studies of cold compacting the "as received" materials, it was found that the low bulk density and the amorphous nature of the calcined Idaho Chemical Processing Plant simulated wastes presented serious problems in their consolidation to high density bodies. Experiments on this material form were not pursued any further than necessary. For the record, however, the following procedure is noted:

As received, granules were compacted in a one-half inch diameter cylindrical steel die, with top and bottom punches compressed between the platens of a "Carver"-type laboratory hydraulic press. Pressures up to 70 t.s.i. were used to produce discs approximately 1/2" thick. Measurements of compacted densities were made on these discs. Table III contains the description of representative samples and their densities.

As will be noted from a comparison of the preceding table and the bulk density of "as received" materials, that densities of such materials have not been increased significantly by either the cold compaction or a combination of cold compacting, binders and sintering.

2) Particle Size Optimization of Calcined Wastes

Because of the results noted above it was felt that if appreciable beneficiation of densities of such materials were to occur, the nature of the starting materials would have to be altered. Optimization of the particle size was felt to be the answer to this problem. By ball milling the "as received" materials and classifying them, one can increase the particle density and maximize the packing density.

As a result, all subsequent experimentation on simulated Idaho Chemical Processing Plant calcined wastes incorporated a preliminary milling operation. This reduced the

TABLE III

SAMPLE NO.	PROCESSING DESCRIPTION	COMPACTED	OBSERVATIONS
		DENSITY GMS/CC	
1	MATERIAL EXACTLY AS RECEIVED	1.09	DIFFICULT EJECTION OF PRESSED PIECE FROM DIE
1A	SAME AS SAMPLE NO. 1 EXCEPT FIRED AT 1250°C FOR 3 HOURS AT PEAK TEMPERATURE	1.15	* SEE NOTE BELOW
2	MATERIAL AS RECEIVED, MOISTENED WITH 6% WATER FOR PLASTICIZING	1.19	MATERIAL HAS EXTENSIVELY HIGH AFFINITY FOR WATER
2A	DISCS FROM SAMPLE NO. 2 CRUSHED AND RESULTANT POWDER (-10 MESH) LUBRICATED WITH 1/8% BARIUM STEARATE	1.29	

* NOTE: IT WAS OBSERVED IN THIS AND ALL SUBSEQUENT EXPERIMENTS WHERE A FIRING TEMPERATURE EXCEEDED APPROXIMATELY 1100°C, THAT THE DISCS EMERGED WITH CONSIDERABLE CRACKING, CONSISTING OF A FINE NETWORK OF "CHECKER-BOARD"-TYPE CRACKS.

calcined granules to a fine powder. The milling procedure followed was: A "Bacilli" (.41 Gallon) size laboratory jar mill containing a 2/3 charge of 3/8 inch diameter porcelain balls was used. The Batch consisted of 500 grams of Idaho Chemical Processing Plant product, 700 grams of water and .5 grams of Polyfon T. Milling times of 6 hours were used in initial experiments, however, subsequent particle size analyses indicated the need for a longer milling period and a time of 18 hours was used on subsequent experiments. Particle size measurements were made by a modification of the hydrometer method described by E. E. Bryant and G. H. Johnson (33). In conjunction with the milling of this product, it was found that after a degree of fineness had been achieved, the material required continued agitation to retain it in a slurry form. If allowed to stand for any appreciable period, the water became absorbed in the solid, forming a congealed mass. This affinity for water necessitated the emptying of mills immediately upon completing of the prescribed milling time, before the above-described "setting-up" could take place.

For the experiments where an inorganic additive was included, primarily as a ceramic fluxing agent, the addition was made directly to the jar mill after the prescribed grinding time. The milling was allowed to continue an additional two hours to insure intimate mixing of the additive.

The material after discharge from the jar mills, was dried in trays in a laboratory oven. The resultant dry cake was extremely soft and was readily broken up into fine powder by being pushed through a 60 mesh screen. In this powder form, the material was placed in a laboratory "dough"-mixer and an organic binder added. Several types of such binders were investigated. The material was then dried, granulated by being pushed through a 12 mesh screen, and classified into whatever selected fraction was to be pressed. Any lubricant to be used was added at this point. Green compacts were then made in a manner similar

to that described previously with various mixtures of Idaho Chemical Processing Plant calcined wastes and fluxes, binders and lubricants. A tabulation of the more significant results is shown in Table IV.

It will be noted from Table IV, samples 3A through 3D and 5A and 5B, are a marked improvement in density over the results of cold compact studies of "as received" materials. Figure 9 shows a comparison of the "as received" bulk material⁽¹⁾ with compacted pellets with (3 and 4) and without⁽²⁾ particle size optimization. Densities were increased by 60 to 70 percent in the better cases. With the additions of various flux additives even high densities were achieved. Densities of 2.2 g/cc and 2.9 g/cc were achieved consistently with pyroceram #25 and calcium fluoride respectively. This is a three to four fold increase over anticipated bulk densities of Idaho Chemical Processing Plant calcined wastes. While it is true that this overall density does not reflect the true densification factor for the calcined Mixed Fission Products, themselves; it still raises it by at least 20 percent more than otherwise would have been achieved for the case of calcium fluoride flux additions. In addition, specimens prepared using such fluxes will have better thermoconducting characteristics than those of a more porous nature, and may be inherently more stable due to flux coating of the particles.

3) Investigation of Slip Casting Techniques

A preliminary investigation of the preparation of slips from Idaho Chemical Processing Plant materials and the casting of them was made during this phase of the program. Although a number of trials were made at incorporating this material into a suitable slip for casting, none met with any degree of success. It was felt that this was primarily due to the nature of the materials.

The Idaho Chemical Processing Plant simulated calcined

TABLE IV

Sample	MILLING TIME HOURS	ADDITIVE	BINDER: PLASTICIZER: LUBRICANT	PARTICLE SIZE	COMPACTING PRESS i.s.i.	SINTER CYCLE	DENSITY GRAMS/CC
3A	6	NONE	B.-.5% Menthyl Cellulose P.-3% Ethanolamine I.-None	-18 Mesh	15.5	500°C-1 Hr.	1.40
3B	"	"	"	"	31	"	1.45
3C	"	"	"	"	47	"	1.50
3D	"	"	"	"	62	"	1.50
3E	"	"	"	-18 + 100 Mesh	"	"	1.80
3G	"	"	B.-Same as above P.- " " " L.-1% Zinc Stearate	-18 + 60 Mesh	"	"	1.85
3H	"	"	B.-Same as Above P.- " " " L.-5%Zinc Stearate	-60 + 100 Mesh	"	"	1.90
4A	"	"	B.-4.5% Phenolic Resin P.-Acetone L.-5% Zinc Stearate	-12 + 60 Mesh	"	150° C-1 Hr.	2.08

TABLE IV

Sample	MILLING TIME HOURS	ADDITIVE	BINDERS: PLASTICIZER: LUBRICANT	PARTICLE SIZE	COMPACTING PRESS i.s.i.	SINTER CYCLE	DENSITY GRAMS/ CC
4B	6	NONE	B.-4.5% Phenolic Resin P.-Acetone L.-5% Zinc Stearate	-12 + 60 Mesh	62	500°C-1 Hr.	1.81
5A	18	"	B.-1% Polyvinyl Alcohol P.-4% Wax L.-5% Zinc Stearate	-18 + 60 Mesh	"	"	1.91
5B	"	"	"	-60 + 100 Mesh	"	"	1.92
6A	"	25% Pyraceram (Corning Glass)	B.-None P.-None L.-5% Zinc Stearate	-12 + 60 Mesh	47	"	2.24
6B	"	"	B.-1% Gum Arabic P.-4% Wax L.-None	"	"	"	1.93
6C	"	"	B.-2% Polyvinyl Pyrrolidone P.-None L.-None	-30 + 60 Mesh	"	"	1.95
7A	"	25% Pemcofrit #AL-619	B.-None P.-None L.-5% Zinc Stearate	-12 + 60 Mesh	"	"	1.85
8A	"	25% Pemcofrit #S-948	"	"	"	"	1.83

TABLE IV

Sam- ple	MILLING TIME HOURS	ADDITIVE	BINDERS: PLASTICIZER: LUBRICANT	PARTICLE SIZE	COMPACTING PRESS i.s.i.	SINTER CYCLE	DENSITY GRAMS/CC
8B	18	25% Pemcofrit #S-948	B.-None P.-None L.-5% Zinc Stearate	-12 + 60 Mesh	47	775°C-NO Soak	1.96
9A	"	12.5% Pyroceram #S-948	B.-None P.-Water L.-5% Zinc Stearate	-30 + 60 Mesh	"	500°C.- 1/2 Hr.	1.90
9B	"	"	"	"	"	570°C.- 1/2 Hr.	1.93
9C	"	"	"	"	"	650°C - 1 Hr.	1.93
9D	"	"	"	"	"	950°C - 1 Hr.	Specimen Cracked
10A	"	20% Calcium Fluoride	"	"	62	1320°C - 1 Hr.	2.90
10B	"	None	"	"	"	"	1.70
11A	"	10% Ammonium BiFluoride	"	"	47	265°C - 1 Hr.	1.85

wastes were found to contain a high percentage of amorphous alumina and were very porous. As a consequence, it was observed that these materials had a strong affinity for water and that they would not remain in suspension despite the use of numerous dispersing and deflocculating agents. A wide range of pH's were also tried without satisfactory results being obtained.

It was felt that if such materials could be converted primarily to the alpha crystalline structure, that they could be slip cast successfully. However, this type of material was not available from the Idaho calciner at this time.

E. DISCUSSION

During this brief investigation of the methods of consolidating Idaho Chemical Processing Plant type calcined mixed fission products densities were increased by a factor of three over that of bulk materials. Techniques were developed for densification of these materials by cold compacting and sintering. An appreciation of problem areas concerning the slip casting of such materials was obtained.

After review of the results of this preliminary study and consultation with other eminent authorities in the field such as Dr. J. Koenig of Rutgers School of Ceramics, it is felt that even higher densities are achievable with further investigation. Such techniques as atmosphere sintering, hot pressing and centrifugal casting should be explored. Changes in the crystalline structure of the calcined alumina wastes by slight alterations of processing conditions might yield materials with even better consolidation characteristics.

IV. INVESTIGATION OF LIFE CHARACTERISTICS OF LOW TEMPERATURE THERMOELECTRIC MATERIALS

A. OBJECTIVE OF TESTS

The purpose of this phase of the program was to evaluate the elevated operation of high figure of merit thermoelectric materials and techniques for bonding them. This is important in the use of a diffuse heat source since these high figure of merit, but temperature limited materials, must be used to obtain useful output power.

Bismuth telluride has long been recognized as one of the more valuable thermoelectric materials, especially for heat pumping and refrigeration devices. Recent advances in the development of alloying techniques have yielded ever increasing figures of merit and are extending the useful temperature ranges of such materials. For this reason, this material was thought to be particularly well suited for low power density sources such as mixed fission products and it was selected as the basic semiconductor material for use in this program. However, while much data was known about the physical properties of this material for low temperature applications, very little information was available about its life characteristics in the temperature ranges of 100°C to 250°C. Therefore, as part of the overall program it was considered necessary to include an investigation of bismuth telluride properties; including the effects of various bonding methods.

B. DESCRIPTION OF EXPERIMENTAL PROGRAM AND PROCEDURES

Bismuth telluride type materials are available from many commercial sources at this time. Initially it was planned to evaluate materials from several independent sources; specifically Melcor, Needco, Merck and Ohio Semiconductor. While these vendors were chosen because of their position in the field as commercial suppliers of bismuth telluride;

in the end, material were received from only the first three vendors. These materials are presently being prepared for testing.

A brief survey of the literature regarding current contact bonding techniques was made. Rather than get deeply involved in developing new methods for making low resistance electrical contacts, it was decided to adapt methods currently being studied by other investigators. After preliminary investigation, the following methods for bonding bismuth telluride materials to base metals were selected for further development and test thermocouple fabrications:

1. Reducing atmosphere, soldering of Bi_2Te_3 to Nickel with:
 - a) pure bismuth solder
 - b) 80 Bi - 20 Sb alloy solder
2. Nickel plated Bi_2Te_3 soldered to Ni or Cu with 95Pb-5Ag solder
3. Flame sprayed Bi_2Te_3 with molybdenum and nickel coatings, then solder soldered to Ni or Cu with 95-Pb-5Ag solder
4. Soldering of Bi_2Te_3 to Ni or Cu with a gold alloy solder.

With selection of semiconductor materials and solder alloys made, methods for fabricating the experimental thermocouples were developed. The thermoelement, as fabricated, consist of an insulation strip (#3, Figure 10), two Cu Extenders (#4, Figure 10), P and N semiconductor materials (#5, Figure 10) and a hot shoe (#6, Figure 10).

With regards to the evaluation of these thermoelements, two special test fixtures and an electrical control console were designed and fabricated for this purpose. The test units and control console are shown in Figure 11.

In essence the test fixture is a thermopile with constant

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temperature hot and cold junctions. It is composed of two concentric cylinders which are capped on either end. The inner portion of these concentric cylinders contain an insulated, thermostatically controlled resistance heating element and the outer portion, bounded by the inner and outer cylinder walls, is a temperature monitored, water-cooled jacket. The cylindrical shells are pierced by a series of 24 tubes which function as individual thermocouple test holders. The whole assembly was dipped brazed together and electrically insulated by "hard coating" both internally and externally.

The electrical control console consists of a series of low resistance switches for monitoring the open and closed circuit voltages and short circuit current outputs from each individual thermoelement. In addition, the controllers for the electrical heaters are also located on the same panel.

C. DISCUSSION

After installation and initial testing of individual thermoelements in the test fixture is completed, measurements, of open and closed circuit voltage, short circuit current hot and cold junction temperatures and hot resistance will be made periodically for each thermocouple. Test will be continued until failure occurs or 10,000 hours of test time has been accumulated. At such a time, the thermocouples will again be examined visually, electrically and by metallography. An addendum to this report covering results of this task of Phase I will be issued at that time.

To date, materials for the thermoelement fabrication have been procured and are presently being fabricated into thermocouples. Test fixtures specifically designed to aid in the evaluation of bismuth telluride materials have been designed and fabricated. A control console for the monitoring of thermoelement thermoelectric properties has also been designed and fabricated.

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V. PARAMETRIC INVESTIGATION

A. PURPOSE OF PROGRAM

An important part of the Phase I effort was the optimization of thermoelectric generator design utilizing the diffuse heat from a mixed Fission product source. A diffuse heat source suffers very large extraneous losses when subjected to high temperature differences. Yet it is precisely required for efficient operation of thermoelectric convertors, as noted in the equations following. The goal of the parametric analysis is to optimize these these conflicting factors.

Optimization involves the careful consideration of the following parameters:

- η_c = Carnot efficiency
- η_E = Thermoelectric materials efficiency
- η_M = Module efficiency
- $(\delta e_f)_t$ = Fission product energy density
- K = Thermal conductivity of insulation
- V and S = Generator and heat source configuration

Each of these parameters is limited by such factors as the thermoelectric state of the art, engineering, and projected characteristics of developmental processes for the fixation of mixed fission products. They may also be defined mathematically, which makes this study possible and conducive to computer solution. The IBM 704 was used because the number of cases computed ran close to a million. (See appendix II for the Fortran program). Because a complete reduction of this material would be a task outside the scope of a feasibility study, only the data on certain specific cases were reduced. This approach aims to develop trends for the problem areas which would be important in the design of thermoelectric convertors. Complete reduction of the data was planned

for the second phase of this program, since sufficient time and funds were not available to accomplish this during Phase I.

B. DERIVATION OF EQUATIONS

The maximum potential efficiency of a thermoelectric convertor η_g is defined as the product of the Carnot efficiency and the thermoelectric material efficiency. (See equation (7))

$$\eta_g = \eta_c \cdot \eta_e \quad (7)$$

and will be defined as

$$\eta_g = \left[\frac{\theta_a - \theta_b}{\theta_a} \right] \left[\frac{M-1}{M + \frac{\theta_a}{\theta_b}} \right] \quad (8)$$

where θ_a is the hot junction temperature of the thermocouple and θ_b is the cold junction temperature. M is primarily dependent upon the thermoelectric material used. This expression defines "maximum efficiency". The first factor represents the thermodynamic efficiency of a reversible engine, and the second describes the reduction of this efficiency as a result of irreversible losses due to heat conduction and Joule heat.

Another factor which must be considered in the design of thermoelectric convertors is that of thermoelectric module design efficiency η_m . Such things as thermal impedances at the junctions, junction resistance and non-uniform temperature and resistivity gradients in the thermoelectric material are included in this factor. The value for this, unless tested for a specific case, must be estimated from previous experience. A value of 0.9 was assigned on the basis of our past experience regarding thermocouple design.

The mixed fission product heat source consists of radioactive constituents having differing half-lives. The energy density of these products may be defined as

$$(\delta \dot{e}r_0)_\tau = \delta \Sigma (e r_0)_x \left(\frac{1}{2}\right) \left(\frac{\Delta \tau}{\tau_{1/2x}}\right) \quad (9)$$

where

- δ = Density of the fission product mixture
 $(\dot{e}r_0)_x$ = Instantaneous rate of radioactive energy release at time $\tau = 0$ for a given radionuclide
 $\tau_{1/2x}$ = The half life of a specific radioisotope X
 $\Delta \tau$ = Number of days of useful generator life

The product of the energy density and volume represent the potential power or heat of a source $(\delta \dot{e}r_0)^\circ V$

Any mixed, nonseparated, fission product heat source necessarily contains a large amount of inert materials. Thus while pure radioisotopes have a very high energy density, this type of heat source is extremely diffuse. It is this fact which is the core of the problem in harnessing the energy in mixed fission products. The extraneous heat loss from this diffuse source, $K S \Delta \theta$, is a function of:

- K = Thermal conductivity of insulation
 S = Shape factor of container configuration
 $\Delta \theta$ = Temperature difference between heat source and heat sink

With the efficiency, heat source, and heat loss now defined, the power output will be that portion of the net heat available for conversion by a thermoelectric generator of particular efficiency. The net heat is thus defined as the amount of available heat minus losses:

$$[(\delta \dot{e}r_0)_\tau \cdot V - K S \Delta \theta] \quad (9A)$$

and it's conversion to power (P) is defined by the general equation

$$P = \eta_G \eta_M \left[(\delta \epsilon r_o)_T \cdot V - K S \Delta \theta \right] \quad (10)$$

It was this equation which was programmed for the IBM 704.

C. PROGRAM FOR 704 COMPUTER ANALYSIS

1) Parameter Limits

The numerical limits of the various parameter used in the IBM 704 program are listed in Table V.

- a) The temperature limit of 40°F for the cold junction was chosen to represent the average ocean bottom temperature. Hot junction temperature values of 140°F to 1040°F correspond to potential operating temperatures for bismuth and lead telluride materials.
- b) The figure of merit M for the materials considered, depends on the type of material, the doping levels and methods of manufacture. Z^1 for the present day thermoelectric materials is of the order of 0.003°C^{-1} for bismuth telluride up to 200°C. and 0.001°C^{-1} for lead telluride up to 600°C. In the near future one should see considerable variations in material ranges in with temperature and the limits used in this analysis have tried to encompass such changes.
- c) Energy density of $.0002 \text{ W/cm}^3$ was selected to correspond to that calculated for calcined Idaho Chemical Processing Plant waste products. With the advent of power reactor fuels and the development of consolidation techniques for their calcined fission product wastes, energy densities of the order of 0.05 W/cm^3 are a distinct possibility.
- d) The insulator thermal conductivity of $0.0002 \text{ Watts/cm}^2\text{-}^\circ\text{C./cm}$ was selected to correspond to the presently available, "better" insulations and vacuum-insulation combinations such as Johns-Manville's Min-K and vacuum.
- e) Cases where vacuum alone is used as an insulation required a modification of the general equation. In these cases, the value for the total emissivity of the surfaces

TABLE V

TABLE OF PARAMETER LIMITS

NO.	PARAMETER	SYMBOL	MINIMUM	MAXIMUM
1	TEMPERATURE			
a	HOT END $^{\circ}\text{R} (^{\circ}\text{C})$	θ	600 (60)	1500 (560)
b	COLD END $^{\circ}\text{R} (^{\circ}\text{C})$	θ	500 (4)	500 (4)
2	FIGURE OF MERIT $^{\circ}\text{R}^{-1}$ $(^{\circ}\text{C})^{-1}$	Z	0.0005 0.0009	0.0015 0.0027
3	ENERGY DENSITY BTU/HR.FT^3 (WATT/CC)	$(\delta \epsilon r_o)_c$	20 0.00024	10000 -01.2
4	THERMAL CONDUCTIVITY $\text{BTU/HR.FT}^{\circ}\text{R}$	K	0.1	1.0
5	RADIUS			
a	INNER SHELL FT	r_a	0.05	1.0
b	OUTER SHELL FT	r_b	$1.25 r_a$	6.0
6	EMISSIONIVITY	ϵ	0.018	0.018
7	MODULE EFFICIENCY	η_M	0.9	0.9

was taken to be that of gold, silver, or polished electrolytic copper, 0.018.

The number of generator configurations studied were three:

1. A sphere within a sphere
2. A cylinder within a cylinder
3. A cylinder within a sphere (vacuum case only)

The module efficiency is an empirical value and is more or less a design criterion. It will be considered constant in all cases studied. A value of 0.9 was assumed for this study.

2) Preparation of General Equation for Computer Solutions

Starting with the general equation derived for power output of an isotope fuel generator, the following steps are used in the IBM-704 solution of the problem:

General equation

$$P = \eta_G \eta_M (\delta \epsilon r_o)_T \cdot V - K S \Delta \theta \quad (10A)$$

$$\text{where } \eta_G = \left[\frac{\theta_a - \theta_b}{\theta_a} \right] \left[\frac{M-1}{M+\theta_a} \right] \quad (11)$$

$$\text{and } M = \left[1 + \frac{Z}{2} \theta_a + \theta_b \right]^{1/2} \theta_b \quad (12)$$

with $\eta_M = 0.9$, constant

and $\theta_b = 280^\circ \text{K}$, constant,

Using first values of K , ϵ_a , Z^1 , and $(\delta \epsilon r_o)_T$, reduces the general equation to

$$P = C_1 V - C_2 S \quad (13)$$

where C_1 , C_2 are computed constants for the following parameters V and S . Next step is to use first values r_a and r_b , which are inner and outer shell radii respectively.

For a sphere insulated within a sphere

$$V_s = \frac{4}{3} \pi r_a^3 \quad (14)$$

$$S_s = \frac{4\pi r_a r_b}{r_b - r_a} \quad (15)$$

For a cylinder insulated within a cylinder where length
 $= 2r$

$$V_c = 2\pi r_a^3 \quad (16)$$

$$S_c = f(6\pi r_a^2) \quad (17)$$

$$f = \left[.79 \left(\frac{r_b - r_a}{r_a} \right) + 1 \right] \quad (18)$$

Then print out P from:

$$P = C_1 V_s - C_2 S_s \quad (19)$$

$$\text{and } P = C_1 V_c - C_2 S_c \quad (20)$$

Incrementally increase θ_a to second value, and holding other parameters at their first value, recompute C_1 and C_2 .
 Print and so forth.

When θ_a has reached its highest value, change ($\delta \epsilon r_o$) to its second value. The process repeats until the entire ranges of all the parameters have been used in the computer study.

As was stated earlier, in the cases of vacuum alone being used to insulate the inner container of fission products, the heat losses must be defined in a different manner. For these cases the equation now reads

$$P = \eta_g \eta_m \left[(\delta \epsilon r_o)_{\tau} V - \frac{\sigma A_a \left[\left(\frac{\theta_a}{100} \right)^4 - \left(\frac{\theta_b}{100} \right)^4 \right]}{\frac{1}{\epsilon_a} + \frac{A_a}{A_b} \left(\frac{1}{\epsilon_b} - 1 \right)} \right] \quad (21)$$

Similar procedure may be taken in this case also. Using first values

$$P = C_1 V - C_2 A_a \quad (22)$$

where C_1 , C_2 are computed constants for the following parameters V and A

For concentric spheres

$$V_s = 4/3\pi r_a^3 \quad (23)$$

$$A_{as} = 4\pi r_a^2 \quad (24)$$

$$A_{bs} = 4\pi r_b^2 \quad (25)$$

And for concentric cylinders where length = diameter

$$V_c = 2\pi r_a^3 \quad (26)$$

$$A_{ac} = 6\pi r_a^2 \quad (27)$$

$$A_{bc} = 6\pi r_b^2$$

The same iteration process is required in this case. The Fortran print-out of this program can be found in Appendix II.

D. DISCUSSION OF THE RESULTS OF PARAMETRIC DATA REDUCTION

The amount of data produced in the IBM-704 digital computer program was so great, that its analysis required far more time and effort than had originally been allotted. Thus, it was decided to reduce only that data which were based on parameters restricted by the present state of the art in thermoelectrical power generation and within practical limitation in economy and size. A large amount of data is still to be analyzed and additional improvements in the digital computer programming are desirable. Trends and specific data that have been reduced to date are discussed in the following paragraphs.

The computer results were broken down into families of curves having constant fuel container dimensions (r_a) and varying outer shell dimensions (r_b). Electrical power output was then plotted as a function of the various generator configurations, thermoelectric materials, figure of merits, radioisotope power densities, hot junction temperatures and insulation thermal conductivity. Four specific cases were studied. They were: 1. a sphere within an insulated sphere, 2. a sphere within an evacu-

ated sphere, 3. a cylinder within an insulated cylinder and 4. a cylinder within an evacuated cylinder. In addition a fifth case, a cylinder within an evacuated sphere was analyzed mathematically by manual calculations to correlate shape factor interrelationships. Limits for the various parameters may be found in Table V .

In general, the net electrical power output is a function of a number of factors (see equation 10), but for any configuration there is an optimum size where maximum power output is obtained for a given Mixed Fission Product energy density. Figures A-1 through A-4, shown in Appendix III, illustrate the maximum power obtainable for various radioisotope energy densities and geometrical configurations. From these curves one can see that for the maximum efficiency configuration, that of a sphere within an evacuated sphere, power output ranges from about 3 watts to about 500 watts for Mixed Fission Product energies of 0.001 and 0.05 Watts/cm³ and a unit size of about two feet in diameter. These isotope energies correspond to consolidated, higher level, Idaho Chemical Processing Plant aluminum wastes and future power reactor fuel element wastes. Even higher level electrical power outputs can be expected if container sizes are increased. It must be noted, however, that a point of diminishing returns will be reached shortly as sizes are increased. At this point the heat losses became larger than added radioisotope energies.

Power output also varies proportionately with the figure of merit (Z) of the thermoelectric materials used. This is illustrated in Figure 12 where the variation in power output is plotted against temperature for various figure of merits (Z) and radioisotope energy densities. Z's of $1.0 \times 10^{-3}/^{\circ}\text{C}$ and $3.0 \times 10^{-3}/^{\circ}\text{C}$ correspond to better lead and bismuth telluride alloys. For the specific case shown in Figure 12, it can be seen that power outputs of

PARAMETER STUDY

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CASE: INSULATED SPHERE WITHIN A SPHERE

FIGURE 12

approximately 50 and 3 watts can be obtained from the maximum energy densities shown. An energy density of $0.0005 \text{ Watts/cm}^3$ corresponds approximately to the power level of Idaho Chemical Processing Plant wastes. Numerous other cases of power output as a function of Z for insulated and evacuated spheres were also reduced and show this same general trend.

A comparison of performance as a function of insulation thickness and thermoconductivity was also made as part of the computer study. Results indicate that only the best insulators can be used for diffuse heat sources such as Idaho Chemical Processing Plant - Mixed Fission Products. Thermoconductivities of 0.0002 to $0.0004 \text{ Watts/cm}^2\text{-}^\circ\text{C./cm}$ required if usable amounts of power are to be obtained. In general, as the insulation thickness is increased, heat losses are decreased, and power outputs are increased for a given design. However, there are diminishing returns; that is, there is a point where increasing insulation thickness will not increase power output. This point is illustrated in Figure 13 where the effect of increasing insulation thickness causes increased hot junction temperatures and slowly increasing electrical power output. With regards to vacuum versus insulation, vacuum is to be preferred analytically over the best insulations because of higher output yields and decreased outer shell diameters and weights. This can be readily seen by comparing the two specific cases presented in Table VI, curves in Appendix III, and Figures 12 and 14.

Reduction of the parameter data also showed the relationship of radioisotope power density to electrical power output. From the general equation (1) it can be seen that the use of increasingly higher energy density Mixed Fission Products will result in increased electrical power outputs for any given configuration. Efficiency, however, may not be increased since heat losses become greater as tempera-

TABLE VI *

M F P ENERGY DENSITY WATTS/CM ³	POWER OUTPUT (WATTS ELECTRICAL)			
	SPHERE WITHIN A SPHERE		CYLINDER WITHIN A CYLINDER	
	VACUUM	INSULATION	VACUUM	INSULATION
0.0005	3.3	-	5.3	-
0.0001	8.2	1.5	11.7	2.0
0.005	45.2	26.5	69.5	4.1
0.01	88.5	64.5	138	94
0.05	455	380	720	440
0.1	910	820	1400	970

* Abstracted from Appendix III curves

POWER OUTPUT VS HOT JUNCTION
TEMPERATURE FOR VARIOUS
THICKNESSES OF INSULATION

FIGURE 13

PARAMETER STUDY

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POWER OUTPUT VS HOT JUNCTION TEMPERATURE

CASE: INSULATED CYLINDER WITHIN A CYLINDER

FIGURE 14

CLT 076

tures are increased by use of higher energy density radioisotopes. The effect of increased radionuclide energy density for two different cases can be seen in Figures 12 and 14 and Appendix III.

With regard to size and shape factors versus power output, Appendix III-"An Analytical Comparison of Power Output for Various Configurations", and Figures 12, 13, and 14 point out the significant trends. From the five cases studied-:

1. sphere within an insulated sphere
2. sphere within an evacuated sphere
3. cylinder within an evacuated sphere
4. cylinder within an insulated cylinder
5. cylinder within an evacuated cylinder,

the best configuration appears to be the case of the sphere within an evacuated sphere. Lowest containment weights and highest conversion efficiencies are obtained for this case. The cylinder within a cylinder appears to offer higher power outputs from data tabulated in Table VI, but this is a false impression due to fuel capacities being larger by a factor of approximately one-third for the geometrical comparison where the diameter of the sphere equaled the diameter and length of the cylinder. The case of a cylinder within a sphere is the poorest of the configurations studied because of wasted space which might otherwise be used for fuel storage. Future analysis should be based upon specific application requirements such as power output, allowable weight and bulk volume. The analytical results obtained may then be applied to the specific requirements and yield the best configuration, approximate generator size and operating temperatures. The specific design would then be optimized utilizing reiterative techniques in order to account for contact resistance and other losses.

The bulk of the data which has been reduced to graphical form has aided in the development of generator design philosophies. This analysis has enabled the designers to quickly optimize all the many parameters necessary for a practical, economical solution of the problems.

E. WEIGHT ANALYSIS VERSUS DEPTH FOR UNDERSEA APPLICATIONS

Devices utilizing Mixed Fission Products as heat source materials for thermoelectric power generators are best suited for underwater applications where water can be used advantageously as both a radiation shield and heat sink. Special designs, however, may permit the use of Mixed Fission Products fueled thermoelectric devices for terrestrial applications.

Therefore, as part of the parameter study, an analysis was made to determine pressure vessel wall thicknesses and weights as a function of generator dimension, depth and geometrical shape. In making this analysis certain assumptions were made, they were:

1. The outer shell was stressed for 20,000 feet depth; however, in practice this shell will be designed for mission depth requirements.
2. The inner vessel or Mixed Fission Products container must withstand hydrostatic pressures for depths to 20,000 feet, the extreme most design application depth.
3. Maximum allowable fiber stress of 50,000 p.s.i., this corresponds to structural steel boiler code limits.
4. Densities of 0.29, 0.072 and 0.013 lbs/cu. in. for steel, radioisotope and insulation, respectively.
5. A length equal to the diameter for cylindrical configurations.
6. Minimum outer shell radius of $1.414 r_a$, where r_a equals inner shell radius.

7. The weight of the thermoelectric material is negligible compared to the total weight.

Calculation for this analysis took into account the weight of the outer pressure vessel (W_o), the weight of the inner fuel container (W_i), the weight of the radioisotope (W_R) and the weight of the insulation (W_I).

Unit weight was calculated for various depths in the following manner:

After selecting a certain radius for the outer shell, there exists some inner fuel shell which will yield the maximum net heat for subsequent conversion to electricity. The solution to this is found simply by letting

$$\frac{(dP)}{(dra)} = 0$$

and holding all the other variables constant.

It was this method which was used to determine the radii for a five (5) watt generator of various geometrical configurations. Knowing the optimum radii for inner and outer shell, the weight of the shells was calculated as a function of depths. Equations used for total unit weight calculations are shown in Appendix IV and the results are shown in graphical form in Figures 15, 16 and 17. From these graphs it is apparent that the case of a sphere within a sphere is the minimum weight configuration and that vacuum is superior to the best insulation from a weight optimization viewpoint. It is also obvious that the higher power density Mixed Fission Products are more suitable for extreme depth applications from a weight and cost standpoint, since their use minimizes shell radii. Energy densities of 0.001, 0.005 and 0.05 W/cm³ correspond to the products of the most promising fixation processes.

WEIGHT VS DEPTH
CONCEPTUAL 5 WATT GENERATOR
CASE: SPHERE WITHIN A SPHERE

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FIGURE 15

200 000

WEIGHT VS DEPTH OF CONCEPTUAL 5 WATT GENERATOR CASE: CYLINDER WITHIN CYLINDER

FIGURE 16

WEIGHT VS DEPTH FOR CONCEPTUAL 5 WATT GENERATOR CASE : CYLINDER WITHIN SPHERE EVACUATED ONLY

FIGURE 17

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In addition to the development of the general equations used in the estimation of unit weight versus depth for the 5 watt case presented, a general study of pressure vessel weight versus depth was made for spherical configurations. Data from this study is presented in Figure 18 in the form of a series of isobar curves of vessel weight versus vessel radii. From these curves it is apparent that for use at great depths one imposes a severe economic and weight penalty for any conceptual design having a radius much greater than two feet.

OUTER SHELL WEIGHT VS SHELL RADIUS AND FOR VARIOUS OCEAN DEPTHS

FIGURE 18

VI CONCEPTUAL GENERATOR DESIGN

A. DESIGN OBJECTIVES

The main goal of the design studies performed during Phase I was the evolution of a conceptual thermoelectric convertor design which would utilize a Mixed Fission Product Heat source with measurable degrees of safety, economy and efficiency. Problem areas pointed up by this study are:

- (1) Sealing
- (2) Structural integrity
- (3) Efficiency and economy
- (4) Temperature flattening
of the heat source
- (5) Power flattening
- (6) Heat transfer
- (7) Radiological health hazards

Our approach to the general solution to these problem areas is embodied in a series of conceptual designs. In general all conceptual designs are (1) hermetically sealed, (2) structurally strong in order to minimize failures due to handling, environment, and credible accidents, and (3) doubly contained to minimize radiological hazards.

Thermoelectric convertors as applied to these heat sources were optimized for temperature and the energy density of the various Mixed Fission Power sources by the parametric analysis. Mechanical and structural requirements necessary to complete the intended mission were incorporated into the design. Efficiency and economy were realized by the use of optimized insulation, selection of containment alloys, use of organic protective films for corrosion, and optimization of containment geometry for lightweight and lowest fabrication cost consistent with safety and mission requirements.

B. DISCUSSION OF CONCEPTUAL DESIGNS

Principal parts common to all designed generators are:

- (1) Outer shell
- (2) Mixed Fission Products source
and container
- (3) Thermoelectric convertor
- (4) Support structure for heat source
- (5) Thermal insulation

1. Outer Shell

The outer shell provides water tight integrity at immersion depths for the duration of time required by mission and safety considerations. It is shown as a thick wall sphere in all figures to indicate the optimization necessary for great depths. When used at more moderate depths, other shapes can be considered.

The use of vacuum insulation will permit a smaller insulation space than shown; consequently a smaller outer shell. The shell is pierced by electrical leads and an evacuation tube. Possibility of leakage is minimized by a protective cap over the tube and by a high pressure conduit around the electrical leads which connects the power utilization package to the generator. The leads pass through two high pressure water tight seals to further reduce the possibility of leakage. The outer shell is also an integral part of the thermal system, acting as a cold side heat distribution surface to efficiently pass waste heat from the generator cold side to the sea water. Terrestrial application generators are air cooled as shown in Figure 19. Because radiation levels from the radioisotopic heat source are reduced by the shielding effect of the outer and inner shell and decrease as shell thicknesses increase, high power density heat sources are better suited to deep sea applications than low power heat sources. For the terrestrial application the containment

may be buried, taking advantage of the earth as natural shielding.

2. Mixed Fission Products Sources and Container

Several different sources of Mixed Fission Products have been considered for these applications, all of which require careful containment due to their radiological characteristics. The container must be designed to minimize possible leakage of the radioisotope. It must also function as a pressure vessel which will be safe even if accidentally operated below designed mission depths. While the wall thickness of the pressure vessel will largely be determined by external pressure; corrosion (internally due to isotope and externally due to sea water) must also be taken into account. Sea water corrosion will exist only if the outer shell leaks, but must be considered for safety reasons.

3. Thermoelectric Converter

The thermoelectric converter receives heat by some suitable method from the mixed fission products heat source and rejects heat to the outer shell by conduction. The thermoelectric couples placed between, and in good thermal contact with both the hot and cold heat exchangers comprise the converter. Conduction on the cold side is improved by the use of a thermally conductive sealant in the interface and by a compensating bellows which produces constant force on the cold side surface, thereby minimizing the effect of thermal expansion and other small movements. Suitable hot side heat transfer methods include conduction across specially prepared interfaces as shown in Figure 20 or a convective heat exchange system as shown in Figure 21.

Methods having specific application advantages (See figures 19, 20, 21, which illustrate specific methods) are determined by the energy density of the mixed fission products source, type of isotope, the location of generator relative to heat source, and mission requirements.

GROSS FISSION PRODUCT FUELED GENERATOR FOR TERRESTRIAL APPLICATIONS

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FIGURE 19

011 088

GROSS FISSION PRODUCT FUELED GENERATOR FOR UNDERWATER APPLICATION DIRECT HEAT CONDUCTION

GROSS FISSION PRODUCT FUELED GENERATOR FOR UNDERWATER APPLICATION

FLUID FLOW INTERNAL HEAT EXCHANGER

Conduction type (figure .20) convertor applications using high power density Mixed Fission Products results in a small compact unit which permits simpler, more economical and higher efficiency heat transfer methods. However, the hot and cold surfaces must be carefully prepared to reduce interface thermal impedance to a minimum. The support structure must position the heat source containment, with respect to the outer shell, with a higher degree of accuracy than is required when convective heat transfer is used. In addition, the mass of conduction members, shown as "thermal extenders" in figure (20), become very heavy when the power density is low and dimensions of the radioisotope container are large, or when the generator is placed at some distance from the hot or cold side. Heat source temperature flattening is provided by metal conductors which reduces the centerline temperatures. This is required for mixed fission products sources for reasons discussed in preceeding parts of this report. Power flattening cannot be incorporated in the conduction heat transfer system but may be applied as a separate system.

Convection heat transfer offer advantages over conductive transfer when:

- 1) Power flattening will be incorporated in the system.
- 2) The generator is located some distance from the heat source.
- 3) The structural flexibility of the piping can be used to reduce shock loading on the generator due to handling, etc.

In this case it is desirable to extract heat from the radioisotope without raising the container temperature. Figure 21 shows a coil buried in the radioisotope source which extracts heat from the central region of the heat source and acts as a temperature flattening device and provides higher temperatures to the generator's hot side,

near the "end of life" of the isotopes. Not all isotopes can be loaded into a container with a coil placed as shown; further study will determine which isotopes may be used in this way.

4. Support Structures

The support structure (legs) may be designed with greater flexibility for convective designs than with conduction designs because the flexibility of the piping permits larger relative movements of the radioisotope container and thermoelectric convertor than with conduction methods. All methods mentioned above require the convertor to be placed with accuracy between the hot side surface and the cold side surface to insure minimum temperature drop across the interfaces. The placement of the components (outer shell, convertor and heat source container) relative to one another, is the function of the support structure. In addition to locating the components the support structure must be stiff enough to prevent inertial forces from subjecting the generator to loads in excess of design limits. Extraneous heat loss through the structure must also be minimized. Unless extreme care is taken in the design of the support structure, failure of the structure can cause interruption of the heat path through the convertor with subsequent overheating of the heat source. This is especially true with high power density mixed fission products source applications.

5. Insulation

In the design of concentric containers enveloped by an infinite heat sink, only two modes of heat transfer are present, conduction and radiation. The function of insulating the inner container of radioactive material is one of minimization of thermal losses from the heat source.

Three general methods of insulating were studied: vacuum, vacuum and insulation, and insulation. With only a vacuum

insulation, the heat losses are purely by radiation. The heat transfer varies with the fourth power difference in temperature, surface area and emissivity. In this case losses are reduced by the minimization of surface areas and by the application of high reflectivity films.

Vacuum plus a bulk insulation lowers the heat path if the insulation has a lower thermal conductance loss than that due to surface emission of radiation. Bulk insulation is the least effective of the three in minimization of heat loss.

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APPENDICES

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APPENDIX I

NOMENCLATURE

NOMENCLATURE

A	=	Area - sq. ft.
C	=	Constant
d	=	Density - lbs/cu. in.
F	=	Correction factor for end losses for short cylinder
h	=	Hydrostatic heat - inches
K	=	Thermal conductivity - Btu/hr. ft °R
M	=	Performance parameter
P	=	Pressure - lbs/sq. in.
Po	=	Power Output - Btu/hr.
r	=	Radius - ft. unless otherwise specified
S	=	Surface, shape factor - sq.ft./ft.
t	=	Wall thickness - in.
V	=	Volume - cu. ft.
W	=	Weight - lbs.
Z	=	Modified figure of merit
γ	=	Density of M.F.P. - lb./cu. ft.
ϵ	=	Normal total emissivity
η	=	Efficiency - percent
θ	=	Temperature - degrees Rankine
σ	=	Stefan - Boltzmann constant - Btu/sq.ft.-hr.-°R ⁴
τ	=	Time - years
$\tau_{1/2x}$	=	Half life of specific radioisotope x
(e_r)	=	Instantaneous rate of radioisotope energy release - Btu/hr.

Subscripts

a	=	Mean radius, inner container
b	=	Mean radius, outer container
C	=	Carnot
E	=	Thermoelectric
G	=	Generator
i	=	Inner
I	=	Insulation

M = Module
o = Outer
R = Radioisotope
S = Steel
T = Total
 τ = Time

APPENDIX II

704 FORTRAN CODE

FOR

THERMOELECTRIC PARAMETER STUDY

A. 704 PROGRAM NOMENCLATURE

NTA = Number of values of T_a
 ATA = First (lowest) value of T_a
 ZTA = Last (.95 times highest) value of T_a
 DTA = Increment in T_a
 NZP = Number of values of Z^1
 AZP = First (lowest) value of Z^1
 ZZP = Last (.95 times highest) value of Z^1
 DZP = Increment in Z^1
 NRA = Number of values of R_a
 ARA = First (lowest) value of R_a
 ZRA = Last (.95 times highest) value of R_a
 DRA = Increment in R_a
 NRB = Number of values of R_b
 ZRB = Last (.95 times highest) value of R_b
 NK = Number of values of K
 AK = First (lowest of value YK from print out) K
 ZK = Last (.95 times highest) value of K
 DK = Increment (from previous data card 4 or print out) of K
 NGET = Number of $FE_t = GET$
 AGET = First (lowest or print out) value of GET
 ZGET = Last (.95) times highest) GET
 DGET = Increment (previous data card 4 or print out) of GET
 TB = T_b

B. FORTTRAN CODE FOR IBM-704 PROGRAM

```
C      PROGRAM TO COMPUTE POWER OUTPUT, BTU/HR., FOR
      THERMOELECTRIC GENERATOR PARAMETRIC EQUATIONS
      FOR AEC CONTRACT AT(30-1) 2605)
C      GENERAL INSTRUMENT CORP.          F. LEHMAN  NOV 60
      DIMENSION PPO  (48)
      N = 0
      READ 5, TEST, CTEST
5      FORMAT (2F4.1)
      IF (TEST) 70.70.10
70     PRINT 1,N
      PRINT 2,N
      GO TO 11
10     WRITE OUTPUT TAPE 6,1,N
      WRITE OUTPUT TAPE 6,2,N
1     FORMAT (99H1 POWER OUTPUT BTU/HR. THERMOELECTRIC
      GENERATOR PARAMETR
      XIC EQUATIONS FOR AEC CONTRACT AT (30-1)2605 15)
2     FORMAT (114H0 IN.SPH IN.CYL DW.SPH DW.CYL IN.SPH
      IN.CYL DW.SPH DW.C
      XYL IN.SPH IN.CYL DW.SPH DW.CYL IN.SPH IN.CYL
      DW.SPH DW.CYL 12) IF (TEST)11,11,60
11     READ 6,ATA,AZP, ARA, ARB, AK, AGET,TB
6     FORMAT (F7.1,F6.4,F4.1,F4.1 F5.3,F6.1,F7.1) GO TO 12
60     READ 3,NTA,ATA,ZTA,DTA,NZP,AZP,ZZP,DZP,NRA,ARA,
      ZRA,DRA,NRB,ZRB
      READ 4,NK,AK,ZK,DAK,NGET,AGET,ZGET,DAGET,TB
3     FORMAT (13,3F7.1, 12,3F6.4,13,3F5.2,12,F4.1)
4     FORMAT (12, 3F5.2,12,F5.1,F9.1,F6.1,F7.1)
12     GET = AGET
      DGET = DAGET
13     YK = AK
      DK = DAK
22     J=J+1
      SD=SDC
      V=VC
      GO TO 21
23     J=1
      IF (TEST) 63,63,64
63     PRINT 8,TA,TB,ZP,RA,RB,YK,GET, (PPO)K),K=1,4)
```


B. FORTRAN CODE FOR IBM-704 PROGRAM (continued)

```

8      FORMAT (5H0 TA=F6.1,4H TB=F6.1,4H ZP=F6.4,4H
RA=F5.2,4H RB=F5.2,4H
XYK=F6.3,5H GET=F6.1/4F8.1)
PRINT      7,CI,SIS,SDS,VS,VC,SDC,SIC,SM,EG,ER
7      FORMAT (5H0 CI=F4.2,5H SIS=F5.2,5H SDS=F5.2,4H
VA=F5.2,4H VC=F5.2/5
XH SDC=F5.2,5H SIC=F5.2,4H SM=F5.2,4H EG=F5.2,4H
EP=F5.4)
TEST = TEST + 1.
GO TO 60

64     IF(I-NTA) 24,25,25
24     I=I+1
TA=TA+DTA
IF(TA-ZTA) 17,17,71
71     IF(SENSE SWITCH 6) 72,25
72     PRINT      9,ZP,RA,RB,YK,GET,DK,DGET, (PPO(K),K-1,48)
25     WRITE OUTPUT TAPE 6,9,ZP,RA,RB,YK,GET,DK,DGET, (PPO(K),
K=1,48)

9      FORMAT (5H0 ZP=F6.4,4H RA=F5.2,4H RB=F5.2,4H
YK=F6.3,5H GET=F9.1,4H
X DK=F6.3,6H DGET=F9.1/(16F7.0))
IF(ZP-ZZP) 26,27,27
26     ZP=ZP + DZP
GO TO 30
27     IF(RB-ZRB) 28, 29,29
28     RE=RB*RRB
GO TO 15
29     IF(RA-ZRA) 30,31,31
30     RA=RA+DRA
GO TO 51
31     IF(YK=ZK) 32,33,33
32     YK=YK+DK
DK= 2.*DK
GO TO 14
33     IF (GET-ZGET) 34,35,35
34     GET=GET+DGET DGET=3.*DGET
GO TO 13
35     READ 80,EN1
80     FORMAT (F4.1)
IF (EN1) 36,36,60
36     END FILE 6
STOP 77777
END (0,1,0,1,0)

```

APPENDIX III

COMPARATIVE ANALYSIS OF POWER OUTPUT OPTIMIZATION

FOR

VARIOUS DESIGN CONFIGURATIONS

In the general equation for power output, P_o is a function of many mutually independent variables. Being independent, a number of changes may take place simultaneously in a non-restrictive manner as it was done in the IBM computer study. Each case studied, however, was simply a calculation of the inputs. There was no inference as to whether or not that calculated power output represented the best combination of variables. No optimization could be made because of the non-restriction of variables. The larger the generator, the greater the power output.

In looking over the study, the question of optimization, that is, the most power for the least package, did arise. Minimization of the package meant restricting the outside radius, r_b , of the shell. Selection of a thermoelectric material also restricted the study by restricting the operating temperatures. By using the above restrictions and only the general equation can then be reduced to

$$P = f \left\{ (\delta \dot{e} r_o)_\tau \cdot r_a \right\} \quad (1)$$

It follows naturally that one should set

$$\frac{dP_o}{dr_a} = 0 \quad (2)$$

because $(\delta \dot{e} r_o)_\tau$ is a function of availability and cannot be dealt with mathematically.

The results of the equations are found in the appendix where they are expressed graphically, P_o being the maximum for a selected r_b .

SYMBOLS

A	=	Surface area - ft^2
F	=	Correction factor for end losses (40)
K	=	Thermal conductivity - $\text{Btu}/\text{ft} \cdot ^\circ\text{R}/\text{ft}^2$
M	=	Performance parameter
P_o	=	Power - $\text{Btu}/\text{hr}.$
r	=	Radius - $\text{ft}.$
S	=	Shape factor - $\text{ft}^2/\text{ft}.$
V	=	Volume - ft^3
x	=	$(\delta e r_o)$, energy density - $\text{Btu}/\text{hr} \cdot \text{ft}^3$
Z^1	=	Modified figure of merit
Δ	=	Difference
ϵ	=	Normal total emissivity
η	=	Efficiency
θ	=	Temperature - $^\circ\text{R}$

Subscripts

a	=	Inner container surface
b	=	Outer container surface
G	=	Generator
M	=	Material
o	=	Output

Sample Computations

1. General equation for insulated containers:

$$P_o = \eta_G \eta_M \left[(\delta \dot{e} r_o) \cdot V - K S \Delta \theta \right] \quad (1.1)$$

$$= \left[\frac{\theta_a - \theta_b}{\theta_a} \right] \left[\frac{M-1}{M + \frac{\theta_b}{\theta_a}} \right] \quad (1.2)$$

$$M = 1 + \frac{Z^1}{2} (\theta_a \theta_b)^{1/2} \quad (1.3)$$

$$\text{Let } \theta_a = 800^\circ R, \theta_b = 500^\circ R, Z^1 = .0015^\circ R, \eta_M = .90$$

$$K = .01 \text{ Btu/Hr.Ft.}^\circ R, (\delta \dot{e} r_o) = x \text{ Btu/Hr.Ft.}^3$$

Substituting

$$P_o = 0.0774 [xV - 3S] \quad (1.4)$$

- a) For concentric spheres

$$V = 4/3 \pi r_a^3 \quad (1.5)$$

$$S = \left(\frac{4\pi r_a r_b}{r_b - r_a} \right) \quad (1.6)$$

Differentiating (1.4) with respect to r_a holding r_b constant

$$\frac{dP_o}{dr_a} = x \frac{dV}{dr_a} - 3 \frac{dS}{dr_a} = 0 \quad (1.7)$$

for a maximum power output.

$$\frac{dV}{dr_a} = 4\pi r_a^2 \quad \frac{dS}{dr_a} = \frac{4\pi r_b^2}{(r_b - r_a)^2} \quad (1.8)$$

Substituting back in (1.7)

$$x r_a^2 - \frac{3 r_b^2}{(r_b - r_a)^2} = 0 \quad (1.9)$$

MAXIMUM POWER vs OUTER SPHERE RADIUS

CASE: INSULATED SPHERE

FIGURE A-1.

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Solving for r_a

$$r_a = \frac{r_b - \sqrt{(r_b^2 - 4r_b^3/x)}}{2} \quad (1.10)$$

b) For concentric cylinders where length equals diameter.

$$V = 2\pi r_a^3 \quad (2.1)$$

$$S = F \frac{(6\pi r_a^2)}{(r_b - r_a)} \quad (2.2)$$

$$F = \left[.79 \left(\frac{r_b - r_a}{r_a} \right) + 1 \right] \quad (2.3)$$

$$\text{or } S = \frac{4.74\pi r_a r_b + 1.26\pi r_a^2}{(r_b - r_a)} \quad (2.4)$$

Differentiating

$$\frac{dV}{dr_a} = 6\pi r_a^2 \quad (2.5)$$

$$\frac{dS}{dr_a} = \frac{4.74r_b^2 + 2.52r_a r_b - 1.26r_a^2}{(r_b - r_a)^2} \quad (2.6)$$

Substituting in equation (1.7)

$$6\pi r_a^2 - 3 \left\{ \frac{4.74r_b^2 + 2.52r_a r_b - 1.26r_a^2}{(r_b - r_a)^2} \right\} = 0 \quad (2.7)$$

Solving for r_b (in this case it is much simpler to pick on r_a and solve for r_b)

$$r_b = \frac{2r_a + \frac{1.26}{xr_a} + \sqrt{\left\{ \left(2r_a + \frac{1.26}{xr_a} \right)^2 - 4 \left(1 - \frac{2.37}{xr_a^2} \right) \left(r_a^2 + \frac{0.63}{x} \right) \right\}}}{2 \left(1 - \frac{2.37}{xr_a} \right)} \quad (2.8)$$

2. General equation for evacuated containers:

$$P_o = \eta_G \eta_M \left[(x \dot{e} r_o) V - \frac{\sigma A_a (\theta_a^4 - \theta_b^4)}{\frac{1}{\epsilon_a} + \frac{A_a}{A_b} (\frac{1}{\epsilon_b} - 1)} \right] \quad (3.1)$$

MAXIMUM POWER vs OUTER SHELL RADIUS

CASE: INSULATED CYLINDER

FIGURE A-2

$$\eta_G = \left[\frac{\theta_a - \theta_b}{\theta_a} \right] \left[\frac{M - 1}{M - \frac{\theta_b}{\theta_a}} \right] \quad (3.2)$$

$$M = \left[1 + \frac{Z^1}{2} (\theta_a + \theta_b) \right]^{1/2} \quad (3.3)$$

Let $\theta_a = 800^\circ R$, $\theta_b = 500^\circ R$, $Z^1 = .0015^\circ R^{-1}$, $\eta_M = .90$
 $\epsilon_a = .018$, $\epsilon_b = .012$, $\sigma = .173^\circ / C^5$ (BTU/FT.²Hr^{°R})⁴

Substituting

$$P_o = 0.0774 \left[xV - \frac{7.31A_a}{0.58 + \frac{A_a}{A_b}} \right] \quad (3.4)$$

a) For concentric spheres

$$V = \frac{4}{3}\pi r_a^3 \quad (3.5)$$

$$A_a = 4\pi r_a^2 \quad (3.6)$$

$$A_b = 4\pi r_b^2 \quad (3.7)$$

By inspection, the maximum power output is reached as $A_b = A_a$, therefore differentiating was not necessary. In this study

b) For concentric cylinders:

$$V = 2\pi r_a^3 \quad (4.1)$$

$$A_a = 6\pi r_a^2 \quad (4.2)$$

$$A_b = 6\pi r_b^2 \quad (4.3)$$

As for maximum power output, the same holds true for this case as it did with the concentric spheres.

MAXIMUM POWER vs OUTER SPHERE RADIUS

CASE: EVACUATED SPHERE

FIGURE A-3

MAXIMUM POWER vs OUTER SHELL RADIUS

CASE: EVACUATED CYLINDER

FIGURE A-4

APPENDIX IV

CALCULATIONS OF UNIT WEIGHT VERSUS DEPTH

FOR

THERMOELECTRIC GENERATOR SEA APPLICATIONS

SYMBOLS

h = Hydrostatic head-inches
P = Pressure - lbs/in.²
r = Radius - inches
S = Stress - lbs/in.²
t = Thickness - inches
w = Weight - lbs.
d = Density - lbs/in.³

subscripts

i = Inner shell
I = Insulation
o = Outer shell
R = Radioisotope
S = Steel
T = Total

Sample Calculations

Inner shell Weight

Using

$$S = Pr_a / 2t \quad (1)$$

Assume $P = 8790$ psi, $S = 50,000$ psi

$$\text{Then } t = .0879 r_a \quad (2)$$

Weight therefore is

$$W_i = A_a t d_s \quad (3)$$

Substituting (2) in (3)

$$W_i = .0879 A_a r_a d_s \quad (4)$$

Density for steel, $d_s = .0290$ lbs/cu.in.

$$W_i = 0.025 A_a r_a \quad (5)$$

Outer Shell Weight

Again using

$$S = Pr_b / 2t \quad (6)$$

Where $S = 50,000$ psi

$$t = Pr_b \times 10^{-5} \quad (7)$$

However P is now a function of ocean depth $P = d_o h$ where d_o = density of ocean, h = ocean depth, inches

Therefore

$$t = d_o h r_b \times 10^{-5} \quad (8)$$

Weight is again

$$W_o = A_b t d_s \quad (9)$$

Substituting (8) in (9)

$$W_o = A_b d_o d_s r_b h \times 10^{-5} \quad (10)$$

or with $d_o = 0.037 \text{ lbs/cu. in.}$

$$W_o = 0.011 A_b r_b h \times 10^{-5} \quad (11)$$

Weight of Radioisotope

$$W_R = d_r V_a \quad (12)$$

using density of radioisotope, $d_R = 0.072 \text{ lb/cu. in.}$

$$W_R = 0.072 V_a \quad (13)$$

Weight of insulation (if used)

$$W_I = (V_b - V_a) d_I \quad (14)$$

using density of insulation, $d = 0.013 \text{ lb/cu. in.}$

$$W_I = 0.013 (V_b - V_a) \quad (15)$$

Total weight now becomes

$$W_T = W + W_o + W_R + W_I \quad (16)$$

Substituting (5), (11), (13), (15) in (16)

$$\begin{aligned} W_T = & 0.025 A_a r_a + 0.011 A_b r_b h \\ & \times 10^{-5} + 0.072 V_a + 0.013 \\ & (V_b - V_a) \end{aligned} \quad (17)$$

For a sphere within a sphere, insulated

$$\left. \begin{aligned} A_a &= 4\pi r_a^2 \\ V_a &= 4/3 \pi r_a^3 \\ A_b &= 4\pi r_b^2 \\ V_b &= 4/3 \pi r_b^3 \end{aligned} \right\} \quad (18)$$

Substituting (18) in (17) and collecting like terms

$$W_T = 0.562 r_a^3 + (.054 + 0.138H \times 10^{-5}) r_b^3 \quad (19)$$

where r_a , r_b , and h are in inches

For sphere within a sphere, evacuated, equation (15) is zero, and $r_a \approx r_b$ therefore

$$W_T = (0.616 \times 0.138 h \times 10^{-5}) r_a^3 \quad (20)$$

For a cylinder within a cylinder, insulated where length = diameter

$$\left. \begin{aligned} A_a &= 4\pi r_a^2 \\ V_a &= 4\pi r_a^3 \\ A_b &= 4\pi r_b^2 \\ V_b &= 2\pi r_b^3 \end{aligned} \right\} \quad (21)$$

Substituting back in (17) with (21) and collecting like terms

$$W_r = 0.684 r_a^3 + (0.082 + 0.138 h \times 10^{-5}) r_b^3 \quad (22)$$

For a cylinder within a cylinder, evacuated where $r_a \approx r_b$

$$W_r = (0.766 + 0.138 h \times 10^{-5}) r_a^3 \quad (23)$$

For a cylinder within a sphere, evacuated

$$\left. \begin{aligned} A_a &= 4\pi r_a^2 \\ V_a &= 2\pi r_a^3 \\ A_b &= 4\pi r_b^2 \end{aligned} \right\} \quad (24)$$

$$\text{where } r_b = 1.414 r_a \quad A_b = 5.6\pi r_a^2 \quad (25)$$

Substituting back in (17)

$$W_T = (0.766 + 0.274 h \times 10^{-5}) r_a^3$$