FOREWORD

This is the final report covering the work performed by the General Electric Company for the United States Air Force under Contract No. AF33(616)-5281 entitled "Thermopile Generator Feasibility Study." This program was carried out by several components within the Company under the overall cognizance of the Aircraft Accessory Turbine Department. The contract was administered under the direction of the Aeronautical Accessories Laboratory of Wright Air Development Center (now designated Flight Accessories Laboratory, Wright Air Development Division), Wright-Patterson Air Force Base, Ohio. Lt. R. G. Leiby was Task Engineer during the early part of the contract, and Mr. R. N. Cooper acted as Task Engineer during the remaining portion.

This report is written in four parts, of which this is Part I. It covers the entire period of the contract, from 1 July 1957 through 31 March 1960.

In addition to the editor of Part I, R. L. Gessner, those who contributed materially to the writing of this part of the report include: Dr. J. H. Bredt, D. L. Kerr, and Dr. R. H. Vought. The very helpful consulting assistance of Dr. R. W. Fritts and Dr. J. D. Richards of the Minnesota Mining and Manufacturing Company is gratefully acknowledged. Other General Electric Company personnel who made significant contributions to the work performed on the contract include:

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ABSTRACT

This report contains a detailed description and summary of a research and development study to determine means of employing thermopile generators as sources of electrical power in future air and space weapon systems. The following major areas of work were involved: 1) Materials development, 2) Junction fabrication and test, 3) Thermoelectric generator applications studies, and 4) Thermoelectric generator design.

The report consists of four parts as follows:

Part I - Summary - This presents an over-all summary of the entire program.

Part II - Materials Investigations - This contains the details of the work on materials development.

Part III - Performance Studies - This presents in detail the work on thermoelectric generator applications studies as well as the more general aspects of thermoelectric generator design.

Part IV - Generator Design - This contains the details of the work on fabrication and test and thermoelectric generator design for specific applications.

This is Part I of the report. It contains a coordinated presentation and discussion of objectives, procedure, major results, and conclusions and recommendations broken down according to the categories defined by Parts II, III, and IV.

PUBLICATION REVIEW

The publication of this report does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published only for the exchange and stimulation of ideas.

FOR THE COMMANDER:

G. W. SHERMAN, Chief
Flight Vehicle Power Branch
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m = Ratio of external electrical resistance to internal electrical resistance of thermoelectric materials, dimensionless

M = Value of resistance ratio, m, for maximum efficiency, dimensionless

Defined by:

$$M = \sqrt{1 + \frac{Z}{2} (T_1 + T_2)}$$

P_N = Net power output, watt or kw

S_n = Thickness of thermoelectric elements, inch

S_p = Thickness of thermoelectric elements, inch

T_1 = Temperature at hot end of thermoelectric elements, K

T_2 = Temperature at cold end of thermoelectric elements, K

W = Weight, lb

Z = Figure of Merit, K^{-1}

η_N = Overall thermal efficiency, dimensionless

INTRODUCTION

In preparing this report, two objectives have been kept in mind: 1) To make a complete and detailed presentation of the work performed on this contract, and 2) To arrange the material in such a way as to make it as convenient as possible for those who read it to obtain the information they are seeking, even though these readers may vary widely in both field and depth of interest. This latter objective was felt to be necessary because of the large quantity of information contained in the report. It is believed that it will be useful to describe briefly the report format that was chosen in an effort to meet this objective.

Basically, the report has been arranged both according to work category and amount of detail as follows: Part I is the summary. It is in turn divided into four sections. Section I is an over-all summary containing the major results, conclusions, and recommendations, all presented as briefly as it seemed reasonable to do. Sections II, III, and IV of Part I amplify on Section I by providing additional, summarized detail for each of the major work categories. Finally, Parts II, III, and IV contain complete details under each of the major work categories.

For various reasons, there were some changes in emphasis and redirection of the program during the course of the contract. These changes caused some modification in the nature of the end results in comparison with the original plans. For those interested in more detail, these developments are discussed under Background in this Part of the report.

Items and materials used in the study, and called out in the four parts of this report by trade name or specifically identified with a manufacturer, were not originated for use in this specific study or for the applications necessary to this study. Therefore, the failure of any one of the items or materials to meet the requirements of the study is no reflection on the quality of a manufacturer's product. No criticism of any item or material is implied or intended. Nor is any indorsement of an item or material by the United States Air Force implied or intended.

Manuscript release August 1960 for publication as a WADD Technical Report

BACKGROUND

Although the basic objectives of the work performed on this contract have remained constant, there have been some shifts in emphasis and redirection of effort which should be described in order to place the work in its proper perspective.

Work on the contract began in July of 1957 and was to be carried out in the following major work areas: 1) Materials Development, 2) Junction Fabrication and Test, 3) Thermoelectric Generator Applications, and 4) Thermoelectric Generator Design. At that time there was some expectation that thermoelectric materials then available might be shown to have promise in some air or space weapon systems applications. The intent, therefore, was to select these materials and the applications considered suitable, carry out junction fabrication and test work on these materials, and make rather detailed generator designs based on these materials and junction techniques for the applications considered to be practical. Such designs would then form the basis for quite realistic performance estimates which could be used as a means of evaluating the possibilities of thermoelectric generators in these applications. Some work was planned on obtaining improved materials, but this was not strongly emphasized.

Due to various budgetary considerations, work on the contract was suspended for a period of several months between September 1957 and March 1958. At the time work was again begun, it had become obvious that a re-direction of effort was necessary. This was occasioned by the fact that in the interim period it has become apparent that the thermoelectric generator applications of particular interest to the Air Force were those involving space vehicles plus consideration of a boost-glide mission. For such applications, studies performed during the initial contract work showed that extremely high temperatures of operation would be required. This in turn placed such severe requirements on materials that it was felt that the key to the whole program was a vigorous Materials Development effort, with such developments guided as to requirements by the Thermoelectric Generator Applications work. Junction Fabrication and Test work was to be performed only on those materials whose basic properties were such that the results of the applications studies showed them to be very promising. In this connection, it was anticipated that it would be possible to obtain from the Air Force requirements for several space missions which could be considered typical. The major emphasis in Thermoelectric Generator Design work, in turn, was to be on using those materials which warranted attention in Junction Fabrication and Test.

Such was the planned approach at the time the work was re-instituted, and this approach was basically maintained, with even further emphasis on Materials Development, when the program was expanded in July of 1958. It should be mentioned, however, that by this time it had become apparent that there was so much uncertainty regarding typical space mission requirements that it was decided that it would be impractical to endeavor to base the Thermoelectric Generator Applications studies on specific missions. Instead, it was decided that it would be better to remain more general and make evaluations for a wide range of power levels and durations of flight.

In the early spring of 1959, most of the Materials Development work as planned at the time of the program expansion were essentially completed. At that time, an evaluation and review of the entire program was made in order to determine the direction of effort for the remainder of the contract. Although some of the materials approaches were showing promise, it was decided that they could not be brought to fruition within the time and funds remaining. Therefore, a decision was made that all of the work performed up to that time should be completed as expeditiously as possible and that the remaining work should concentrate primarily on achieving two objectives which were:

1. Preparation of specifications for a 100 watt solar thermoelectric generator suitable for use in space applications using materials then available.

2. Construction of a small (approximately 5 watt net power output) model generator using materials then available.

The remaining portion of the program was therefore directed entirely toward the achievement of these objectives. One consequence of this decision was that it was not possible to carry out some of the previously begun investigations to the extent that had originally been contemplated. One example of this lies in the Thermoelectric Generator Applications area, where studies of complete thermoelectric generator systems and comparisons of the performance of these systems with systems using other methods of energy conversion were not carried out to the extent originally planned.

Viewed in its over-all perspective, then, the various changes in emphasis of the program over its lifetime had the following effects in comparison with the original plans.

1. The area of investigation was shifted almost completely to space applications instead of both air and space applications.

2. Some of the original plans were cut back to some extent in order to concentrate effort on the 5 watt model generator and the 100 watt solar thermoelectric generator specifications. The major modification here appears to have occurred in the Thermoelectric Generator Applications area where studies of complete systems and investigation of the comparative performance of complete systems were not carried out to the extent originally contemplated.

3. Considerable effort was devoted to efforts to construct a small generator whereas original plans contemplated no hardware construction other than that connected with fabrication and test of individual junctions.

SECTION I

SUMMARY

INTRODUCTION

This Section is an over-all summary of the work performed on the contract and has been separated into two parts: 1) Major results, and 2) Conclusions and recommendations. Each part has been further subdivided in accordance with the three major work categories: 1) Materials Investigations, 2) Performance Studies, and 3) Generator Design.

MAJOR RESULTS

MATERIALS INVESTIGATIONS

The work which was done under this division of the contract falls naturally into three principal parts, divided according to the type of work which was undertaken and the sort of results which were obtained: namely, surveys of several classes of materials which were thought to have some promise for high temperature thermoelectric applications, two rather specialized investigations which differed in most respects but were alike in that their points of departure were from specific laboratory techniques rather than classes of materials, and three programs aimed at developing instruments and techniques for measuring the relevant properties of thermoelectric materials at high temperatures. We shall follow this classification scheme in the following summary of the principal results of the program, and revert to the subject headings which were employed in the original proposal and the technical progress reports for the more detailed summaries of the work done in each area which appear below.

Since the survey work done under this contract was designed to investigate materials suitable for use in thermopiles operated at temperatures up to 1000°C, its purview was necessarily limited to the "high melting" metals and the refractory compounds based on them. In view of the fact that practically all of these materials either exhibit metallic conduction (which implies a low Seebeck coefficient) or are reasonably good insulators at room temperature, they would not appear to be an especially promising class of thermoelectric materials, but the almost complete lack of Seebeck coefficient data left the question of the existence of some thermoelectrically useful refractory substance or substances open, and several vague or enthusiastic notices of particular thermocouple systems which had been gleaned from the literature appeared to offer reasonable guidelines for the investigation without by any means exhausting its proposed field. The work on metals and metal-hydrogen systems consisted entirely of literature surveys and of experiments designed to test claims which had been published for particular systems. The upshot of the survey was to show that the best presently available metallic thermocouple system consists of the alloys 82Ni-18Mo and Constantan, both of which are used for temperature measuring thermocouples. The system would have an approximately constant value of the dimensionless parameter ZT (product of the thermoelectric figure of merit and the absolute temperature; see the detailed summary titled "Thermoelectric Properties of Metallic and Semiconducting Borides, Carbides, Silicides and Nitrides" for its relation to the energy conversion efficiency of a thermocouple) equal to about 0.05 (the maximum value of this parameter attained at present by compound semiconductors is about 1.0). Like the metals, the fairly extensive list of metallic borides, carbides, and nitrides which were screened all exhibited Seebeck coefficients which were so low as to remove them from serious consideration as thermopile materials. The silicides, on the other hand, showed some promise, apparently because the large relative size of the silicon ion prevents these compounds from forming interstitial-type metallic lattices. In particular, $MnSi_2$ was found to have a Seebeck coefficient of approximately the size (about 180 microvolts/°K) which various authors* have claimed is necessary for the attainment of a maximum thermoelectric figure of merit, and that of $CrSi_2$ was nearly as great (120 microvolts/°K). The rather small figures of merit

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* In this connection, see A. F. Ioffe, <u>Semiconductor Thermoelements and Thermoelectric Cooling</u> (Inforsarch, London, 1957) p. 69 and H. J. Goldsmid, J. Electronics, <u>1</u>, 218 (1955).

calculated for these materials result mainly from their high resistivities, so that there seems to be some prospect that their thermoelectric properties might be brought into the useful range by doping with suitable impurities. Several of the metal oxides which were surveyed had Seebeck coefficients reaching into the hundreds of microvolts/$^{\circ}$K, but all of them had resistivities which were much too high for practical use. Some doping experiments were performed on Cr_2O_3 and the cobalt oxides, but these did not disclose any means of lowering their resistivities to desirable levels. The same was found to be generally true of the many titanates and ferrites which were screened using the "S-Rho meter" (see below), and neither doping, reduction, nor the two combined were found to produce useful properties in the materials on which they were tried. A few isolated instances of treatments which simultaneously increased the Seebeck coefficient and decreased the resistivity were observed, however.

The first of what we have chosen here to call "specialized" investigations had to do with techniques of enclosing thermoelectric materials in airtight capsules in order to extend their useful temperature ranges by protecting them from oxidation, loss of material by sublimation, and breakdown due to melting. Two such systems were tried at the outset of the program, and both were successful; the better one of the two consisted of a Forsterite tube with iron end caps sealed to it by a eutectic bonding technique. This success was exploited by a series of measurements on a variety of the materials for which the latter system was suitable without modification, and it was found that enclosure in the capsules extended the temperature range in which they were useful by as much as 200°K. Moreover, the thermoelectric figures of merit for enclosed PbTe and ZnSb were found to reach maximum values which were higher, and were reached at higher temperatures, than those for the same materials exposed to the atmosphere. These measurements were carried up to temperatures above the melting points of the materials tested; all of them became p-type in the molten state, with rather small Seebeck coefficients and approximately constant resistivities (except for As_2Se_3, which seemed to be an intrinsic semiconductor). The only substance which seemed to have possibilities as a liquid semiconductor was InSb, whose Seebeck coefficient above the melting point increased linearly with the temperature.

The other "specialized" investigation made use of an existing apparatus for the measurement of low-temperature thermal conductivities to throw some light on the mechanisms of heat conduction in the transition metal oxides. The thermal conductivities of MnO, CoO, and NiO were measured in the temperature range between 3°K and 300°K; it was found that at low temperatures the thermal conductivities of these paramagnetic oxides are held to rather low values by the scattering of lattice vibrations by disordered atomic magnetic moments, and that at elevated temperatures they may be expected to approach those of the diamagnetic metal oxides.

Two of the efforts toward the development of devices for high temperature measurements of thermoelectric properties were principally concerned with the problem of measuring the thermal conductivity; for reasons given in the detailed summaries, this is considerably more difficult than the measurement of the Seebeck coefficient or resistivity. Models of the thermal conductivity device invented by R. W. Powell and the "Z meter" system developed by T. C. Harman and M. J. Logan were constructed and tested, and it was found that although both systems could be operated successfully at room temperature, their usefulness was limited to temperatures below about 100°C by the effects of radiative heat transfer and, in the case of the Powell apparatus, the near impossibility of maintaining a reliable calibration. A considerable amount of analysis was devoted to the radiation problem in both systems, and a design for a high temperature thermal conductivity apparatus was produced as well.

The "S-Rho meter" mentioned above was developed for use in the screening measurements on titanates and ferrites. In essence, it was a heated jig provided with thermocouples and with current and potential leads, in which the Seebeck coefficient and electrical resistivity of a specimen could be measured for the temperature range between 20°C and 1000°C. Two models were constructed; one was heated by a radio-frequency induction heater and had potential leads which were connected to the current leads at the point where the latter made contact with the specimen, while the other was heated by windings of resistance wire and had potential leads which made direct contact with the specimen. Both models were designed with a view to rapid, simple operation, and their success in this respect is attested by the large volume of data which was obtained for the substances which were screened by their use.

PERFORMANCE STUDIES

Fundamental Relations

Performance studies of thermoelectric generators and systems require as basic tools certain fundamental relations giving the performance of the thermoelectric elements, such as efficiency and power output per unit volume, in terms of a number of pertinent variables such as material properties, operating temperatures, and load resistance, to name but a few.

Therefore, in order to carry out the performance studies required on this contract, a compilation of these fundamental relations was prepared and is included as a part of this report. Although some of these relations are readily available in the literature, their derivation was verified in all instances before including them here. Relations not readily available in the literature were derived independently.

One of the major problems involved in making theoretical performance predictions for actual materials is that of taking into account the variation of material properties with temperature. Most of the literature treats only the case of constant material properties. Consequently, early in the program an approximate procedure was developed for handling variable material properties, and this was used extensively in the performance studies. Later, an exact procedure was developed which is applicable to the particular case where the Seebeck coefficient varies in such a manner that the Thomson coefficient is constant. Finally, toward the end of the program, an exact, completely general procedure was developed for handling variable material properties. This procedure was then applied to several test cases in order to check the accuracy of the previously developed approximate procedure. This check indicates that results of the performance studies reported herein based on the approximate procedure lie well within the accuracy requirements considered necessary. This report contains a complete description and summary of each of the procedures discussed above.

Optimization Studies

Recognizing the importance of weight in space applications, these studies were carried out for two purposes: 1) To develop procedures for minimizing the weight of a thermoelectric generator system in space, and 2) To utilize these procedures to estimate the minimum weights possible with presently available materials and better hypothetical materials. With these ends in view, procedures were developed for minimizing the weight of the system by concentrating on the generator and radiator package. Presentation of the minimum weight of these two components as a function of thermal efficiency permits the combination of this information with data regarding various heat sources to determine the approximate minimum weight of all three major components of the system.

Since the radiator will play a major part in determining the weight of the complete system preliminary studies for the purpose of minimizing radiator area were made. The results graphically indicate the importance of high radiator temperatures ($>$ 500 - 600 K) and also show that the amount of absorbed solar radiation is of secondary importance at radiator temperatures of practical interest (again $>$ 500 - 600 K).

In the generator-radiator weight minimization studies two basic configurations hereafter called the sandwich type and the side fin type were considered. Both types have the radiator and generator combined into one package in such a manner that circulating fluids are not required on the cold side. A combination of these two configurations called the side fin-sandwich type was found to have the lowest weight.

These studies have shown that the optimization involved results in significant weight reductions as compared to an unoptimized approach. For example, in the sandwich type configuration for any given materials, hot junction temperature, and thermoelectric element thickness, the weight that might be obtained using no gap between the elements can be as much as 100 times greater than the minimum weight determined here. On the other hand, it was found that neither the relative dimensions of the p- and n-type elements nor the ratio of load resistance to internal resistance of the thermoelectric materials exert a very strong influence on performance as long as values in the vicinity of the optimums for maximum power output or maximum efficiency are used. However, as could be expected, the effects of both hot junction temperature and Figure of Merit are extremely important. It was also found that minimum weight was a function of the thickness of the elements with very thin wafers being most desirable.

The most important single result of the optimization studies is that it appears theoretically possible, using presently available lead telluride thermoelectric materials, to achieve specific weights in the neighborhood of 30 lb/kw for the generator and radiator at a thermal efficiency of 3-4%. Substantial improvement in performance could be expected with relatively modest improvements in temperature capability and Figure of Merit of thermoelectric materials.

Heat Sources

Studies of the following sources of heat were made in connection with this program, the emphasis being on heat sources suitable for space weapon systems applications:

1. Solar heat sources
2. Chemical heat sources
3. Radioisotopes
4. Nuclear reactors
    a. Solid, homogeneous type
    b. Forced circulation type

The objectives of these studies were to obtain a better understanding of the characteristics, problems, and performance possibilities of these heat sources, particularly with reference to their use with thermoelectric generators.

The work on solar heat sources was restricted to consideration of concentrating, parabolic collectors focusing energy on a hot absorber to which the thermoelectric or similar generator would be coupled. The following tentative conclusions were reached:

1. Attainment of the required collector geometrical accuracy in a lightweight structure is believed to be the major problem area.

2. Meteorite damage could conceivably limit the useful life to much less than a year. More reliable data on meteorite density is needed.

3. It is doubtful if cylindrical collectors will find practical use at temperatures of interest for thermoelectric applications because of low collection efficiency. Spherical collectors are to be preferred.

4. Cavity (i.e. aperture) type absorbers appear to have better performance than selective surface absorbers for temperatures of interest in thermoelectric applications.

Results of the study of chemical heat sources show that such sources are too heavy to be of interest except when the required operating time is very short, i.e. on the order of minutes or a few hours.

Based on a number of criteria considered to be of importance, the characteristics of four radioisotopes were investigated. Results indicate that some of these are quite promising on the basis of weight. Handling problems and launch and re-entry hazards are serious. Shielding weight also complicates the picture, and total power output available from present production is not very large.

The solid, homogeneous reactor was investigated because of the potential simplicity of systems based on it. In this concept, the reactor core is surrounded by thermoelectric elements or some other static energy converter, and the heat generated in the core is transferred by conduction to the hot junctions of the generator. Basically, no moving parts are required.

Four types of reactors were considered as follows:

1. U-metal, fast reactor
2. UO_2-ceramic, fast reactor
3. U-Be, thermal reactor
4. UO_2-BeO, thermal reactor

Of these, the U-Be reactor was found to have the least weight per unit thermal output (neglecting shielding) for temperatures of interest for thermoelectric applications. However, it was also found that the requirement of removing heat solely by conduction through the reactor core severely limits the heat outputs obtainable..

The study of forced circulation reactors restricted itself to consideration of fast UC or UO_2 reactors using sodium or potassium as coolants. Results indicate that such reactors are capable of achieving much lower weight per unit thermal output than can be obtained with the solid, homogeneous reactors.

As a result of these studies, some tentative estimates were made of the weight of these various heat sources when applied to thermoelectric generator application. These are tabulated in Table 6 of Section III. Except for the chemical heat sources, these weights are surprisingly close, indicating that a greater degree of refinement is necessary in order to really evaluate weight possibilities.

Practical Weapon Systems Applications

In keeping with the belief that the greatest need for development of electrical power supplies lies in space applications, the primary emphasis has been placed on consideration of space weapon systems applications. In this connection, it has become apparent that there is no specific applications area where thermoelectric generators or any of the other possible energy conversion methods has a clear cut advantage or disadvantage. This situation exists primarily because of lack of operating experience of the various equipments, not only under conditions which are a reasonable facsimile of those which they will face in space, but in many instances because of inadequate operating experience in a ground environment as well. This in turn occurs because both the field of application and many of the conversion methods being investigated are so new.

Therefore, it is possible to reach only some fairly general conclusions regarding the applicability of thermoelectric generators to space weapon systems applications. These are as follows:

1. Viewed strictly in terms of their potential ability to operate reliably in space for extended periods of time with little or no maintenance, thermoelectric generators are believed to rank at or near the top in comparison with other possible energy conversion methods.

2. Based on presently available material properties and fabrication techniques, the weight of thermoelectric generators does not look very promising when compared with weight predictions of some of the other possible energy conversion methods.

3. For application to space weapon systems, it appears that thermoelectric generators will not be competitive with other systems unless: a) Significantly improved thermoelectric materials are developed, or b) Some of the potential problem areas involved in the other energy conversion methods fulfill their threat of seriously affecting the performance of these systems, or c) the relative performance predictions of the various energy conversion methods, when compared to actual performance, turn out to place the thermoelectric generator in an unduly pessimistic light.

GENERATOR DESIGN

Design Concepts

Two basic thermoelectric generator design concepts suitable for space applications were developed during the course of the contract. These configurations have been called the sandwich type and the side fin type. A combination of the two, referred to as the side fin-sandwich type, has been shown to have the least weight. Both of these concepts have the generator and radiator as an integral unit and do not require circulating fluids for waste heat rejection. Both are flexible as to the source of heat used, whether it be by radiation from a solar collector, by direct conduction from a radioisotope, or by the circulation of hot fluids using solar or nuclear energy as the primary heat source. The sandwich type and the side fin-sandwich type configurations have both been utilized in design studies and efforts to construct a model thermoelectric generator.

Materials Selection

For the purposes of constructing a 5 watt model generator and preparing a specification for a 100 watt solar thermoelectric generator p- and n-type lead tellurides were selected as the best available materials. This selection was based on considerations of performance, availability, and status of technology with regard to practical application.

Fabrication Problems

For the purpose of constructing a model thermoelectric generator of the sandwich type configuration using lead telluride thermoelectric materials, solutions to a number of fabrication problems were required. These problems are:

1) Diffusion Barrier - Provision of a suitable diffusion barrier between the thermoelements and the conductors.
2) Junction Formation - Deposition of the diffusion barrier material on the thermoelements so as to form a suitable junction.

3) Sublimation and Oxidation - Provision of a coating for protection of the thermoelements against oxidation and sublimation.
4) High Temperature Glue - Development of a high temperature adhesive suitable for bonding the generator to a structural member.
5) High Emissivity Coating - Provision of a radiator surface having high thermal emissivity.
6) Conductor Joining - Bonding of the conductors to the thermoelements (via the diffusion barriers) and to the thermal insulation.
7) Materials Fabrication - Formation of the thermoelectric materials into the small, wafer-like elements desired.

Progress toward the solution of these problems was such that most appeared amenable to solution within a reasonable time. Solutions to fabrication problems 1), 5), and 7) that appear satisfactory are available. Problem 4) may be solved, but the proposed solution is not completely evaluated. However, satisfactory solutions to problems 2) and 3) were not forthcoming. Moderate success was achieved in depositing the diffusion barrier (iron) on n-type lead telluride, but efforts to deposit an adequate barrier on the p-type were unsuccessful. Also, a method for applying a thin, impervious protective coating for the lead telluride at high temperatures was not found. Had these problems been solved, the resulting sandwich type model was expected to have a specific weight of 52 lb/kw at an efficiency of about 2.5%. Failure to solve these problems without extensive development of fabrication techniques necessitated revision of the model generator program toward a more conventional design.

Model Thermoelectric Generator

The design of the model generator based on more conventional construction techniques utilized pressure contacts, elements which are large with respect to the wafers heretofore considered, and enclosure of the structure containing the elements in a gas tight envelope filled with an inert or reducing atmosphere. The pressure contacts necessitated a relatively heavy containment structure in which the pressure contact forces were applied by inserting the elements between the jaws of a C ring which acted as a spring. Mica sleeves were used for sublimation protection and the configuration selected was of the side fin-sandwich type.

Initial performance estimates for this model (neglecting end effects) indicated a specific weight of about 70 lb/kw at a thermal efficiency of approximately 3.4%. Experiments have indicated pressure contact junction resistances approximately an order of magnitude higher than the approximately 30×10^{-6} ohm cm^2 anticipated. This has been the primary cause of a revision of the performance estimate for this model so that, neglecting end effects, a specific weight of about 120 lb/kw at a thermal efficiency of approximately 2% is now expected. The model has not actually been built, so this estimate has not been confirmed by test of a complete generator.

Specifications - 100 Watt Solar Thermoelectric Generator

The experience gained on this contract has been reflected in a set of specifications which have been prepared for a 100 watt solar thermoelectric generator. These specifications are contained in an appendix of Part IV of this report. They cover the design, construction, and ground feasibility test of a generator whose ultimate application would be as a source of power for space applications having a lifetime of at least one year. The specifications apply to the thermoelectric generator only. They do not apply to the other subsystems which would be required for a complete power system, such as the collector sub-system, an orientation sub-system, a voltage regulation sub-system, and an energy storage sub-system. The specifications do, however, define certain requirements that the collector and orientation sub-systems can be assumed to meet, since such information is necessary in order to design the generator.

The following performance requirements are believed to be realistic and are incorporated into the specifications.

Minimum power output - 100 watts
Maximum weight of generator - 20 pounds
Maximum envelope volume of generator - 3400 cubic inches
Minimum generator efficiency - 2%

CONCLUSIONS AND RECOMMENDATIONS

MATERIALS INVESTIGATIONS

The principal effect of the materials investigations carried out under the present contract has been to confirm the a priori lack of promise of the conventional refractory metals and compounds for thermoelectric application which was alluded to above. The root of the difficulty appears to be that in order for a substance to have a high melting point, it must have either metallic binding, which involves free electrons and a low Seebeck coefficient, or else very tight ionic or covalent binding, which leads to a large band gap and high resistivity. The second type of substance is the only one which seems capable of yielding useful high temperature semiconductors, for nothing much can be done to decrease the number of free electrons in a metallic material, while the number of carriers in a compound having a large band gap can be increased by doping. This approach to the problem depends, however, on the discovery of materials in which the carrier mobility is great enough so that a reasonably low resistivity can be obtained without introducing so many carriers as to lower the Seebeck coefficient to impractical values. Thus it appears that any future attempts at the development of high-temperature thermoelectric materials should concentrate on the class of nonmetallic refractory compounds, and should include precise measurements of the Hall Effect in these substances as a means of evaluating the carrier mobility and determining whether any improvement can be obtained by doping. While this may seem to be a rather ambitious recommendation for what amounts to a program of engineering research, it should be noted that virtually all of the solid state materials and effects which have interesting technical applications have been discovered by the methods of fundamental research. Moreover, such an approach would certainly be more fruitful, and would probably be more economical of money and time, than the trial and error method, in which the ratio of errors to trials may easily approach unity.

The encapsulation method developed under this contract for semiconductors has been so successful that it certainly deserves to be pursued, and in fact further work along these lines is currently under way under a contract awarded by the Navy Bureau of Ships (NObs 78403, Optimization of Thermoelectric Energy Converters). Further testing of known thermoelectric materials in the capsules will be done, bonding techniques for different cap materials and higher temperatures are being investigated, and means of minimizing the heat conductance of the capsules and matching their thermal expansion coefficients to those of the enclosed thermoelectric substances will be developed. In addition, the causes of the rather unexpected improvement which was obtained in the performance of PbTe will be investigated, in the hope that a like effect can be produced in other materials.

A moment's reflection on the relative degrees of success attained by the two thermal conductivity devices and the "S-Rho meter" will suffice to point up the comparitive difficulty of measuring the thermal properties of solids at high temperatures without any need for further comment here. However, the problem of measuring thermal conductivities at high temperatures does not seem to be an insoluble one, and as we have pointed out in the detailed summaries covering the work on the Powell device, knowledge of the thermal conductivity of a thermoelectric substance is essential for the engineering of its practical applications. The Powell device and the "Z meter" both fail at high temperatures because they depend on the realization of ideal operating conditions which are virtually impossible to obtain above about 100°C, and the same discouraging result can be expected of any system in which the radiation problem is not treated with extreme care. Under the circumstances, the approach which seems to offer the best prospect of success is a "brute force" method which satisfies the following requirements:

1. Establishment of a one-dimensional temperature gradient in the specimen, eliminating side losses, and

2. Measurement of the flux of heat across both ends of the specimen, in order to correct for whatever side losses cannot be eliminated. On account of the difficulty of securing calibrated standards in the appropriate range of temperatures and thermal conductivities, an absolute measurement is to be preferred.

An apparatus meeting these requirements could be modified in an interesting way: if leads were attached to the specimen so that a known electric current could be passed through it and the potential difference across it could be measured, direct measurements of the specimen's thermal efficiency as a heat pump or electrical generator could be secured. Such measurements would possess considerable theoretical interest, and would constitute the most valuable kind of engineering data as well; for this reason it would be very desirable to develop the necessary apparatus. However, because the main necessity for the success of the enterprise would be a continuous and fairly intense effort lasting until the experiment was made to work, it would be quite difficult to carry out under a fixed-appropriation contract. From the standpoint of the Air Force's interest in thermoelectricity, the most satisfactory arrangement would doubtless be to find some laboratory (for instance, the National Bureau of Standards, or some similar organization) which was interested in carrying out such experiments on its own account, and to contract with it for evaluation work on promising materials.

PERFORMANCE STUDIES

Fundamental Relations

The fundamental relations and procedures developed on this contract for determining the theoretical performance of thermoelectric generator elements for both constant and variable material properties are believed to be sufficiently basic that they can be used by other investigators studying a wide variety of applications. It is believed, moreover, that they are presented in a form convenient for such use, and it is hoped that they will prove valuable in this connection.

Optimization Studies

The relations and procedures developed for determining the minimum weight of thermoelectric generator and radiator packages in space power systems have shown that there is considerable opportunity for weight reduction through design optimization. It is believed that these procedures may prove valuable to other investigators in the field of thermoelectric generators in space applications.

From the results of these studies it is concluded that by careful attention to design it is theoretically possible, using presently available materials, to achieve specific weights of about 30 lb/kw for the generator and radiator at thermal efficiencies of 3-4%.

Heat Sources

Disregarding chemical heat sources, which are definitely shown to be too heavy to be of interest for long-lived applications, the study of heat sources has pointed up the difficulty that exists in making realistic evaluations of such sources with respect to problems and performance possibilities. The basic reason for this is lack of information based on operating experience. (A possible exception to this, of course, is the use of radioisotope heat sources, on which a great deal of ground, but no space, experience has been gained.)

Consequently, the main conclusion to be drawn is that no conclusion can be drawn as to which sources are the best, and development work on all of the sources considered, except chemical, should be continued until their status can be more clearly defined. Actually, each will probably find a place of usefulness.

In this connection, current solar collector hardware development programs are considered vitally necessary in order to obtain realistic data on collector performance and weight. More accurate determination of meteorite density should also be actively pursued since the answer to this question is fundamental to the feasibility of solar collectors. Finally, in connection with the shielding of nuclear sources, it would seem highly desirable to carry out shielding studies by considering the overall space vehicle, taking into account simultaneously with the nuclear source the ionizing radiation already present in space and the effect this has on overall shielding requirements.

Practical Weapon Systems Applications

Thermoelectric generator systems, like a number of other possible systems, are believed to warrant continued consideration for any space applications having mission durations longer than a few hours. Because the need for improved power supply systems is so great and the uncertainties involved in the prospects for all systems are so large, it would seem prudent, moreover, to implement such consideration by maintaining a continued active interest in and development of thermoelectric generators for space weapons systems applications.

GENERATOR DESIGN

Model Thermoelectric Generator Construction

Efforts to construct a model generator are reported under several headings in Part IV of this report, namely, Design Concepts, Materials Selection, Fabrication Problems, and Model Thermoelectric Generator. Since conclusions reached and recommendations to be made as a result of experience gained in the course of all the work directed toward the construction of a model generator are interrelated, they are summarized here under one heading.

It is concluded that the use of pressure contacts results in generator-radiator weights of 2-3 times those which could be obtained using bonded contact construction. This occurs for three reasons: 1) A heavy containment structure is required to provide pressure contact forces, 2) Application of the pressures required practically precludes the use of the thin elements desired for minimum weight, and 3) The junction resistance is apparently much higher than could be achieved with bonded contacts. It is recommended that in future development of thermoelectric generators for space applications every effort should be made to develop bonded contacts suitable for high temperature, either for lead telluride or for better materials that may become available.

It is also thought that the development of coatings suitable for protection against oxidation and sublimation should be pursued for lead telluride or for any better materials that become available, should they require such protection. The combination of mica sleeves and a sealed enclosure containing an inert atmosphere will provide the required protection for thick cylindrical elements of lead telluride. However, mica sleeves are not suitable for the thin elements desirable for space applications, and a coating that would also permit elimination of the sealed enclosure would represent a significant advance over present methods.

Specifications - 100 Watt Solar Thermoelectric Generator

The performance requirements incorporated into the specifications are based on the use of lead telluride thermoelectric material. They also contemplate the use of pressure contacts and include an allowance for the high junction contact resistances encountered in efforts to build the 5 watt generator. Consequently they are believed to be quite realistic, but at the same time, use of better materials or a solution of the junction problem should make it possible to make significant improvements in the specified performance.

SECTION II

MATERIALS INVESTIGATIONS

INTRODUCTION

The following text is intended to give a brief but reasonably complete account of the work which was accomplished under each of the formally designated materials investigations tasks performed under the terms of the contract. In each summary, references are made to one or more corresponding appendices; these are collected in Part II of this report, and consist of the original text and figures from reports prepared by the people who actually did the work. For purposes of ready reference, the numbers and names of the tasks are listed along with the corresponding appendices below:

Materials

1.1 - Metallic Alloys and Transition Metal Hydrides:

Appendices A, B, C, D

1.2 - Metallic and Semiconducting Borides, Carbides, Silicides, and Nitrides:

Appendices E, F, G

1.3 - Oxidic Semiconductors - (Oxides and Sulfides):

Appendices H, I, J

1.4 - Oxidic Semiconductors - (Titanates and Ferrites):

Appendix K

1.5 and
1.6 - Intermetallic and Liquid Semiconductors:

Appendix L

Measurements

1.7 - Thermal Conductivity: Powell Apparatus:

Appendices O, P

1.7 - Thermal Conductivity: Z - Meter:

Appendices Q, R

1.8 - Thermal Conductivity of Transition Metal Oxides:

Appendix M

MATERIALS

METALLIC ALLOYS AND TRANSITION METAL HYDRIDES

If one substitutes the Wiedemann-Franz-Lorentz value for the product of the electrical resistivity and the thermal conductivity of a free-electron solid in the denominator of the well-known expression for the thermoelectric figure of merit, the result is a formula which characterizes the potentialities of metallic thermocouple systems reasonably well, viz.,

$$Z \simeq 0.4 \times 10^8 \frac{S^2}{T}$$

Where S is the Seebeck coefficient and T is the absolute temperature. From published values of the properties of metals tabulated in Appendix A, it appears that deviations from the Wiedemann-Franz-Lorentz law tend to be relatively small, so that the maximum value which might be attained by the coefficient in the above formula would be about 1×10^{-8}. Moreover, it appears that in general the deviations which occur among metals with large Seebeck coefficients are such as to make the coefficient smaller rather than larger. For known high-output thermocouple materials, the maximum value of S^2 is of the order of 10^{-9} $\text{volt}^2/{}^{\circ}\text{K}^2$ and is approximately independent of the temperature; thus the figures of merit of the best known thermocouple metals are to be found in the range between $10^{-1}/T$ and $10^{-2}/T$.

These are rather unimpressive values by practical standards; in order to be useful for energy conversion or heat pumping, a metal thermocouple system would need to have a figure of merit about ten times as large as that of the best conventional systems. Because the Wiedemann-Franz-Lorentz law is only violated to a limited extent in metals, this improvement can probably be obtained only from a thermocouple system whose Seebeck coefficient is about three to four times as great as that of present-day high-output temperature measuring thermocouples.

The excellent mechanical properties and the high melting points of most metals and metal alloys would make such a system highly desirable for thermopile generator applications. It has also been shown, by a calculation which is given in detail in Appendix B that the very low electrical resistivities of metals give metal thermocouples a high ratio of power output to volume of material used in the thermocouple. This property could be advantageous for applications where a high power output was desired, low efficiency could be tolerated, and the desired temperature difference could be easily maintained across the thermocouples in spite of their high thermal conductivity.

The results of the preliminary literature survey detailed in Appendix A suggested a few guides for experimental work along the lines of investigating the variation of Seebeck coefficient as a function of composition in various alloy systems and following up reports of metallic systems which were supposed to produce larger than ordinary thermal emf's. In conformity with the considerations outlined above, measurements of the Seebeck coefficient were used almost exclusively to evaluate the materials which were investigated.

Two metal alloy systems were investigated in this way. The first, nickel-tungsten (reported in Appendix C) was found to have an average Seebeck coefficient of +34.9 microvolts/°K versus nickel for the best composition (74 Ni, 26 W) which was tested. This was almost, but not quite, as good as that of a 82 Ni-18 Mo alloy which is commonly used in temperature control thermocouples and has a Seebeck coefficient of +38.4 microvolts/°K versus nickel. The other was a Cu +3.1% Co alloy which had been reported to have outstanding properties. The evaluation of this alloy is reported in Appendix D; thermal emf's of Cu containing 1.5%, 3.1%, and 5.0% Co were measured versus a copper standard, and were found to be only about 20% as great as that produced under the same circumstances by a constantan wire. Appendix D also includes tabulations of the Seebeck coefficients of a number of high-output thermocouple alloys and standard materials, and a reference to a report of a Pt, Pd, Au alloy of unspecified composition which is supposed to have a Seebeck coefficient in the neighborhood of 50 microvolts/°K; the latter was found too late for investigation in the present program.

In addition to the alloys, three metal hydride systems were investigated. The addition of hydrogen to zirconium metal (see Appendix D) was found to produce a monotonic increase in Seebeck coefficient with increasing hydrogen content, from +12.9 microvolts/°K for pure Zr to +22.2 microvolts/°K for $ZrH_{1.91}$. Hydrided palladium (see Appendix C) exhibited Seebeck coefficients of from -19 to -24 microvolts/°K at elevated temperatures when the hydrogen was in equilibrium with the palladium; a value of -66 microvolts/°K was observed in an experiment in which the specimen was giving off hydrogen fairly rapidly during the measurements. Some trial measurements (reported in technical progress report No. 10 and not included in the appendices) were made to see if improved performance could be secured by thermal cycling of hydrogen-saturated palladium in a hydrogen atmosphere; the maximum Seebeck coefficient obtained was -36 microvolts/°K, which was not large enough to justify further work. Measurements were also made on titanium hydride (reported in technical progress report No. 9 and not included in the appendices); the maximum Seebeck coefficient obtained was +7.1 microvolts/°K.

Thus none of the new materials tested were found to be as good as the best conventional thermocouple alloys, which are 82Ni-18Mo (about +40 microvolts/°K) and 45Ni-55Cu (about -40 microvolts/°K). With these materials a thermocouple having a figure of merit of about 0.05/T could be made.

THERMOELECTRIC PROPERTIES OF METALLIC AND SEMICONDUCTING BORIDES, CARBIDES, SILICIDES, AND NITRIDES

The efficiency E of a thermocouple whose figure of merit is Z, operating between a hot reservoir at temperature T_1 and a cold reservoir at temperature T_o and delivering maximum power (i.e., connected to a matched load) is given by the following formula:

$$E = \frac{1 - \frac{T_o}{T_1}}{\frac{3}{2} + \frac{1}{2}\frac{T_o}{T_1} + \frac{4}{ZT_1}}$$

A moment's consideration of this formula will show that two approaches are possible if one wishes to construct a device which will generate power at reasonably high efficiencies. One of these is to construct the thermocouple of materials which have a high figure of merit. The functional dependence of E upon Z shows, however, that the gains obtainable by increasing Z are limited by the fact that for present day materials the maximum obtainable value of ZT_1 appears to be of the order of unity (see Appendix L, Fig. L-17). The other possible approach is to increase the efficiency by increasing the temperature of the heat source; with $T_o/T_1 = 1/5$ and $ZT_1 = 1$, for instance, the efficiency would rise to 1/7. From these considerations, it is evident that a rather low figure of merit can be tolerated in a thermoelectric material which can be used at high temperatures, and this is why the thermoelectric properties of refractory materials are of special interest for thermopile generator applications.

Early in the history of the contract, a survey of the available literature on refractory thermocouple materials of all types was carried out; a report of the results of this survey is given in Appendix E. The Appendix is divided into two principal parts, which roughly conform to the work outline which was subsequently adopted. The first of these contains some material on thermocouples in which graphite is used, but deals mainly with oxides and sulfides; the second is concerned with the class of materials known as "refractory hard metals" because of their electrical properties; i.e. metallic borides, carbides, silicides, and nitrides. In addition to these two principal divisions, a certain amount of miscellaneous information which seemed of possible interest was included.

Although only fragmentary thermoelectric data were available for most of the materials surveyed, some comparisons of the usefulness of various materials for power generation with the known properties of Bi_2Te_3 were possible, and it was concluded that for sheer quantity of power generated with a given temperature drop, irrespective of any other consideration, $MoSi_2$ was far superior to any of the other materials surveyed. Other promising materials were CrS, Cu_2O and SiC.

Appendices F and G describe the experimental work which was carried out on the "refractory metals". For screening purposes, measurements of the Seebeck coefficient versus platinum leads were relied upon exclusively, as this parameter largely governs the maximum power which can be obtained from a thermocouple. Of the materials which were selected as representative and tested, the borides, carbides, and nitrides all exhibited Seebeck coefficients which were so low as to deprive them of almost all promise for practical thermoelectric applications. Some of the silicides, on the other hand, were found to develop thermal emf's which were large enough to make them appear worthy of consideration for actual use. The relatively large thermal emf's appeared to be correlated with the structures of the materials to some extent. When the radius of the non-metal ion in one of these compounds is less than 0.59 times that of the metal ion, the structure is of a normal interstitial type based on the structure of the metal, and when the non-metal ion has a radius larger than this critical value, more complicated structures result. It was found that in the silicides the Si ion was always larger than the critical size, while the non-metal ion was generally smaller than or just equal to the critical size in the other compounds which were investigated.

By far the largest Seebeck coefficients were obtained from the two disilicides $MnSi_2$ (180 microvolts/^oK maximum) and $CrSi_2$ (120 microvolts/^oK maximum); the Seebeck coefficients of the other silicides which were tried were all in the same range as those obtained with metals, and the effect of the impurities which were tried as doping agents was to lower the thermal emf somewhat in all cases. Of the two best materials, $MnSi_2$ appears to be better than $CrSi_2$ because of its lower resistivity and higher average Seebeck coefficient over the temperature range in which it might be operated as a thermocouple element; assuming equal values of the thermal conductivity for both materials, the room temperature figure of merit was estimated as about 7 x $10^{-4}/^{o}K$ for $MnSi_2$ and about 6 x $10^{-5}/^{o}K$ for $CrSi_2$.

The approximate formula for the figures of merit of metals which is given in the previous section indicates that $MnSi_2$ would have a room temperature figure of merit of about 3 x $10^{-3}/^{o}K$ and $CrSi_2$ would reach a value of 0.6 x $10^{-3}/^{o}K$ if the electrical and thermal conductivities of these materials had the values which are found in metals. Thus one promising avenue for further development of these materials would be to investigate means of increasing their electrical conductivities; if the large values of their Seebeck coefficients could be maintained, the accompanying increase in their thermal conductivities could be tolerated. Since the thermal conductivities of $MnSi_2$ and $CrSi_2$ are probably mostly due to lattice conduction, it would also be worth while to look into means of decreasing them by modifying the crystal structures of these materials or introducing imperfections of suitable types. It should also be noted that the estimates of the figure of merit which are quoted above rest on an assumed value of the thermal conductivity of $MnSi_2$ and an unconfirmed published value for that of $CrSi_2$; it will be necessary to secure more precise measurements on both substances if the promise which they have shown in the present study is to be confirmed.

OXIDIC SEMICONDUCTORS - (OXIDES)

A number of metal oxides are known to have semiconducting properties; the most familiar example is Cu_2O, used in the manufacture of rectifiers. Although little or no data were available in the literature about their thermoelectric properties, it was expected that they should have rather large Seebeck coefficients, as other semiconductors do; available data indicated that their electrical resistivities might in some cases reach values low enough to be "practical" at elevated temperatures. In addition, these compounds have high melting points, which would make them useful for thermopile power generation with high grade heat sources, the techniques for producing ceramic bodies from them are well understood, and their electronic properties can be manipulated in a relatively simple and convenient way by alteration of their oxygen content as well as by more conventional doping techniques. The program of measurements which was undertaken to determine the usefulness of metal oxides for thermoelectric applications is described in Appendices H, I and J.

This study relied almost exclusively upon measurements of the Seebeck coefficients of sintered compacts of various compositions for screening. At the beginning of the program, the Seebeck coefficients of Cr_2O_3, Co_3O_4, NiO, ZnO, Cu_2O, and Fe_2O_3 bodies were measured between 595°C and 925°C; the highest values were found for Cu_2O (690 to 850 microvolts/°K) and Cr_2O_3 (480 to 570 microvolts/°K). Because Cu_2O exhibited great sensitivity to the nature of the atmosphere surrounding it at high temperatures, and also because its properties had already been studied by other investigators, it was not studied in detail; in the subsequent work, the most attention was given to the properties of Cr_2O_3.

Measurements on the pure Cr_2O_3 showed that its resistivity ranged from 34 ohm cm at 310°C to 6.0 ohm cm at 880°C; the specimens had about 60% of the theoretical density, and it appeared that resistivities in the useful range could not be obtained by densification alone. Some increase in density was attained by hot pressing specimens in a graphite mold, and a resistivity of 0.3 ohm cm was measured at 980°C, but this procedure also decreased the Seebeck coefficient considerably, probably because the specimen interacted with the mold to form carbides. The effects of a number of metallic impurities, added to the compacts as oxides or compounds which decomposed during sintering to form oxides, were also studied, and it was found that impurities which increased the Seebeck coefficient increased the resistivity also, while those that decreased the resistivity decreased the Seebeck coefficient as well. In general, increases in impurity content were accompanied by decreases in both the Seebeck coefficient and the resistivity, which would indicate (as shown by P. J. Price, Phys. Rev. 104, 1223 (1956)) that optimum doping was to be found at quite small impurity levels. None of the compositions studied had resistivities which were low enough to be useful for thermoelectric applications.

Some effort was also devoted to the study of the cobalt oxides, since previous work reported in the literature had indicated some promise that useful properties could be developed in them. Specimens having nominal compositions corresponding to Co_3O_4 and to CoO were prepared and their properties were measured: the Seebeck voltage of CoO was found to be about twice that of Co_3O_4, but the former showed a considerable sensitivity to oxygen in the atmosphere around it at temperatures around 900°C and below. This was presumably due to oxygen absorption effects connected with the fact that Co_3O_4 is the stable form below 900°C; it was found that the resistivity and Seebeck coefficient of the CoO decreased sharply at temperatures below 900°C in air and that the resistivity was smaller during cooling than during heating. This effect was not observed in Co_3O_4 below 900°C, nor in CoO heated in an argon atmosphere. Several doping agents were tried in CoO specimens, but as with the Cr_2O_3 specimens, none resulted in useful properties; the lowest resistivity was obtained by the addition of lithium, which also decreased the Seebeck coefficient.

OXIDIC SEMICONDUCTORS - (TITANATES AND FERRITES)

Published work on this class of compounds had indicated that it exhibited the same sort of semiconducting properties as those of the simple oxides, and that some control could be exerted over these properties by variation of the oxygen content and the use of doping agents. On account of the general desirability of semiconducting materials which remain stable at high temperatures for thermoelectric power generator applications, a program of evaluation measurements was carried out on a selection of representative titanates and ferrites. The results of this work are described in Appendix K.

The properties measured were the resistivity and the thermoelectric power, and the temperature range covered was from 25°C to 1000°C; a special apparatus was developed for this purpose and is briefly described below as the "S-Rho Meter." From the standpoint of practical applications, the results which were obtained were discouraging; the ferrites and titanates studied* were generally characterized by resistivities which were too large for useful thermoelectric materials, coupled in several cases with rather small Seebeck coefficients. All of them behaved as intrinsic semiconductors at high temperatures, and some, notably $SrTiO_3$ and $BaTiO_3$ + 5% $BaFeO_3$, exhibited indications of impurity-type conduction below 800°C; the lowest resistivity measured for any of the materials tested was about 0.4 ohm cm, for some Ni-Zn ferrites at 1000°C.

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* These included $FeTiO_3$, $SrTiO_3$, $BaTiO_3$, $BaFeO_3$, $CoTiO_3$, $BaCoO_3$, $2CoO{\cdot}TiO_2$, $2Cr_2O_3{\cdot}TiO_2$, $MnFe_2O_4$, and some complex ferrites.

Two doped $BaTiO_3$ specimens were investigated; $BaTiO_3$ + 5%$CuSnO_3$ had a relatively high Seebeck coefficient at high temperatures, but even at 1000°C its resistivity was somewhat greater than 1000 ohm cm, and $BaTiO_3$ + 5%$BaFeO_3$ exhibited a Seebeck coefficient which was less than 50 microvolts/°K over the whole temperature range covered in the experiment. On the other hand, it was found that both the resistivity and the Seebeck coefficient of $Ni_4Zn_3Fe_{18}O_{36}$ doped with 5 mol.% Co_2O_3 were better, from the thermoelectric point of view, than those of undoped $Ni_7ZnFe_{24}O_{48}$; this was taken to indicate that there might be some hope of attaining useful figures of merit in compounds of this type by doping.

A series of experiments was also conducted in order to evaluate the usefulness of reduction as a means of altering the properties of these compounds. The most complete data were obtained with $SrTiO_3$, specimens of which were reduced by heating in both vacuum and a hydrogen atmosphere. The lowest resistivity was obtained with a hydrogen-reduced specimen which had been made of C.P. grade material; it ran between 3 and 4 ohm cm over the whole range of temperatures and was coupled with a slowly increasing positive Seebeck coefficient which reached nearly 200 microvolts/°K at 1000°C. The unreduced material, on the other hand, showed intrinsic conduction properties and had a high resistivity (which was decreased only to 100 ohm cm at 1000°C) and a large Seebeck coefficient. Vacuum reduction decreased the resistivity and increased the Seebeck coefficient of the C. P. material, but both properties appeared to tend toward limiting values which were still outside the useful range as the degree of reduction increased. The effects of vacuum reduction on an "ultra pure" specimen were of the same general character, although both the resistivity and the Seebeck coefficient of this specimen were considerably lower than the values found for the C. P. material.

On account of this apparent saturation effect, it was concluded that reduction alone would not suffice to bring the properties of this class of compounds into the useful range, and trials were made on the effect of vacuum reduction on doped specimens. Two "ultra pure" specimens were prepared with 1% additions of niobium and antimony, respectively, and their resistivities were measured before and after a one hour vacuum reduction. The doped, unreduced specimens had resistivities which were somewhat lower than that of the undoped "ultra pure" material as expected, but the effects of vacuum reduction on the two were strikingly different. The antimony-doped specimen showed a reduction of its resistivity on vacuum annealing which was of the same order of magnitude as had been produced in the "ultra pure" specimen by comparable treatment, but the resistivity of the niobium-doped specimen was increased by a factor of about 20. No explanation of this effect seemed possible on the basis of the available data. While it would evidently be worthy of investigation by anyone who was interested in elucidating the electronic properties of the titanates, the conclusion to be drawn in the context of the present investigation is that the combination of doping and vacuum reduction has not so far shown itself to be a means of producing thermoelectrically useful titanates.

The general conclusions which seem to be established by this investigation are that pure titanates and ferrites of stoichiometric composition are not promising as thermoelectric materials because of their high resistivities, and that the development of doping techniques to secure useful properties would require a considerable amount of investigation because of the unpredictable effects of impurities in these compounds.

INTERMETALLIC AND LIQUID SEMICONDUCTORS

The object of the work done in this area was to develop a practical method of enclosing specimens of promising thermoelectric materials in capsules so that they could be used under environment and temperature conditions in which unenclosed materials would sublime or melt, and to carry on investigations of the changes in the properties of materials as they change from the solid to the liquid state. The results of this effort are described in detail in Appendix L.

The most promising techniques and materials for encapsulation appeared to be:

1) Sealing in quartz tubes with thin (about .0025 cm thick) molybdenum ribbon electrodes running through non-graded seals in the walls.

2) Enclosure in Forsterite or alumina tubes with ends sealed by iron caps attached by means of the eutectic bonding techniques which have been developed for use with ceramic enclosed electron tubes.

Studies of the corrosion of various possible contact materials in contact with molten thermoelectric materials of the kinds to be investigated indicated that both molybdenum and pure iron would be suitable for use with a wide range of materials. The iron-Forsterite capsule was chosen for use in the investigation because it offered a configuration in which reasonably accurate measurements could be made of the temperature difference across the enclosed material and because its expansion coefficient was better matched to those of the materials to be enclosed than was that of the quartz. It also seemed that the metal-ceramic type of cell would allow some latitude with respect to materials used, which would permit matching of expansion coefficients for special applications and selection of optimum contact materials.

It was found that the Forsterite-iron cell could be operated at temperatures as high as 1220°C, so that it would be useful over the whole of the range contemplated for high temperature use of thermoelectric materials. As noted in Appendix L, the use of iron electrodes somewhat restricted the domain of materials which could be tested in the cell; the variety of materials for which the Forsterite-iron capsule was satisfactory was broad enough, however, so that the rest of the time and money available for this work could be used for the evaluation of materials rather than for the development of modified capsules. The two principal modifications which appeared to be desirable to extend the usefulness of ceramic and metal cells were contacts made of metals other than iron and reinforced capsule walls for use with materials whose vapor pressures were high at elevated temperatures.

The materials to be evaluated were prepared from the purest constituents which were commercially available, by melting them together in evacuated and sealed quartz tubes. All handling of the materials after preparation was done in a dry, oxygen-free atmosphere, and they were sealed into the cells in vacuum. Since the latter process was carried out above the melting temperatures of the materials, however, there was some opportunity for them to pick up impurities from the cells. In accordance with the philosophy of exploiting the initial success in encapsulation technique by doing as much materials evaluation as possible in this area, little emphasis was placed on the development of measuring apparatus and the measurements were confined to the electrical resistivities and the Seebeck coefficients of the materials studied. Where estimates of the thermal conductivities of promising materials were desired they were taken directly from the literature or extrapolated from published values. The precision of the resistance measurement was estimated as ± 7% and that of the Seebeck coefficient, as ± 12%; these limits were judged reasonable for a screening type of investigation and although some means of improving the measurements were projected during the work, no major effort was made to attain higher precision.

In n-type PbTe doped with 0.1% Bi, in ZnSb (both pure and with various additions), and in a 76% Bi - 24% Sb alloy, the Seebeck coefficient was found to go through a relative maximum and then drop rapidly to very small values near the melting point. The Seebeck coefficient of PbTe reached its maximum of about -200 microvolts/$^{\circ}$K measured against Pt near 1000°C, dropped to zero at 1200°C, and became slightly positive (about 20 microvolts/$^{\circ}$K) in the liquid state. The maximum Seebeck coefficient for the bismuth antimony alloy is evidently found below 300°C, the lowest temperature reached in this series of measurements; in the range covered, the Seebeck coefficient of the alloy measured dropped monotonically from -50 microvolts/$^{\circ}$K at 300°K to about -1 microvolt/$^{\circ}$K at 600°K, the melting point, and remained small and negative in the liquid state. The Seebeck coefficient maximum for the pure ZnSb was reached at a little above 700°K and that for the doped alloy, about 100°K lower; both maximum values were about 180 microvolts/$^{\circ}$K, and for both materials the Seebeck coefficient dropped sharply to a value of about 25 microvolts/$^{\circ}$K at the melting point (about 840°K) and remained approximately constant thereafter.

The Seebeck coefficients of InSb and of two PbSb alloys which were tested behaved in a way which contrasted markedly with that described above. For InSb the Seebeck coefficient reached a maximum of nearly -60 microvolts/$^{\circ}$K near 650°K and then fell rapidly, becoming zero at about 750°K and weakly positive at about 800°K, the melting point. So far, the curve was much like that obtained for PbTe, but above the melting point, the Seebeck coefficient of the InSb increased linearly with temperature, with a slope of about 20 microvolts/($^{\circ}$K)^{2}. Both of the PbSb alloys (one of which was 50 Pb-50 Sb and the other, 76Pb-24Sb) were n-type at room temperature but became p-type below the melting point, which was at about 560°K. The 50-50 alloy changed its carrier type quite close to room temperature, while the 76-24 alloy did so at about 530°K; both alloys had appreciable Seebeck coefficients in the liquid state, reaching about 70 microvolts/$^{\circ}$K for the 50-50 alloy and about 50 microvolts/$^{\circ}$K for the 76-24 alloy at 1000°K.

The resistivity vs. temperature curves obtained for PbTe, InSb, and ZnSb all showed the same general characteristics, rising from the room temperature value to a relative maximum and then decreasing smoothly to a value at the melting point which was somewhat smaller than the room temperature resistivity; beyond the melting point, the resistivities of these materials remained nearly constant. Measurements were also made of the temperature dependence of the resistivity of antimony and arsenic selenides; both of these exhibit an approximately 1/T variation up to the melting point; the resistivity of the Sb_2Se_3 decreasing from 4000 ohm cm at 300°K to 0.4 ohm cm at 880°K, where it melts, and remaining constant up to 980°K. The resistivity of As_2Se_3 was still very high (10,000 ohm cm) at its melting point of 630°K but continued to decrease above the melting point, reaching about 2000 ohm cm at 1000°K. No Seebeck coefficient measurements were made on either of these materials.

Approximate figure of merit calculations were carried out for four of the materials studied, and their results may be summarized as follows: For the PbSb alloys, the maximum figure of merit is reached at 1000°K, and amounts to about $0.1 \times 10^{-3}/^{o}K$; since the Seebeck coefficients of these materials seemed to begin to saturate at this temperature, they do not appear promising for high temperature use. For PbTe, the figure of merit as a function of temperature shows a broad maximum, reaching values slightly above $1.0 \times 10^{-3}/^{o}K$ between 750°K and 900°K. In this temperature range published measurements on unenclosed PbTe[3] lead to figures of merit which decrease linearly from a value of about $0.7 \times 10^{-3}/^{o}K$ at 750°K to about $0.5 \times 10^{-3}/^{o}K$ at 820°K, where the material begins to sublime. Thus the encapsulation technique developed in this program not only extends the useful temperature range of PbTe by about 200°K, but also leads to a considerable improvement in performance over that of the unenclosed material even below the sublimation point. The calculated temperature at which the figures of merit of the enclosed and unenclosed materials become equal is about 650°K, and the figure of merit is about $0.9 \times 10^{-3}/^{o}K$. For encapsulated pure ZnSb, the calculated figure of merit exceeds $1.0 \times 10^{-3}/^{o}K$ between 500°K and 750°K, reaching a maximum of $1.4 \times 10^{-3}/^{o}K$ at about 700°K. Near 550°K, the figures of merit of the encapsulated and unenclosed materials become equal at a value of about $1.1 \times 10^{-3}/^{o}K$, and at higher temperatures[3] the value for the unenclosed material drops steadily, reaching about $0.7 \times 10^{-3}/^{o}K$ near 650°K. The ZnSb specimens containing additives exhibited figures of merit which were about half those for the pure specimen, chiefly because their electrical resistivities were higher.

The enclosure of thermoelectric materials in ceramic and metal capsules for high temperature applications appears to be most promising, for in two cases clear-cut improvements have been found in the performance of thermoelectric materials, and their useful temperature ranges have been extended. It will be well, however, to inject two notes of caution into the consideration of these encouraging results. One is that the improvement in the figure of merit may not be specifically due to the encapsulation, but may rather result from unaccounted differences in composition between the specimens used in the present program and those which supplied the published data with which the present results were compared. The other reservation which one must bear in mind is that the figures of merit quoted here were calculated for the bulk material and neglect the thermal conductance of the capsule in which it is enclosed; proper design can undoubtedly reduce the latter factor to very small values, but nonetheless the overall figure of merit of a system including the capsule will always fall somewhat short of the ideal values obtained for the material alone.

A second result of this work has been to show that some materials at least have noticeable thermoelectric properties in the liquid state; although none of the materials investigated so far has a large enough Seebeck coefficient to be practical for use as a liquid thermoelectric element, one of them, InSb, increases so rapidly in the temperature range which has been investigated as to give some promise of being useful at still higher temperatures. A more serious objection to projecting the use of liquid thermoelectric materials at present is that most materials seem to become p-type when they melt; before proceeding with attempts at further development along these lines, it might be profitable to give some theoretical consideration to the question of whether or not one could expect to obtain molten materials with sizeable negative Seebeck coefficients, and in general to the transport properties of liquid materials.

THERMAL CONDUCTIVITY OF TRANSITION METAL OXIDES

As noted elsewhere, in the sections dealing with the efforts devoted to the development of measuring techniques, the thermal conductivity of a thermoelectric material is the most difficult of the three properties of interest to measure. From the standpoint of a program intended to develop improved materials, it is a very interesting one, for whereas the Seebeck coefficient and electrical resistivity are both bound up with the electronic properties of a solid and cannot be varied independently, some of the heat conductivity results from the transport of energy by lattice vibrations, and these can be influenced by means which have little effect on the electronic properties. At the time of the proposal for expansion of the present contract, the General Electric Research Laboratory possessed a functioning apparatus for measuring low temperature thermal conductivities and was conducting a program of studies whose outlook was apposite to the objectives of this program. In order to take advantage of the apparatus and fund of experience which had already been built up in this field, it was decided to include measurements of the thermal conductivities of some transition metal oxides which possessed practical interest from the thermoelectric point of view in the program. This work is described in Appendix M.

For these measurements, single crystal specimens of MnO and NiO were prepared by the Verneuil (flame fusion) method and by decomposition of metal halide vapor. Although these crystals possessed some substructure, it was felt that they were sufficiently perfect to give values characteristic of the material itself and not materially influenced by structural imperfections or other than intentionally introduced impurities. The domain of temperatures covered in the thermal conductivity measurements was 3^oK to 300^oK, and the method employed was an absolute one. The specimen was mounted in contact with a heat reservoir whose temperature was measured with a helium gas thermometer, and temperature differences between the end of the specimen and the reservoir due to thermal contact resistances were measured directly using a differential thermocouple; another thermocouple junction was mounted on the specimen so that the temperature gradient developed by a heat flow could be measured. A small heater cemented to the upper end of the specimen and otherwise thermally isolated supplied a flux of heat which could be calculated from the values of the current and voltage supplied to it, and this and the value of the temperature difference across a known length of the specimen were used to calculate the thermal conductivity. The whole assembly was enclosed in an evacuated can and was immersed in baths of various liquids which approximately fixed the temperatures of the heat reservoir. The absolute accuracy obtained in measurements of the thermal conductivity was estimated at about ± 5%.

The principal stress in this work was placed on theoretical interpretation of results, and for this reason a preliminary series of measurements was performed on a single crystal specimen of MgO, which is a very good electrical insulator and should therefore exhibit a thermal conductivity which is wholly due to lattice vibrations. The results of these measurements showed good agreement with the only previously published measurements on this material, which had been made at room temperature and above. They also showed satisfactory agreement with theoretical calculations of the lattice thermal conductivity down to the thermal conductivity maximum near 35^oK, and the deviations below that temperature could be attributed to added thermal resistance contributed by crystal imperfections.

Similar measurements were then carried out on high-purity single crystals of MnO, CoO, and NiO in the same temperature range. All of these specimens exhibited smaller thermal conductivities than those which could be predicted on the basis of the simple theory which had been found to suffice for MgO, and this was interpreted as being due to the mean free paths of phonons being shorter than the theoretical expectation. This discrepancy was explained by use of a model of scattering of phonons by the magnetic moments of the metallic ions in the crystals; the argument is given in detail in Appendix M, and can be summarized qualitatively as follows: Above the Neel temperature the magnetic moments of the ions are totally disordered, and their contribution to the scattering of phonons is approximately independent of the temperature; whatever temperature dependence the phonon mean free path has is supplied by phonon-phonon scattering, and if the Neel temperature of the material is below the range in which phonon-phonon scattering has much effect, as it is in MnO, the mean free path may be nearly constant over a temperature interval whose lower limit is the Neel temperature. In this temperature range the thermal conductivity will increase slowly with temperature as the total energy of the lattice vibrations increases. Below the Neel temperature, the magnetic moments become increasingly ordered and their effectiveness as scatterers of phonons decreases; calculations of the variation in thermal conductivity between 300°K and 30°K in MnO using this model show satisfactory agreement with the data. At still lower temperatures, where the ordering of the magnetic moments into antiferromagnetic domains nears completion, the thermal conductivity does not, however, rise to the value defined by boundary and imperfection scattering of the phonons, for the walls of the domains constitute regions in which the magnetic moments remain highly disoriented. The domain walls are thus very efficient phonon scatterers, and the phonon mean free path never increases beyond the dimensions of the domains. In fact, it appears that the observed low temperature limit of the phonon mean free path can be used to provide a value of the domain size in crystals of this type.

It would seem that considerable confidence may be reposed in both the measurements and the model as representing the fundamental properties of the substances involved. Measurements on NiO crystals prepared by the two methods mentioned above, both before and after annealing at 1500°C, showed only such differences as might be expected from changes in crystal perfection, the annealed crystals exhibiting conductivities about twice as great as the unannealed ones at low temperatures. The same result was obtained from measurements made on a Verneuil process MnO crystal before and after annealing; the two curves reproduced each other with considerable fidelity, only small displacements of one from the other being observed.

The effects of impurities on the thermal conductivities of MnO and NiO were also studied. One MnO crystal containing 3 mole % of CaO and another containing 10 mole % of CoO were prepared and their thermal conductivities were measured; although one of these impurities was ferromagnetic and the other was not, they both had approximately the same effect on the thermal conductivity, reducing its room temperature by a factor of about two and depressing the low temperature conductivity maximum by a factor of about 8. The general shape of the curve and the position of the conductivity minimum remained unchanged, however, and because of this it seems that these impurities acted only as point scatterers of phonons. Some added support for this view can be found in the fact that 10% CoO produced the same effect as 3% CaO, for the latter has a limited solubility in MnO while the former will mix with it in any proportions; thus CoO probably produces a smaller distortion of the lattice and is a less efficient point scatterer than CaO.

Nickel oxide specimens containing 1% Li, 5% Co, and 25% Co respectively were also measured. Although the addition of the Li reduced the resistivity of the NiO from about 10^5 ohm cm to about 10 ohm cm at room temperature, there was no noticeable change in the room temperature thermal conductivity. The curve of thermal conductivity vs. temperature at lower temperatures for this specimen was not noticeably different from that obtained for a pure crystal grown by halide reduction and left unannealed. Thus it seems evident that the Li atoms act as point phonon scatterers, as one would expect from the fact that the Wiedemann-Franz law predicts that the added electrons introduced by the Li should make only a negligible contribution to the thermal conductivity. The Co impurity concentrations produced a general reduction in the thermal conductivity over the whole temperature range, in much the same way as the impurities in MnO had done. At room temperature, the thermal conductivity was reduced by a factor of about 2-1/2 by the addition of 5% of CoO and by a factor of 4 by the addition of 25% CoO; from these data it has been estimated that the minimum thermal conductivity in the NiO-CoO system would be about 0.08 watt/cm°K and would be obtained with a concentration of about 50 mole % of CoO. From the data obtained below 10°K, it appears that the dimensions of the antiferromagnetic domains formed in these mixed crystals vary monotonically with composition.

The general conclusions derived from this work are that the conduction of heat in MnO, CoO, and NiO below 300°K is entirely due to the transport of energy by lattice vibrations, and that the low values of thermal conductivity obtained with these compounds as compared with a diamagnetic insulator like MgO arise from interactions between the lattice vibrations and the magnetic moments of the metallic ions. At temperatures well above the Neel temperature this interaction effect is small compared to that of phonon-phonon scattering, so that at high temperatures the thermal conductivities of paramagnetic oxides will approach those of diamagnetic oxides. At temperatures below 10°K the thermal conductivity appears to be limited by the scattering of phonons at the boundaries of antiferromagnetic domains. The addition of substitutional impurities of either magnetic or non-magnetic nature changes the conductivity below 10°K very little in these oxides, but lowers the conductivity at higher temperatures by point impurity scattering.

INSTRUMENTATION

POWELL THERMAL CONDUCTIVITY APPARATUS

Of the three physical properties whose values enter into the figure of merit of a thermoelectric material, by far the most difficult to measure is the thermal conductivity. Formally, the measurement of thermal conductivity is rather like that of electrical conductivity, with temperature differences substituted for voltages and fluxes of heat for electric currents, but although it is reasonably easy to measure temperature differences it is very difficult to make an exact determination of the amount of heat that flows through a specimen of material because it is virtually impossible to confine a flux of heat to a unique path as one may do with an electric current. Consequently, the available data on thermoelectric materials are mainly concerned with the Seebeck coefficient and electrical resistivity, and precise thermal conductivity data are fragmentary.

While electrical measurements can serve as a reliable guide for the selection of useful thermoelectric materials, thermal conductivity data are of crucial importance for the design of functioning thermoelectric devices. The thermal conductivity not only enters directly into the figure of merit, but also largely determines the temperature difference which can be maintained across a thermocouple of given properties in any situation. It is thus almost as important as the figure of merit itself in determining the efficiency and power of a thermoelectric generator or the temperature difference which can be maintained across a Peltier cooler in the presence of a given heat load, and therefore precise measurements of thermal conductivity have an important place in any program of evaluation of materials for thermoelectric uses. A determined effort was made during the period of this contract to develop a technique which would be adequate for this purpose in the range of temperatures (about 300°K to 1300°K) in which thermopile generators might be expected to operate.

The first activity in this area was a survey of the extensive literature which exists on the subject of thermal conductivity measurements in order to find out the present state of the art and to discover promising methods. Most of the systems which have been described are specialized ones designed for use with specific classes of materials, and a realistic estimate of the overall uncertainty in a typical "good" measured value of a thermal conductivity appears to be about ± 10%. Among the experimental methods surveyed, the one developed by R. W. Powell (Journal of Scientific Instruments, 34, 485 (1957)) appeared to be the most promising for the work which was to be done.

In the Powell method a metal ball, initially at a temperature different from that of the specimen, is brought into contact with the specimen surface and its temperature is monitored as a function of time. If conditions are such that the specimen acts effectively as a semi-infinite body, then after a very short time a set of quasistable isothermal contours are set up in it, and the rate of heat transfer from the specimen to the ball becomes a function of the thermal conductivity rather than the thermal diffusivity of the specimen. In the apparatus described by Powell and the ones developed on this contract, a second ball was provided, with a thermal environment identical in all respects to that of the first ball except for the contact with the specimen. The time variation of the second ball's temperature was thus controlled by all of the factors which were effective for the first ball, except for heat exchange by conduction through the contact with the specimen, and it could be used to supply a correction for extraneous heat flows. In practice, the temperature difference between the balls at a fixed time after making contact with the specimen was used as the indication of the specimen's thermal conductivity. The device was developed for use as a calibrated instrument using materials of known conductivity as standards, for the functional relationship between its response and the thermal conductivity of the specimen is an exceedingly complex one. Although this approach involved including errors in the conductivities of the standards in the overall uncertainty in the measurements, it seemed to offer means of making rapid and sensitive comparisons between different materials, using the very small specimens which would usually be available.

Appendix O describes the several models of the comparator which were constructed. The first two models consisted merely of pairs of balls mounted in transite blocks which could be heated above the temperature of the specimen by means of a winding of resistance wire. Preliminary measurements were carried out with these devices, and the results were considered encouraging: After an initial short transient, the cooling rate of the ball in contact with the specimen was about constant for a period of 10 seconds or more if the initial temperature difference was about 70°K, and the results obtained with a given specimen were pretty consistently repeatable. The system was also subjected to an approximate mathematical analysis, described in Appendix P, which indicated that the signal did in fact depend almost wholly on the thermal conductivity of the specimen after the quasi-steady state was reached, provided that the contact area was sufficiently small. Formulae relating this area to the load and to the mechanical properties of the ball were also developed.

In the first operating model of the comparator, two 1/4" phosphor bronze balls were mounted in separate, independently heated transite blocks, and each ball was positioned over a separate specimen. The load on the contact was applied by weights acting against a spring and the whole assembly was shielded from drafts by a cover when in use. It was found that the phosphor bronze balls were unsatisfactory in two respects: Oxidation of the surface of the contacting ball made it impossible to maintain a constant calibration of the device, and the limited thermal conductivity of the phosphor bronze caused a saturation of the response with highly conductive specimens; zinc, aluminum, and copper specimens all produced about the same signal. These difficulties were removed by the substitution of silver balls, and reasonably consistent test results were obtained on a series of specimens having conductivities between 2.4 and 0.15 watts/cm°K. The response was linearly related to the logarithm of the conductivity, within about ± 10% limits for a 200 gm load on the contact. Responses of the comparator using specimens with conductivities between 0.1 and 0.01 watt/cm°K were also measured, but the results were inconclusive as a means of evaluating the performance of the instrument because no precisely calibrated standards were available for this range of conductivities.

A final model of the comparator was constructed of materials capable of withstanding temperatures up to 500°C, with provisions for remote operation so that it could be worked inside a heated enclosure. On account of the time and cost limits on the thermal conductivity program, only trials near room temperature were carried out with this device. The results obtained in these trials were about the same as those yielded by the previous model of the comparator, with one exception: In the earlier model the curve of response versus load for a given specimen had shown a tendency to level off for loads approaching 200 gm, but in the final model the response increased linearly with load for loads above 80 gm.

Although no high temperature tests were performed with any of the comparators, some consideration was given to the difficulties which would be encountered in high temperature operation of this sort of device. Radiative heat transfer between the balls and specimen would be one serious complication, for at moderate temperatures the power transferred by radiation from the specimen to the balls would exceed that transferred to the contacting ball by a specimen of low conductivity. From a rough calculation using data obtained in the testing program, it was concluded that the heat transfers due to radiation and conduction would become equal at about 600°C for a specimen whose conductivity was 0.1 watt/cm°K and at about 300°C for a specimen whose conductivity was 0.01 watt/cm°K. Thus very precise matching of the radiation characteristics of the two balls would be necessary for operation above room temperature with low conductivity specimens. Any mismatch between the rates at which radiation transferred heat to the two balls would introduce a temperature difference whose absolute value was independent of the conductivity of the specimen; this would introduce errors if a room temperature calibration were to be used, and would decrease the sensitivity of the device at high temperatures even if a high temperature calibration were available. On the basis of an estimate that 95% matching was about the maximum that might be obtained, it was concluded that this type of device could be useful only up to about 300°C for insulating materials.

A second difficulty would be that of maintaining constant surface conditions on the balls and the specimens at elevated temperatures. The response of the comparator is very sensitive to the states of the surfaces involved, and it might easily happen that different responses could be obtained from materials whose bulk conductivities were the same, unless extreme precautions were taken and some independent means of evaluating the condition of the surfaces were available. The device could be operated in a high vacuum in order to avoid oxidation, but with most interesting thermoelectric materials etching of the specimen surface by evaporation would be a serious and unavoidable problem at elevated temperatures.

The results of this effort may be summarized as follows: The Powell comparator has been found to yield a response which is a function of the thermal conductivity of the specimen under appropriate conditions, so that it can be used as a calibrated device for measuring conductivity. Because it must be calibrated, it would find its most effective applications as an auxiliary instrument in a materials evaluation program which included means of making absolute thermal conductivity measurements with good precision. In this kind of a program the comparator could be calibrated against standards supplied by the absolute measurement and used to supply approximate thermal conductivity values which could be refined, in the interesting cases, by the absolute measurement. Because of its sensitivity to radiation losses and its dependence on constant surface conditions, it is doubtful that the comparator could be useful at temperatures much above room temperature. The difficulties involved in maintaining the calibration of the device at elevated temperatures and of checking the validity of the results obtained with it would be such that an absolute measurement would be likely to involve less effort and expense, and would be more certain to produce reliable results.

HIGH TEMPERATURE Z-METER

Suppose that a specimen of a thermoelectric material could be isolated so that heat transfers between it and its surroundings were negligible, and an electric current were passed through it. The Peltier effect would cause heat to be absorbed at the junction between the specimen and one current lead, and to be released at the other junction; the temperature difference between the two junctions would increase until the flow of heat from the hot to the cold junction by normal conduction became equal to the heat transport due to thermoelectric effects, and thereafter a steady state temperature distribution would be maintained in the specimen. For suitably simple experimental conditions, it would be possible in principle to calculate the thermal conductivity and the Seebeck coefficient with respect to the current leads of the specimen from measurements of the potential and temperature differences between its ends and the current running through it.

This is the principle of the device which has come to be known in the trade as the "Z meter" because of its prospective ability to furnish measurements of all three of the quantities which directly affect the performance of an ideal thermocouple. On the basis of preliminary information uncovered in a survey of the literature, the Z-meter appeared to be attractive as a rapid materials evaluation instrument, and some effort was devoted to an investigation of its capabilities. The detailed results of this effort are reported in appendices Q and R.

The practical obstacles to successful operation of the Z-meter arise mainly from the presence of unavoidable heat leaks from the specimen to its environment. Great care must be taken to insure that the thermocouples at the ends of the specimen are attached in such a way that the thermal resistance between the thermocouple junction and the specimen is so small that the flow of heat along the thermocouple wires does not produce an appreciable temperature difference between the junction and the specimen. The existence of such a temperature difference falsifies the measurement of the temperature difference across the specimen and introduces errors in the measurements of the Seebeck coefficient and the thermal conductivity. The attachment of the current leads to the specimen must be arranged so that conduction along them to the environment does not allow any degradation of the temperature difference across the specimen. Radiative heat transfer between the specimen and the environment can allow heat evolved in the specimen to escape or can serve as a spurious heat source, thereby complicating the analysis of the data, and the seriousness of this effect increases very rapidly as the temperature increases. In addition to these difficulties, the Z-meter involves all of the usual problems of measuring small temperature differences and low level voltages, and in general these are aggravated when temperature gradients exist in the leads of the measuring circuits.

Part I of Appendix R describes a rather simple Z-meter which was designed and built to obtain empirical estimates of the seriousness of these difficulties by making room temperature measurements on specimens of known properties. In the first arrangement which was tried, pressure contacts were used to attach all of the leads to the specimen. The current, potential, and thermocouple leads to each end of the specimen were fabricated in the form of three parallel flat strips which lay in the same plane. Each group of lead strips was mounted in a frame; the arrangement was such that the specimen, when in place, was held entirely by the lead strips which could be tightened against its ends by relative motion of the frames. The electrical resistivity measurement was separated from the Seebeck coefficient and thermal conductivity measurements and made with no temperature gradient in the specimen by means of an A.C. circuit. A 400 cycle measuring current was used, and the indicating instrument used to detect the amplified signal from the potential leads was a dynamometer wattmeter whose moving coil was supplied with a constant sinusoidal 400 cps current. This arrangement greatly reduced the shielding requirements of the circuit, for the wattmeter acted effectively as a filter of very narrow band width.

While the results of the resistivity measurement were generally satisfactory, it was found that the measurements of the temperature difference developed across the specimen by a direct current were seriously in error because of the high thermal resistance of the pressure contacts employed. When the thermocouple junctions were embedded in the specimen, satisfactory temperature measurements could be made, for it was found that the measured Seebeck coefficient agreed with the known value. The thermal conductivity values obtained with this apparatus remained unsatisfactory, however, and this was attributed to the presence of heat leakage along the leads.

The rest of the work which was performed on this device during the life of the contract was analytical rather than experimental. A simple device was designed for use at room temperature, but was not built because the main objective of the program was to develop a means of evaluating materials at high temperatures; this is described in Appendix R. Two independent calculations of the effects of radiation losses were performed; the more extensive of these appears as Part II of Appendix R, and a more compact one, as Appendix Q. The general conclusion obtained from both of these studies is that $300^{o}K$ is approximately the temperature at which radiation losses become critically important with specimens of low conductivity and high emissivity, and that at any higher temperature extreme care must be taken to secure effective radiation shielding. The calculations also show that even with the best shielding which was considered, operation of the Z-meter as originally described would require the application of very large corrections to the data obtained at temperatures above $500^{o}K$.

It therefore appears that the simplicity and ease of operation offered by the Z meter can be obtained only by sacrificing precision. Even at room temperature the problem of isolating the specimen to the extent required by the underlying assumptions of the design are acute, and measuring techniques of very high precision are necessary to secure good quality results from the low level signals which are obtained. The operation of such a device is thus not particularly easy unless the tolerance limits on experimental error are as wide as ± 20%. The data obtained with the Z meter also require rather complex analysis if good precision is desired, for account must be taken of all of the effective heat leaks in the apparatus, and particularly of radiation. Since the radiation correction is not small in general, a reasonably good value for the emissivity of the specimen must also be secured.

The final conclusion of the people who had concerned themselves with the Z-meter project was that the most practical means of measuring the thermal conductivitie of materials at high temperatures would be one in which the heat flow in the specimen arose from an external source rather than the thermoelectric effects in the specimen. A proposed design for such a device is described in Part III of Appendix R. Attention has been given to the problems presented by radiative heat transfer and thermal contact resistances at the ends of the specimen, and it has been concluded that these difficulties can be overcome in the design which is presented. It is proposed to measure the rate of heat flow through the specimen by measuring the temperature difference across a standard specimen in series with the unknown one. This procedure might involve difficulties, for the standards would have to be calibrated very carefully against specimens of known conductivities, and it would be necessary to devise means of determining whether the conditions which applied during the measurements on an unknown specimen were the same as those under which the calibration had been performed. It would also be necessary to have standards whose thermal conductivities matched those of the specimens reasonably well, for if the temperature gradients in the specimen and the standard differed by a very large amount it would become very difficult to reproduce the temperature distribution well enough in the radiation shield to prevent excessive losses. The estimated precision of this method of measuring thermal conductivities is given at the end of Part I, Appendix R, as ± 13%; about 3/4 of this uncertainty is expected to arise from uncertainties in the calibrations of the standards.

THE S-RHO METER

The opening sections of Appendix K describe the construction of a device intended for preliminary evaluation of materials by measurements of their Seebeck coefficients and electrical resistivities over the temperature range which would be covered in possible applications. This approach is both reasonable and highly useful because of the rather narrow range of thermal conductivities (roughly, from 0.01 to 2 watts/cm^{o}K) encountered in possible thermoelectric materials; unless the quotient S^2/ρ exceeds a threshold value of about 10^{-5} watts/cm$(^{o}K)^2$, a material cannot attain useful values of the figure of merit.

The principal emphasis in the design of the device was given to rapid, easy operation, and high precision was not demanded of the measurements. The resistance of the specimen was measured by passing a small, known dc current through it and measuring the potential difference across it; measurements were made with current flowing in both directions in order to correct for adventitious emf's arising from thermoelectric effects and possible electrolytic action in the specimens at high temperatures. The Seebeck coefficient was determined from measurements of the emf's developed between two platinum leads connected to opposite ends of the specimen when a measured temperature difference was established between them. Two models of the device were constructed, and both of them permitted the Seebeck coefficients and electrical resistivities of two or more specimens to be determined as functions of temperature between 20°C and 1000°C in the course of an eight-hour working day.

The first instrument was designed to be used with rather thin disk-shaped or plate specimens, and was heated by a radio-frequency induction heater. Specimens to be used in it were first completely covered with a sputtered platinum film, and the platinum was then removed from the sides to prevent short circuiting, leaving only the flat faces on the ends covered. They were clamped between two platinum foils to which potential leads and thermocouples were attached, and since the foils made only a pressure contact with the specimens, the resistance measurements included some small contact resistances; these were estimated as amounting to about 5% of the specimen resistance. The assembly of foils and specimen was held between two graphite cylinders which acted as heat sources for the device by absorbing power from the coil of the induction heater, and the temperature difference across a specimen could be varied from zero to about five or ten degrees in either direction by moving the coil so as to change the relative amounts of power dissipated in the two pieces of graphite. The cylinders and specimen, but not the coil, were enclosed in a narrow evacuated bell jar when in use, and were mounted on insulating supports.

This design fully realized the desired advantages of ease of specimen mounting and rapid operation. Prepared specimens had merely to be set in place, and in practice measurements were made with descending temperature so that the specimen could be removed immediately at the end of a run; placement of a new specimen and evacuation of the bell jar required only a matter of minutes. The best evidence of this ease of operation is the quantity of data which is reported in Appendix K; there were, however, some disadvantages in the original design. The most serious was that although the contact resistance error in the measurements was thought to be small, it could not be evaluated; in addition, better control over the temperature and smaller thermal inertia in the hot part of the apparatus were desired. It was also suspected that the presence of the graphite cylinders might cause some reduction of the titanate and ferrite specimens on which the device was used.

These objections were met in the second model, which was built rather late in the life of the contract and used mostly to verify the results obtained with the device described above. In the new design a long thin specimen was used, and electrical contacts were made to a row of four dots of platinum which were sputtered on the surface through a mask. The specimen was placed in a holder which contained four permanently mounted thermocouples whose tips pressed against the platinum dots on the specimen surface; the platinum legs of these thermocouples also served as parts of the electrical measuring circuit. Because of its small size, the holder assembly had a very small heat capacity, and it was found to have a free cooling rate which was about twice as large as that of the graphite cylinder assembly used in the first apparatus; the assembly was heated by coils of resistance wire, and this arrangement was found to improve the control over the specimen temperature.

SECTION III

PERFORMANCE STUDIES

INTRODUCTION

This section contains a coordinated discussion and summary of the work on Performance Studies presented in Part III of this report.

These investigations can be grouped under the following major headings:

1) Fundamental relations for predicting the performance of thermoelectric generators.
2) Optimization studies.
3) Heat sources.

For ease of reference, the appendices of Part III applicable to each of the major headings are listed below.

Fundamental Relations - Appendices A through E

Optimization Studies - Appendices F through N

Heat Sources - Appendices O through T

FUNDAMENTAL RELATIONS

INTRODUCTION AND SUMMARY

Performance studies of thermoelectric generators and systems require as basic tools certain fundamental relations giving the performance of the thermoelectric elements. Performance parameters of primary interest in this connection are efficiency, power output per unit area and volume, and heat input and output per unit area. These are desired in terms of material properties, operating temperatures, relative dimensions of the n- and p-type elements, and the ratio of load resistance to internal resistance of the elements.

Early in the program, therefore, those relations that were readily available in the literature were compiled, and the few additional ones not readily available were derived. This initial work dealt solely with the case of constant material properties. As studies proceeded, however, it became more and more apparent that a means of treating variable material properties would be required in order to predict the performance of actual materials. Therefore, an approximate means of doing this was developed and used extensively.

Some months later, efforts to develop a general, exact procedure for treating variable material properties achieved some success with development of an exact procedure for the particular case when the Thomson coefficient of a material is constant. A series of calculations were then carried out using this method for a wide variety of cases, and results were compared with those obtained for the same cases using the approximate method. The objective here, of course, was to gain a better understanding of the magnitude of the errors that might be involved in the approximate method. Results were quite encouraging and led to increased confidence in the approximate procedure. Indeed, it was felt, as a result of these comparisons, that the accuracy of the approximate method would be quite adequate for the performance studies to be carried out on this contract.

Later, however, about a year prior to the contract expiration date, an exact theoretical procedure was developed for handling the general case where material properties are arbitrary functions of temperature. The accuracy of the approximate procedure previously developed was then checked again by carrying out calculations for a number of cases involving the use of lead telluride and comparing results of the exact and the approximate procedures. Again, the accuracy of the approximate procedure was found to be quite good for the cases investigated. Thus, as a result of these studies there now exist the following:

1. A compilation of useful fundamental relations giving the performance of thermoelectric generator elements when material properties are constant.

2. An approximate procedure for determining the performance of thermoelectric generator elements when material properties are arbitrary functions of temperature. This procedure has been compared to exact solutions for a number of cases and found to be quite accurate. It is, therefore, believed that, except for unusual instances, it will be quite satisfactory for initial performance predictions and for all but the final, detailed design of a generator.

3. An exact method for determining the performance of thermoelectric generator elements when the Thomson coefficients of the materials are constant. This procedure is primarily of academic interest, now, however, due to development of the completely general, exact procedure for handling arbitrary variation of material properties with temperature.

4. A relatively straightforward, exact method for determining the theoretical performance of a thermoelectric generator when material properties are arbitrary functions of temperature. This procedure should find considerable use in detailed design work and as a means of checking the accuracy of the more convenient approximate procedure whenever one begins work based on new materials or uses operating conditions considerably different from those of his previous experience.

Some additional details concerning the various studies just outlined are given in the material that follows.

CONSTANT MATERIAL PROPERTIES

Appendix A of Part III of this report presents in convenient summary form the important fundamental relations for the performance of thermoelectric generators when material properties are constant. The performance parameters involved are efficiency, power output per unit area of thermoelectric material, power output per unit volume of thermoelectric material, and required heat transfer rates. Included are both general expressions and expressions giving maximum attainable values of efficiency, power output per unit area, and power output per unit volume. The corresponding optimum relative dimensions of the thermoelectric materials and optimum load resistance are given in each instance. For a typical case, a numerical comparison is also made between those conditions giving maximum efficiency and those giving maximum power output per unit area.

Appendix B of Part III of this report contains a derivation of all of the relationships summarized in Appendix A of Part III.

APPROXIMATE PROCEDURE FOR VARIABLE MATERIAL PROPERTIES

This procedure is developed and summarized in Appendix C of Part III. It is based on treating variable material properties in a manner that is exact if no current is flowing and then neglecting the effects of current flow when applying it. Thus, the error involved in this procedure would be expected to increase with increasing current. In Appendix E of Part III of this report, this has indeed been shown to be the case in one illustrative calculation.

EXACT PROCEDURE FOR CONSTANT THOMSON COEFFICIENT

This procedure is derived in Appendix D of Part III. Calculations are also carried out in this appendix for a number of different cases, and results are compared with results obtained using the approximate procedure of Appendix C, Part III. This comparison is discussed in some detail on pages 44 and 45 of that appendix. The conclusion reached is that the approximate method provides results of acceptable engineering accuracy for most purposes for all cases investigated except some having very extreme conditions.

While admitting the limited range of conditions investigated, these results in turn provide an encouraging indication that the approximate method of Appendix C, Part III will give acceptable results for most conditions of interest.

Appendix D, Part III also makes a comparison between the exact results and an approximate procedure suggested by Ioffe and finds that in general, for the conditions investigated, the procedure of Appendix C gives better results than that suggested by Ioffe.

EXACT PROCEDURE FOR ARBITRARY VARIATION OF MATERIAL PROPERTIES

This procedure is developed and summarized in Appendix E, Part III. It is based on an extension of an approximate procedure first suggested by Dr. C. Zener. For the case of a single thermoelectric element, determination of efficiency, power output, and temperature distribution resolves itself into a straightforward numerical integration of two simultaneous, first order differential equations with known boundary conditions. Determination of the efficiency and power output for two thermoelectric elements in electrical series and thermal parallel follows by algebraic manipulation of the results for each single element.

The procedure has been checked out numerically by applying it to two cases where the exact results are known by other means, as, for example, the case of constant Thomson coefficients treated in Appendix D, Part III. Excellent agreement is found, substantiating the validity of the approach and calculation procedure.

The method is also applied to the determination of the performance of lead telluride thermoelectric generator elements using actual material properties. These material properties are identical with those which have been used extensively elsewhere in the performance studies carried out in this contract. They are also the same properties used in the design of the 5 watt thermoelectric generator and in the performance studies associated with preparation of the specifications for the 100 watt Solar Thermoelectric Generator. The exact calculations are also carried out for hot and cold junction temperatures which span the range covered by these other studies. Since these other studies were carried out based on the approximate procedure of Appendix C, Part III, a comparison of results between the exact procedure and approximate procedure under these conditions not only provides another check of the latter, but also indicates the accuracy of these other performance studies.

This comparison is made in Appendix E, Part III and is presented in some detail on pages 89-95 and 108-112 of that appendix. It shows that the errors in efficiency and power output involved in the approximate procedure are very small for these conditions, indications being that they are in the neighborhood of 2% or less for cold junction temperatures suitable for space applications.

On the other hand, when cold junction temperatures approach those suitable for water cooling (about 300°K), the errors increase, rising to about 5% error in efficiency and as high as 14% error in power output.

In all cases investigated, the error is such that the approximate procedure of Appendix C gives better performance than predicted by the exact procedure.

this connection, 1% fuel burn-up is a figure which generally appears to be quite permissible, and this corresponds to about 36.5 KW/KG of U-235 over a period of one year. The results in Table T-3 bracket this figure.

From these results and similar studies made in another connection after completion of this investigation, it seems quite reasonable to believe that forced circulation nuclear reactors which can operate for periods on the order of a year or more should be capable of achieving weights appreciably less than 1 lb/kw thermal (probably 0.3 lb/kw or even lower) although not necessarily at low power levels. These weights neglect shielding. It can be concluded therefore that forced circulation reactors can be significantly lighter in weight than solid, homogeneous reactors. This is as anticipated.

Appendix T of Part III also considers shielding weights in an approximate manner, both for shielding against typical transistor equipment and for biological shielding. These results are given in Figures T-7 and T-8 in terms of lb/ft^2 of shielding required for various distances from the reactor of the item being shielded.

COMPARISON OF VARIOUS HEAT SOURCES

From the information just discussed, a brief comparison of the various heat sources considered may be of interest. First, consider the various indications of weight that have been determined. These are given in Table 6 for operating periods of 30 days and one year, assuming hot junction temperatures on the order of 1100° F. It should be emphasized that these estimates are very tentative, and serve only to indicate rough bench marks of performance.

Table 6

Approximate Weights of Various Heat Sources

Heat Source	Approximate Weight - lb/kw of Thermal Output	
	30 day life	1 year life
Solar Collectors [1]	2 - 8	2 - 8
Chemicals [2]	300 - 1900	3500 - 23,000
Radioisotopes [3]	0.4 - 2	1 - 5
Reactor, solid, homogeneous [4]	2 - 5	2 - 5
Reactor, forced convection [5]	0.3	0.3 - 1

Notes:
1) Includes absorber losses.
2) Depending upon chemicals used. 100% combustion efficiency assumed. Structure weight not included.
3) Depending upon isotope used. Container and shielding weight not included.
4) Shielding weight not included.
5) Shielding weight not included. Probably higher for thermal output less than a few hundred kw.

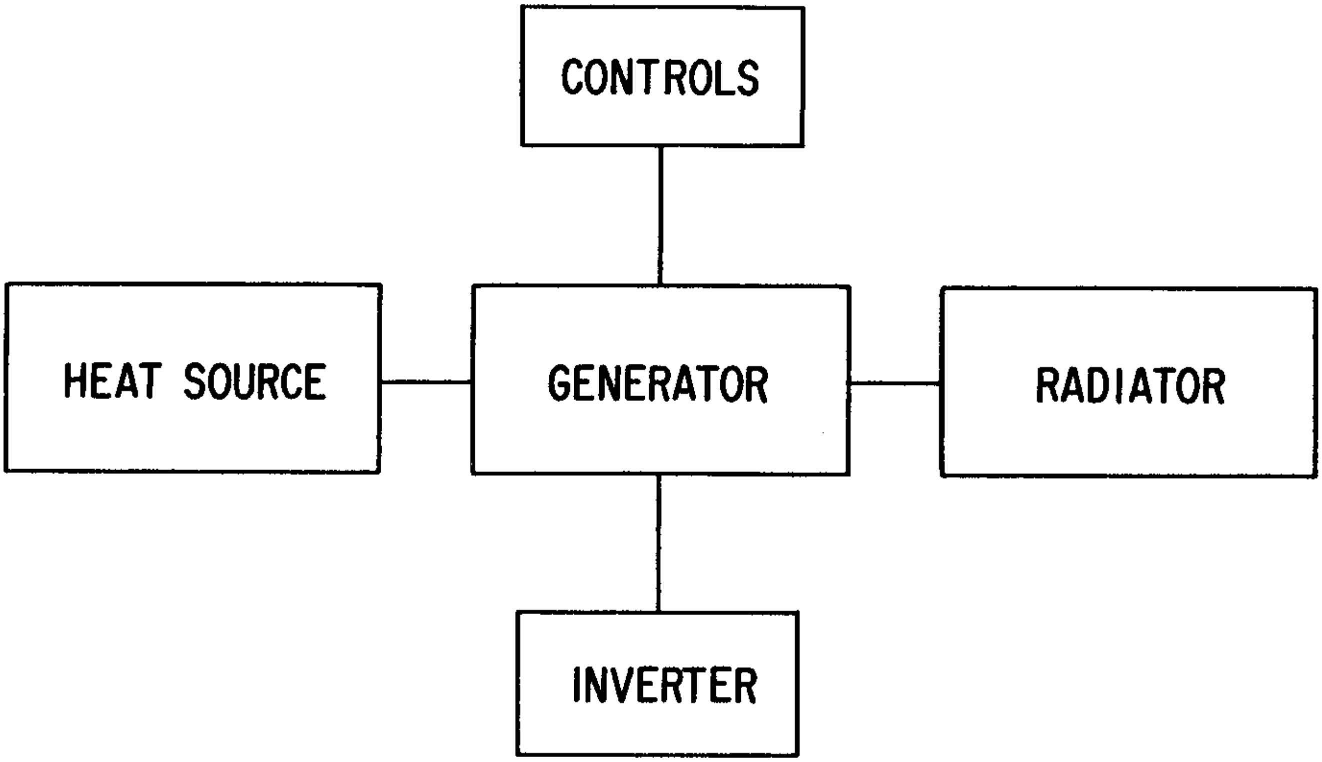

Figure 1: Thermoelectric Generator System.

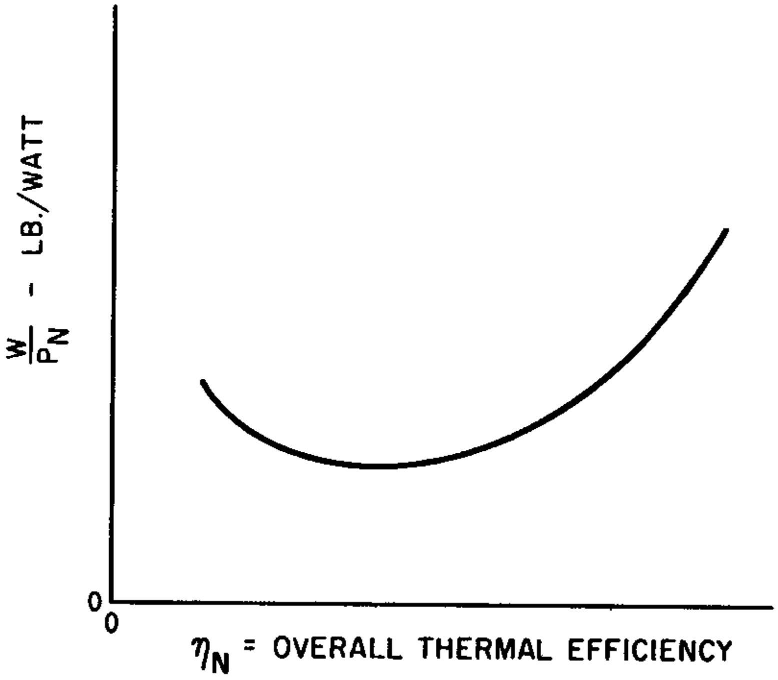

Figure 2: Typical Relationship Between Weight and Thermal Efficiency.

4. In most, if not all, energy conversion systems, the interdependence between weight and efficiency has the form given in Figure 2, assuming given materials and a given type of configuration. This figure is seen to exhibit a particular value of efficiency at which minimum weight occurs, and higher values of efficiency can be obtained only at the cost of increased weight.

The details of the reasons for the characteristic shown by Figure 2 may vary somewhat from system to system. However, such a characteristic can be expected in any energy conversion method involving heat transfer. This is readily indicated in a general way by observing that materials limits or other design problems will fix a maximum practicable heat source temperature, and the environment will specify the temperature of the heat sink. When an energy conversion cycle operates between the heat source and sink, high efficiency will tend to demand a large temperature difference between the maximum and minimum cycle temperatures. On the other hand, this decreases the amount of heat that can be transferred per unit size and weight of the heat exchangers. When these characteristics are coupled with the effect of efficiency on the amount of heat that must be transferred for a given power output, the result is a set of opposing influences which result in the characteristic shown on Figure 2.

The end product of the analysis discussed here is a procedure for determining the minimum weight of the generator-radiator as a function of overall thermal efficiency. Results of calculations using this procedure are suitable for presentation in a form similar to Figure 2 for any given values of materials properties and hot junction temperature. From such information, the corresponding minimum weight of a complete thermoelectric system can be determined as a function of overall thermal efficiency for a variety of heat sources.

MINIMIZING RADIATOR AREA

Since the radiator constitutes a major component of any space power system, consideration of its size and weight is one of the significant problems associated with system design and optimization. Appendix F of Part III discusses in detail one aspect of this problem, - namely, the required area of the radiating surface--with particular reference to thermoelectric generator applications. This section summarizes the information presented there.

Although the design considerations producing minimum radiating surface area will not necessarily result in the minimum weight of the complete system,the weight and hence, the area, of the radiator will generally be a very important factor. Hence it is felt that consideration of radiator area is useful from the standpoint of indicating the nature of the variation of radiator size with material properties and operating temperatures, as well as providing insight into system optimization problems.

If the thermal emissivity of the surface is fixed, the net amount of heat that can be rejected per unit area from a radiating surface is a function of two variables, radiator temperature and the amount of absorbed radiation from external sources such as the sun, earth, etc. On the other hand, the amount of waste heat that must be rejected by a space power system is a function of the net power output and the thermal efficiency. Assuming that the net power output is absorbed and rejected elsewhere, by combining the two functional relationships mentioned above, the net power output per unit of radiator area can be expressed as a function of thermal efficiency, radiator temperature, and absorbed radiation from external sources. The results of calculations based on this relationship indicate the strong effect of radiating surface temperature and that at radiating temperatures high enough to be of interest (>500 - 600 K) the effect of absorbed solar radiation is of secondary importance. (See Part III, Figures F-1 and F-2).

The thermal efficiency of a thermoelectric generator is primarily a function of hot and cold junction temperatures, thermoelectric material properties, and the ratio (m) of the external electrical resistance (load resistance) to the electrical resistance of the thermoelectric material. Assuming that cold junction temperature is equal to radiating surface temperature, the relationships for efficiency and for power output per unit of radiator area can be utilized to show an optimum cold junction temperature for minimum radiator surface area. The ratio of this optimum cold junction temperature (absolute) to the hot junction temperature (absolute) is found to lie between 0.75 and 0.80 for a wide variety of conditions. (See Part III, Figures F-4 and F-5).

The effects on radiator area of the other parameters affecting thermoelectric generator efficiency are also analyzed in Part III, Appendix F. Values of power output per unit of radiating surface area that represent the maximum possible values obtainable from a thermoelectric generator are presented in Part III Figures F-11 and F-12. This information can be useful in preliminary size investigations.

MINIMIZING GENERATOR-RADIATOR WEIGHT

Configurations

Fundamentally, there are two basic types of generator configurations which can be considered, each of which has several variations depending upon details of application. The first is one wherein the generator rejects heat to a circulating heat transfer fluid which in turn rejects this heat to space in a separate radiator. The second is one wherein the generator is an integral part of the radiator, and no circulating fluid is used on the cold side. Depending upon details of construction, both are flexible as to the source of heat used, whether it be by radiation from a solar collector, by circulation of a hot fluid, or by direct conduction from a radioisotope or from the fuel elements of a nuclear reactor.

There are several advantages of having the generator integral with the radiator, however. First, it usually eliminates one circulating fluid circuit. Second, the generator makes use of structural elements which are already required for the radiator with a resultant weight saving. When the generator can be placed inside a reactor, this may not necessarily be an advantage, since a generator inside a reactor can also make use of structural elements already required. Third, thermoelectric elements integral with the radiator can provide a considerable amount of protection against meteorite puncture of the tubes containing the heat transfer fluid, since they will surround those tubes. This again can mean a weight saving.

Considerations such as the foregoing lead to investigation of the generator-radiator type of configuration. Three variations of this configuration have been considered, hereinafter referred to as the "sandwich" type, the "side fin" type, and a combination of the two which is termed the side fin-sandwich type.

The sandwich type construction is indicated in Figure 3. Both cylindrical and planar configurations are shown. The thermoelectric elements, rectangular in shape, are sandwiched between two segmented metal plates. These plates act as electrical conductors between adjacent elements. The hot plate also serves to collect and distribute the heat coming from the heat source, and the cold plate also serves as the radiator. The plates must be segmented in order to accomodate the electrical insulation that is required between adjacent pairs of elements. Any combination of series and parallel electrical connections is possible. To minimize weight, it will usually be true that the cross-sectional area of the thermoelectric elements will be much less than the area of the radiating surface. For this configuration, increased radiator area is obtained by opening up a gap between the thermoelectric elements and filling this gap with thermal insulation or radiation shields to cut down on heat leakage.

The side fin type of construction is indicated in Figure 4. Here the generator elements are wrapped around a tube and are in the form of annular discs or wafers. In the axial direction, these discs are stacked one against another with adjacent discs consisting alternately of n- and p-type thermoelectric material. The axial separation between each disc is just sufficient to provide for a thin layer of electrical insulation. Cylindrical rings on the inner and outer radii of the discs are connected in the proper order to function as current carrying conductors. The direction of current flow is thus radially outward in one disc, then axial, then radially inward through the next disc, then axial, and so on. On the cold side, a radiating fin (side fin) extends out on either side of the tube in order to reject the waste heat. Appropriate electrical insulation is required at the inner and outer radii. Further details on various possible methods of construction and multiple tube arrangements are given in Part III, Appendix N.

The axial spacing between adjacent thermoelectric elements is shown to be very small in Figure 4. Actually, the principle used in the sandwich type construction to obtain increased radiator area could also be used here by increasing the axial spacing between thermoelectric elements and filling the resulting gap with insulation. This combination is the side fin-sandwich type. As will later be shown, it appears that it is the configuration having the least weight.

In accordance with the importance of low weight in space applications, it is now of interest to consider means of minimizing the weight of the generator-radiator combination insofar as this contributes toward minimizing the weight of an overall system.

Minimizing Weight-Sandwich-Type Construction

Consider first the weight of the generator sandwich with heat leakage through insulation and exclude the weight of the heat source. The weight involved, then consists of the combined weight of the thermoelectric materials, the hot and cold plates or conductors, and the weight of the thermal insulation. The procedure used in this study for determining the minimum weight for this type of configuration has been described in Part III, Appendices H, I and K. It is briefly outlined below.

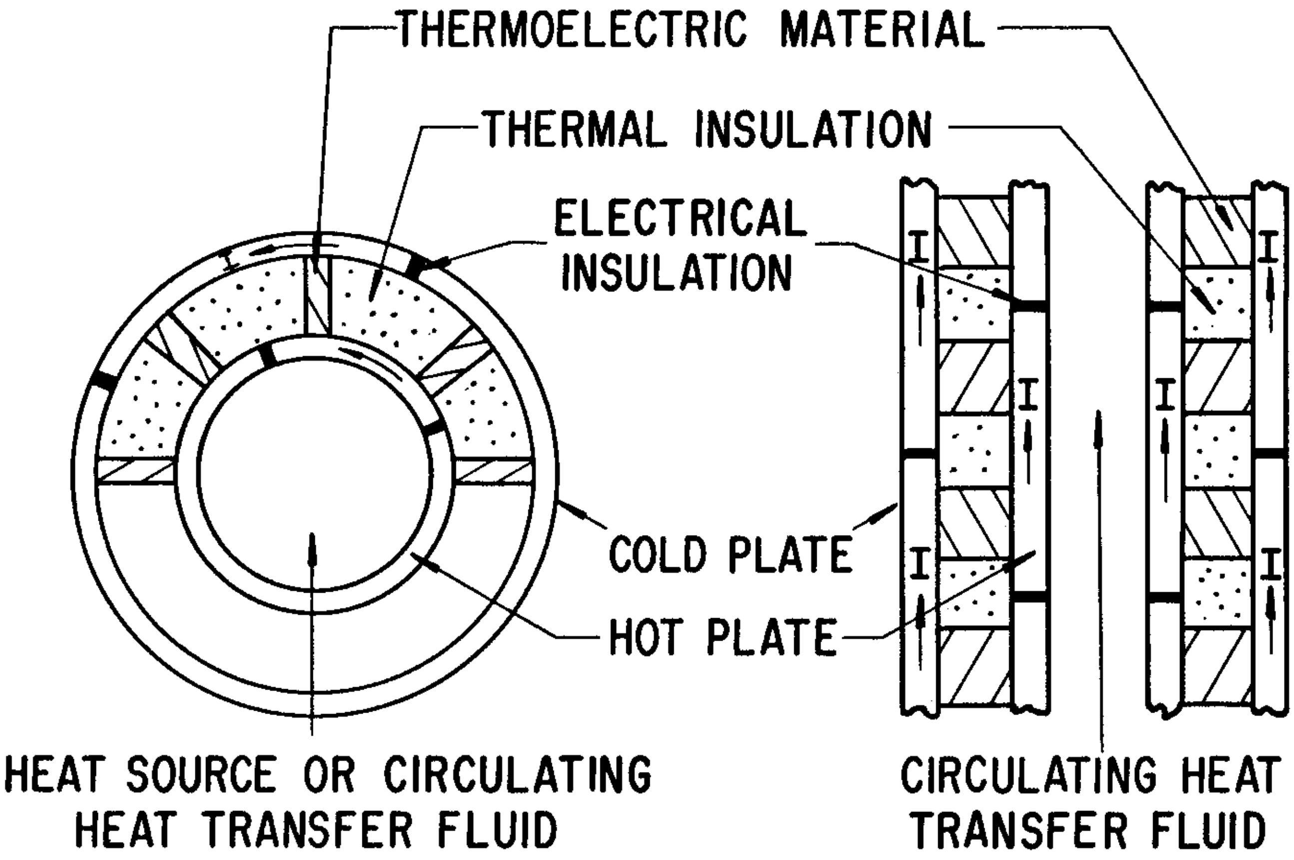

Figure 3: Sandwich-Type Thermoelectric Generator Configurations

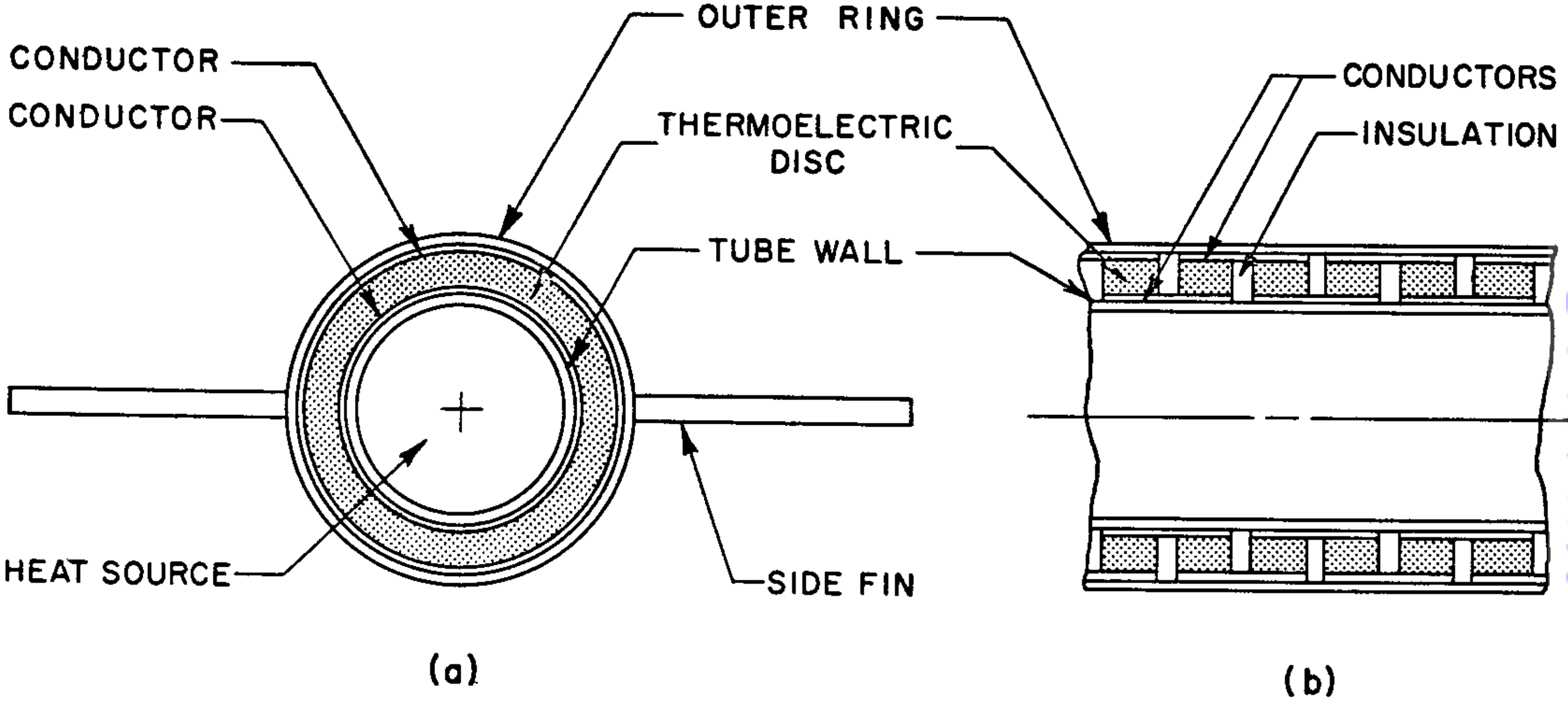

Figure 4: Side Fin Type Thermoelectric Generator Configurations.

For a given set of calculations, the following information is used as input data:

1) Materials and material properties to be used for the thermoelectric elements, the hot and cold conductors, and the thermal insulation.
2) Amount of absorbed solar radiation per unit area of cold plate.

With the above input information constant, the weight per unit net power output of the generator-radiator can be treated as being a function of the following variables:

1) Generator efficiency
(Defined as the ratio of the net power output of the generator to the total heat input to the generator)
2) Hot junction temperature
3) Cold junction temperature
4) Ratio of the cross-sectional area of the n-type material to that of the p-type.
5) Ratio of the electrical resistance external to the thermoelectric elements to the electrical resistance of the elements.
6) Electrical contact resistances between the thermoelectric elements and the hot and cold plates.
7) Ratio of the heat leakage through the insulation to the total heat input to the generator.
8) Ratio of the Joule heating loss in the cold plate to the net power output.
9) Ratio of the Joule heating loss in the hot plate to the net power output.
10) Thickness of the thermoelectric elements
(Obtained by fixing either S_p or S_n in Figure H-2, Part(III)

In the range of possible operating conditions, any eight of the first nine variables can be selected arbitrarily, and the ninth variable is then fixed. Selection of the tenth variable can always be arbitrary subject to whatever practical considerations may apply.

Our studies have indicated that variables 4) and 5) do not exert a very strong influence on optimum performance as long as values in the vicinity of maximum power output or maximum efficiency are used. It is suggested, therefore, that the values used be those giving maximum efficiency of the thermoelectric elements for given material properties and hot and cold junction temperatures. This is the procedure followed here unless noted otherwise.

In the studies herein, the effects of the sixth variable were neglected by assuming zero contact resistances. When the thermoelectric elements are very short, such an assumption becomes invalid, and results are therefore optimistic on this count. A few checks after the calculations were completed, however, indicate that for the calculations reported here and operating condition of interest, this effect is small if contact resistances on the order of 20 micro-ohm cm^2 or less can be obtained.

The effect of using different values for the Joule heating losses in the cold and hot plates is believed to be small. The losses in the hot plate have therefore been assumed to be equal to the losses in the cold plate for these studies.

With the above considerations, the weight per unit net power output can be considered to be a function of the following variables:

1) Generator efficiency
2) Hot junction temperature
3) Cold junction temperature
4) Ratio of the heat leakage through the insulation to the total heat input to the generator.
5) Ratio of the Joule heating loss in the cold plate to the net power output.
6) Thickness of the thermoelectric elements.

In the range of possible operating conditions, four of the first five variables can be selected arbitrarily, and the fifth is then fixed.

Now of the above variables, only the first two, generator efficiency and hot junction temperature, interact directly with the rest of the system and, obviously, do so to a high degree. Therefore, an analysis which restricts itself primarily to consideration of the generator-radiator has the most meaning if the generator efficiency and hot junction temperature are treated as independent variables and results are expressed as functions of these variables. Such results can then be rather readily translated to their effect on a complete system. This is the procedure followed here, and it specifically is one of determining the minimum generator-radiator weight as a function of generator efficiency for various values of hot junction temperature.

Use of such results as input data for a complete systems study would make possible a high degree of systems optimization, but it must be admitted that it would not result in a completely rigorous optimization. This is because this procedure fixes within certain bounds several other parameters which interact with the rest of the system and which, in a rigorous optimization, should be left free to assume their best values from the system standpoint. Illustrative of two of these parameters which are thus fixed within certain bounds are: 1) The heat transfer rates required per unit area of hot plate, and 2) The radiator size. In the case of a circulating fluid on the hot side, the former interacts with the rest of the system insofar as it affects the pumping power and the heat transfer requirements of the heat transfer fluid. The radiator size affects the rest of the system in terms of packaging problems. In addition, in the case of a reactor system, the radiating area would affect, for any given separation distance between reactor and instrument or crew compartment, the required shielding weight, lengths and weights of pipes and headers for the heat transfer fluid, and bus bar lengths and weights.

Recognizing these limitations, which are indicative of the kind one always encounters when considering but one component in a system, we nevertheless proceed as indicated with the thought that much useful information can still be gained with this approach. The procedure for any given set of materials has therefore been as follows:

1) A hot junction temperature is assumed.
2) One or more values of thermoelectric element thickness are assumed.
3) Various values of generator efficiency are assumed covering the range of values which are possible for the given materials and hot junction temperature.
4) The minimum generator-radiator weight attainable at each of these values of efficiency is then determined by finding the optimum combination of cold junction temperature heat leakage through the insulation, and Joule heating loss in the conductors.
5) Results are conveniently expressed in the form of a curve giving minimum generator-radiator weight as a function of generator efficiency for a given hot junction temperature and thermoelectric element thickness,
6) The procedure can then be repeated for various other hot junction temperatures, if desired, thus giving a range of performance information which can be used as input for optimization of a complete system.

In the process of carrying this out, it has been found that the least weight, for any combination of the other variables, is achieved by making the thermoelectric element thickness as small as possible. Thus a theoretical lower limit to the weight obtainable can be determined by letting this element thickness become, in the limit, zero. When this is done, it is found that the thickness of the conductors also becomes, in the limit, zero, and the weights obtained are the same as those that would be given by neglecting the weight and resistance losses of the conductors. This theoretical lower limit to the weight can therefore be termed "the weight neglecting conductors." The extent to which this limit can be approached in reality will, of course, depend on considerations governing the minimum thickness of elements that it is practicable to use.

Before presenting some results obtained by following this procedure, it is of interest to mention that the optimization involved results in significant weight reductions as compared to an un-optimized approach. For example, for any given materials, hot junction temperature, and thermoelectric element thickness, the weight that might be obtained using no gap between the elements can be as much as 100 times greater than the minimum weight values determined here. (See Part III, Figure I-1, for example.)

Results of some calculations for a hypothetical material whose properties are somewhat better than lead telluride are presented in Figure 5. The properties of this hypothetical material are assumed constant with temperature. These results are based on the input data given in Table 1 and show minimum

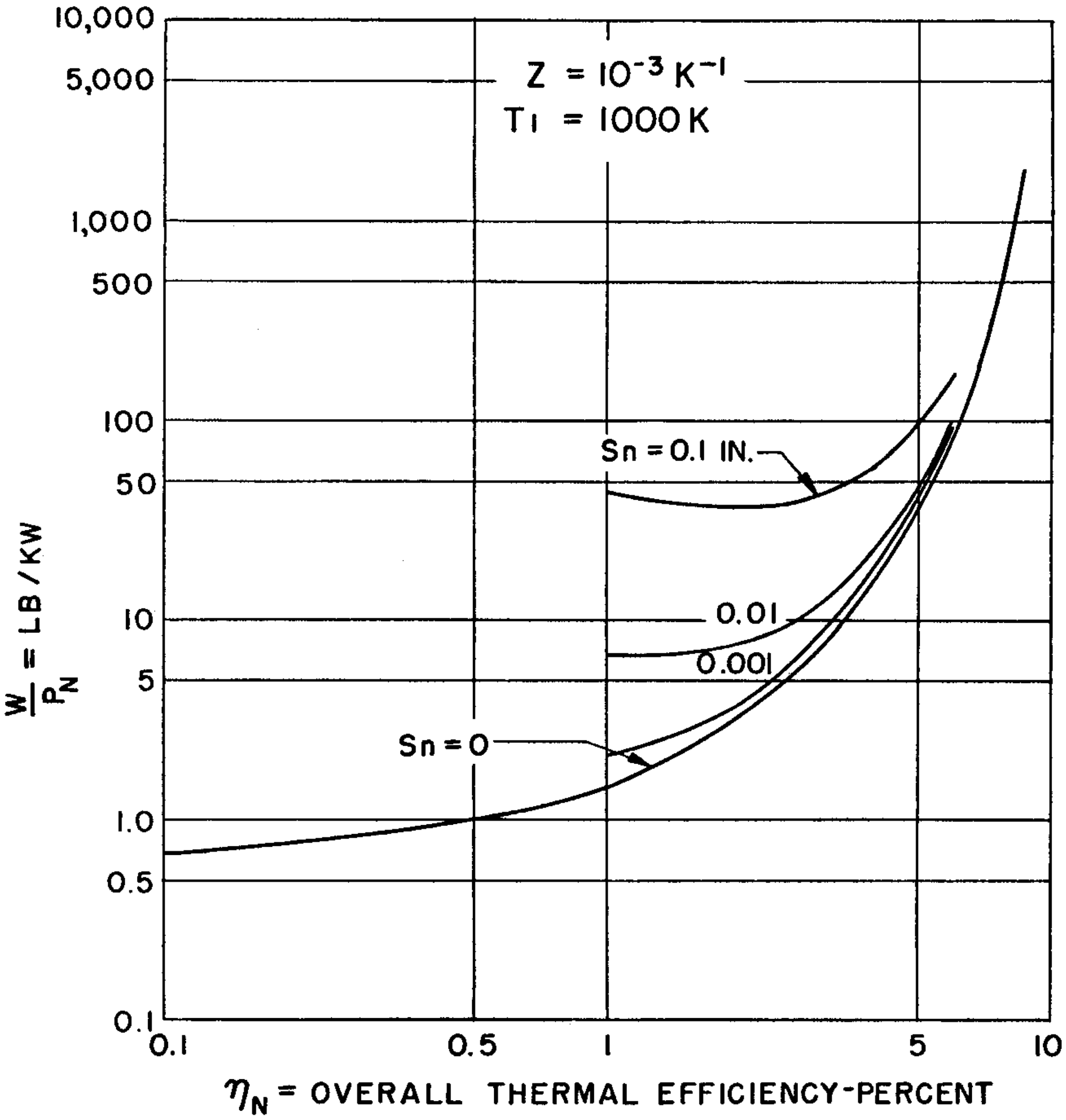

Figure 5: Minimum Generator-Radiator Weight — Sandwich-Type — Heat Leakage Through Insulation.

generator-radiator weight per unit net power output as a function of generator efficiency for four values of thickness of the thermoelectric elements.

Table 1

Input Data for Figures 5, 6, & 7

		Hypothetical Material	
	Lead Telluride* (Figure 6)	Heat Leakage through Insulation (Figures 5 & 7)	Heat Leakage by Radiation (Figure 7)
Hot junction temperature, °K	866	1000	1000
Figure of Merit, °K^{-1}	0.9×10^{-3}	1.0×10^{-3}	1.0×10^{-3}
Thermal conductivity, watt/cm-°K	0.016	0.03	0.03
Seebeck coefficient, volt/°K	225	225	225
Resistance ratio, m	1.3	1	1
Thermal insulation	Potassium titanate	Potassium titanate	Potassium titanate
Absorbed solar radiation, watt/cm^2	0.0418	0	0
Conductors-hot side	Copper, Iron	Copper	Copper
cold side	Copper, Iron	Aluminum	Aluminum
Radiator emissivity	0.9	0.9	0.9
Weight of thermoelectric material, lb/ft^3	509	538	538
Emissivity of interior surfaces of hot and cold plates	Not needed	Not needed	0.1

* p-type - doped with 1.0 at. % Na
n-type - doped with 0.1 mol. % PbI_2

The lower curve of Figure 5 is the limiting case for zero thickness of the thermoelectric elements. The upper three curves illustrate the increase in weight obtained as thermoelectric element thickness is increased.

Results of some calculations carried out for lead telluride are presented in Figure 6. These are based on the input data given in Table 1 and show minimum generator-radiator weight as a function of thermal efficiency for three values of element thickness and two conductor materials. These curves

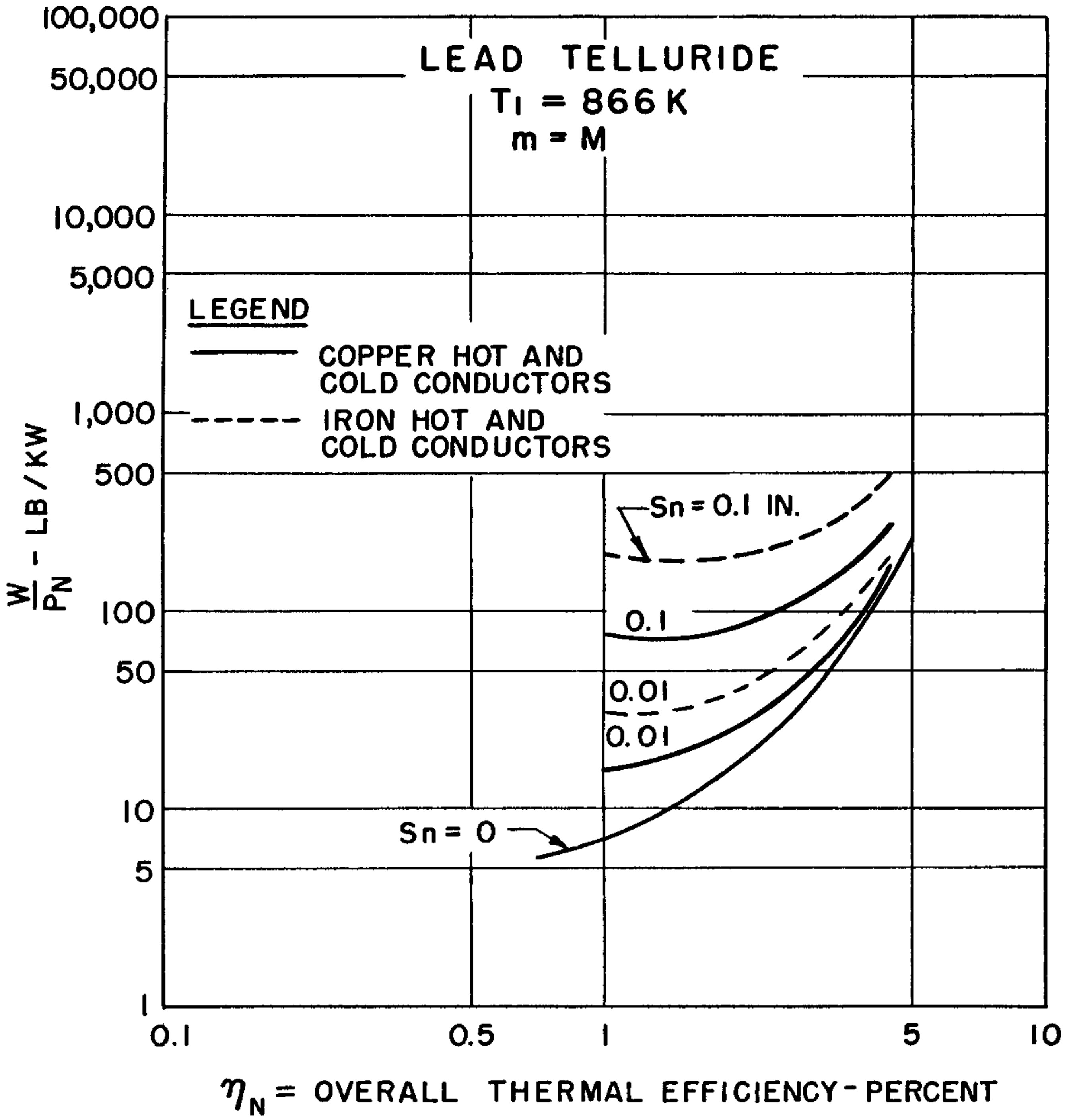

Figure 6: Minimum Generator-Radiator Weight — Sandwich-Type — Heat Leakage Through Insulation.

illustrate the weight penalty associated with the use of a relatively low conductivity material such as iron for the conductors as well as the increase in weight obtained as element thickness is increased.

Comparison of Figures 5 and 6 illustrates the rather substantial improvement in performance for the hypothetical material as opposed to lead telluride. This occurs even though the improvement in properties for the hypothetical material is rather modest and is predominantly in temperature capability rather than Figure of Merit. On the other hand, in retrospect, the thermal conductivity used for the hypothetical material is probably higher than will actually be achieved for such a Figure of Merit, and so the weight shown for it is probably somewhat less than can realistically be expected for materials which achieve that same Figure of Merit and temperature capability.

A possible modification of the sandwich type configuration as considered up to this point is to replace the thermal insulation (see Figure 3) with a vacuum and to coat the interior surfaces of the hot and cold plates of the sandwich with a low emissivity material. In this modification heat leakage from hot plate to cold plate between adjacent thermoelectric elements is by thermal radiation. The procedures used for this heat leakage by radiation case (See Part III, Appendices H, J and L for details) are similar to those used for the heat leakage through insulation case. The results of some calculations for the same hypothetical material used previously for the heat leakage through insulation case are presented in Figure 7. The input data for this figure are shown in Table 1 . Superimposed on the figure are the results from Figure 5 for the heat leakage through insulation case.

Some explanation regarding the case of $S_n = S_p = 0$ when heat leakage is by radiation is in order. For this case, the weight per unit of power output becomes zero at the lower overall thermal efficiencies. This situation represents a limiting case in which the current per element, the thickness of the thermoelectric elements, and the weight of the conductors are zero. When heat leakage by radiation is employed, the total weight considered consists solely of the weight of the thermoelectric materials. At the lower efficiencies, with heat leakage by radiation, as the length of the thermoelectric material approaches zero the weight of the thermoelectric material also approaches zero, but the heat leakage and efficiency are relatively unchanged and the net power output remains finite for the assumed conditions.

The results for finite thermoelectric element thickness indicate that the heat leakage by radiation configuration is somewhat lighter in weight than the heat leakage thru insulation configuration for $S_n = S_p = 0.1$ inch case, and significantly lighter for the $S_n = S_p = 0.01$ inch case. This advantage is, however, somewhat academic because, in the element size range in which the potential improvement is greatest, the problems of fabricating the heat leakage by radiation configuration are most severe. This occurs because this configuration cannot utilize the support afforded by thermal insulation in the assembly of a generator composed of very small thermoelectric elements.

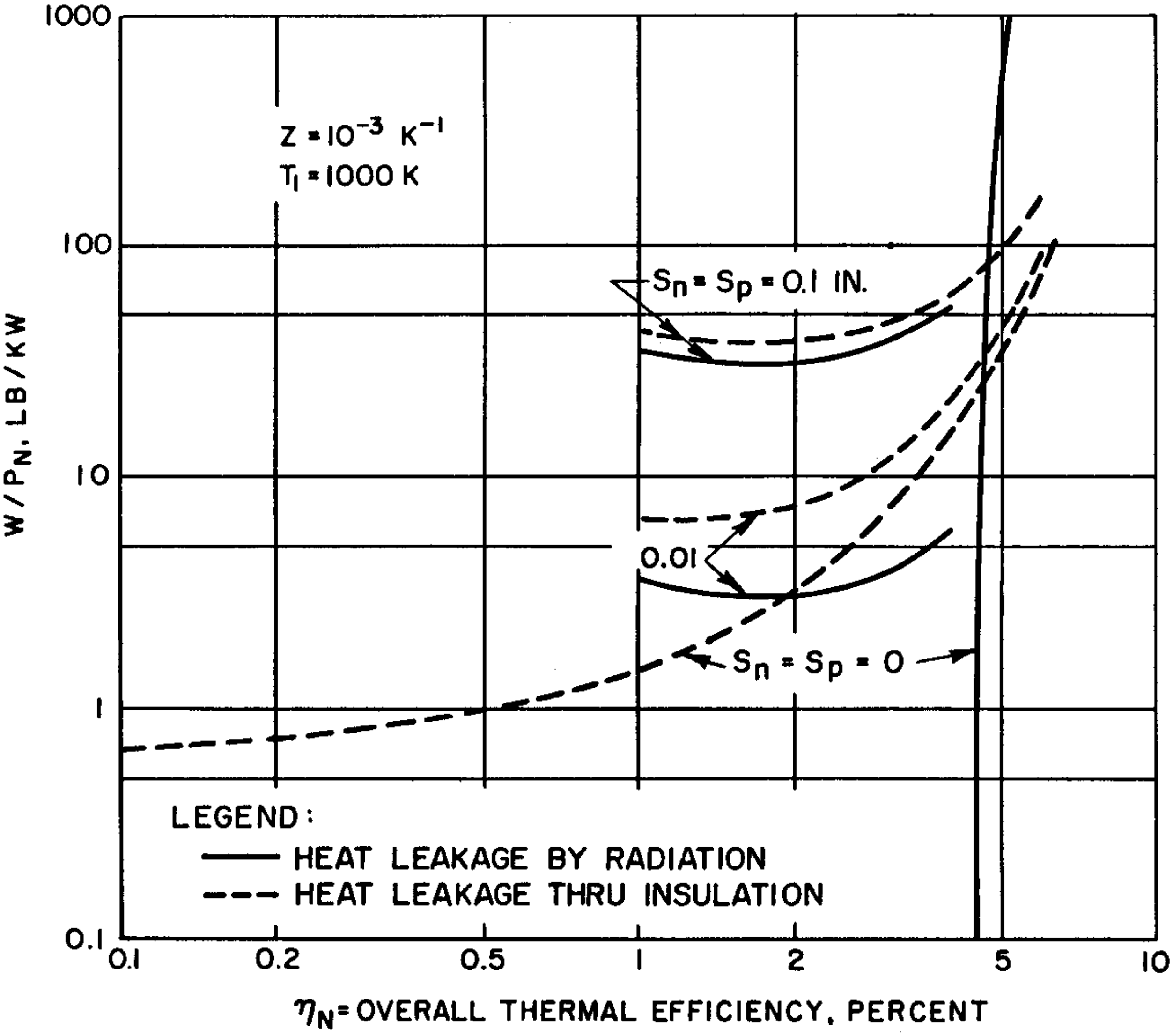

Figure 7: Minimum Generator-Radiator Weight — Sandwich-Type — Heat Leakage by Radiation.

If extended to higher efficiencies, the $S_n = S_p = 0.01$ inch curves for the heat leakage by radiation configuration would approach the $S_n = S_p = 0$ curve asymptotically. Therefore, at the higher efficiencies (greater than about 4.5%) the heat leakage through insulation configuration is the lighter of the two.

Other results for the heat leakage by radiation case with conductor weight neglected ($S_n = S_p = 0$) are presented in Part III, Appendix J. Included are the combined minimum weight envelopes for both heat leakage through insulation and heat leakage by radiation for several Figures of Merit and hot junction temperatures. Also included are the lengths of the thermoelectric elements at the minimum weight conditions.

Referring back to the heat leakage through insulation case, additional results for it are presented in Part III, Appendices I and K. For Example, the effects of variations in the value of m were found to be insignificant, at least for the range of variables investigated. The effect of absorbed solar radiation was also found to be of minor importance. Also included in Part III, Appendix I are some minimum weight results for a number of metallic thermoelectric materials. The values of other parameters of interest for the results shown in Figures 5 and 6 are presented in Part III, Tables K-1 and K-2 respectively.

Minimizing Weight - Side Fin Construction

The particular side fin construction that has been considered for this study is that shown in Part III, Figure N-3, part (b). The analysis of this configuration is very similar to that for the sandwich construction. The major distinction is the presence of the side fins. Instead of varying the gap between adjacent elements in order to minimize weight, as was done in the sandwich case, the heat rejection capacity of the side fins is varied. Tube diameter is, of course, also a variable, and more will be said later about it.

In analyzing the configuration shown in Part III, Figure N-3, part (b), all of the heat rejected is assumed to occur from one side of the side fins. Heat transfer by radiation between the outer tube walls and either the inside or outside surfaces of the fins is also neglected. The combined effect of these assumptions is believed to be conservative, but not significantly so, particularly when the tubes are arranged in banks somewhat as shown in Part III, Figure N-2, part (b). Under these assumptions, the effect of the side fins on the performance of the thermoelectric elements can be expressed solely in terms of the heat rejection capacity per unit length of tube for any given cold junction temperature at the base of the fins. Now, it has been shown (See Part III, Appendix M, References M-1 and M-2) that the dimensions of a rectangular fin radiating to space can be optimized so as to result in a minimum fin weight for given materials, fin base temperature, and heat rejection rate per unit width (tube length in this case) of the fin. This study has made use of such results in order to achieve minimum fin weight for any given operating conditions, feeding these results into the optimization of the complete generator-radiator combination.

The only numerical calculations carried out for the side fin configuration have been for the limiting case where the conductor and structure weight is neglected, so that the weight included is the weight of the minimum number of essential parts which are: the thermoelectric elements, the side fins, thermal insulation in the corners, and a heat transfer fluid. Results of such calculations serve to establish minimum weight values which can be compared directly, for example, with corresponding results for the sandwich configuration neglecting conductor weight. These calculations have been carried out using lead telluride materials operating under the same conditions listed previously in Table I with the following additional input information pertinent to the side fin construction:

Fin material - silver
Dimensions of inner tube - 3/16 inches in diameter
Heat transfer fluid - NaK

Results are given in Figure 8, along with the corresponding results previously obtained for the sandwich construction as given by the lower curve of Figure 6. Also shown are results for the side fin-sandwich configuration that will be discussed later. These results show that the sandwich construction gives lighter weight at low efficiencies, but that the side fin construction is lighter at higher efficiencies. In this connection, however, three additional comments are in order. a) The side fin calculations neglect the effect on efficiency of the heat leakage through the insulation in the corners. However, for the cases considered this leakage is small and therefore does not particularly affect the comparison. b) The comparison is not quite valid in the sense that the side fin results include weight of a heat transfer fluid, while the sandwich calculations do not. However, the weight of fluid is small for the case considered, being about 1 lb/kw, and so this does not particularly affect the comparison. c) The comparison is, however, strongly dependent upon the diameter chosen for the inner tube and will not be as favorable for the side fin construction if larger tube diameters are used. The reason for this is that the fin weight per unit power output is, for all other parameters constant, proportional to the square of the inner tube diameter. The basic reason for this is that, as tube diameter (and element width) increases, the heat rejected per unit length of the tube increases, and the fin characteristics are such that this results in an even greater increase in fin weight.

Minimizing Weight - Side Fin-Sandwich Construction

A configuration which is a combination of the sandwich and side fin types of construction is an obvious possibility in order to further decrease weight. This is the side fin-sandwich type previously referred to and is considered next. As mentioned earlier, it differs from the side fin construction in that increased radiator area is obtained not solely by use of the side fins but also by increasing the axial spacing between thermoelectric elements and filling the resulting gap with thermal insulation. Results of obtaining the minimum weight for this construction, based on the properties of lead telluride, are shown on Figure 8 along with the results previously discussed for the other two types of construction. The combined construction is seen to offer significant weight improvements.

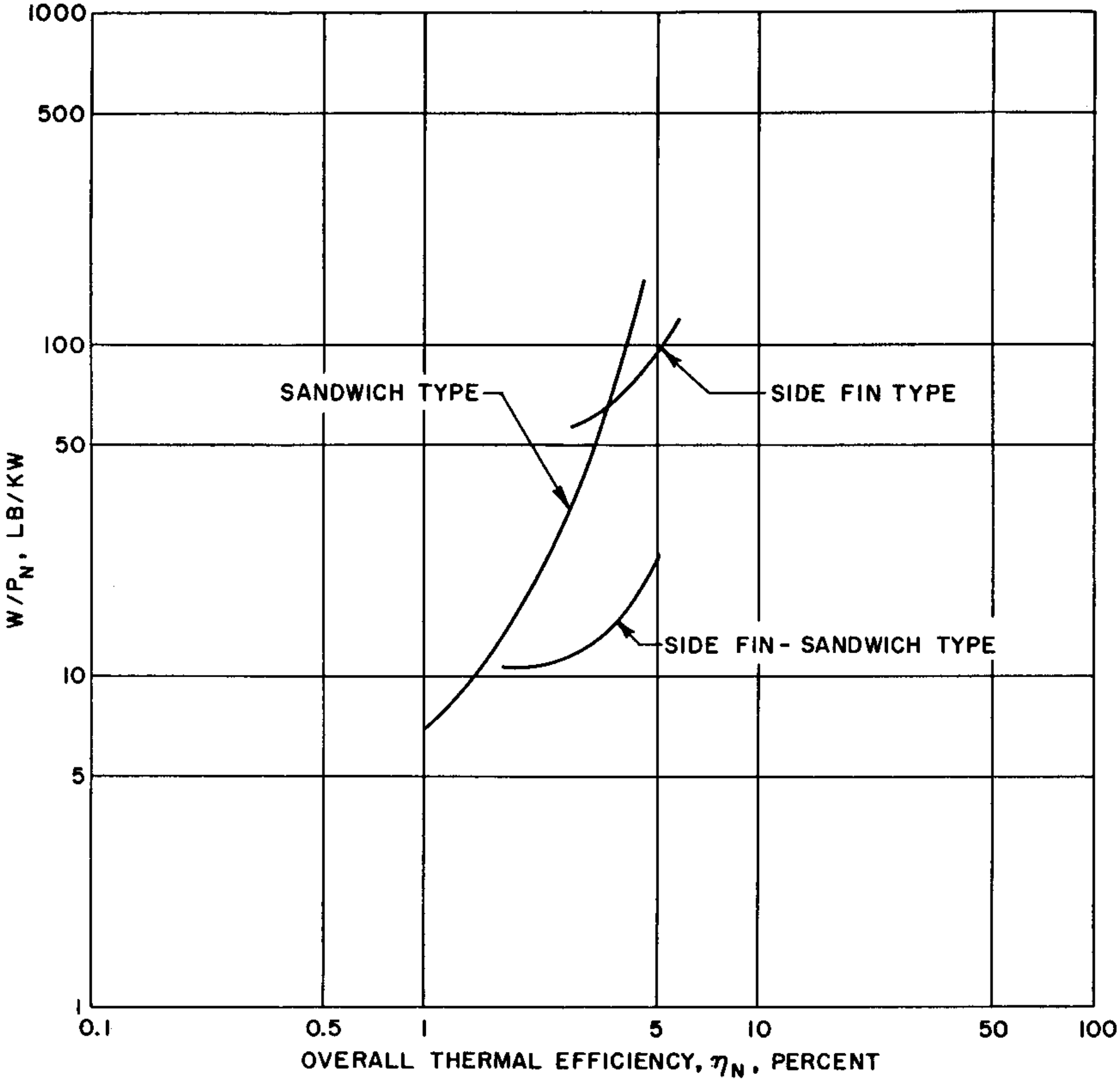

Figure 8: Minimum Generator-Radiator Weight — Lead Telluride. T_1 = 866 K, S_n = 0.

It is now of interest to investigate the weight obtainable with the side fin-sandwich construction when the weight of the conductors is included. This has been done, using the same lead telluride materials, for a generator efficiency of 3% and for various values of the thickness of the thermoelectric elements. This has, moreover, been carried out for two cases, one being that wherein the only weight included over that just presented in Figure 8 is the weight of copper conductors. The other is one wherein the weight of some additional structure is included.

This additional structure weight is equivalent to the following items:

1) An inner tube of stainless steel, 3/16 inch in diameter, square, and with 0.005 inch walls.
2) An adhesive or electrical insulation coating on the inner tube which has a weight equivalent to 0.001 inches of copper.
3) An outer circular tube of stainless steel coated with an electrical insulation. The ratio of the thickness of the tube wall plus insulation to the tube diameter is assumed to be 0.02.
4) A sublimation coating completely surrounding the elements having a weight equivalent to a coating of copper 0.001 inches thick.
5) Iron caps, 0.005 inches thick, on the ends of each element to act as diffusion barriers. The cross-sectional area of the caps is assumed to be equal to the cross-sectional area of the thermoelectric elements.

Results are plotted in Figure 9, showing the variation in specific weight with the minimum thickness, S_n, of the thermoelectric material. Since a limited number of calculated points were determined, these are indicated. The lower curve does not include the structural weight items just tabulated, while the middle curve includes these items. The top curve is a plot of corresponding results for the sandwich construction. From Figure 9, it is seen that at 3% efficiency, use of thermoelectric elements having a minimum thickness of 0.01 inches, for example, increases by only a minor amount the weight obtained by neglecting structure. Inclusion of the structure, however, almost doubles the weight at such small element thicknesses. It should also be noted, however, that these structural weights, though fairly reasonable, are somewhat arbitrary. In an actual case, assuming successful bonding techniques, the outer tube thickness could be decreased to about 0.001-0.002 inches although the resultant weight saving might be partially used to thicken the inner tube somewhat.

From Figures 8 and 9, it is quite apparent that the side fin-sandwich combination gives the prospect of achieving significant reductions in weight as compared to either the sandwich or the straight side fin configurations. In this connection, it should be re-emphasized, however, that the weight of this combination is strongly dependent upon the diameter of the inner tube, and the larger this diameter is, the greater the weight will be. Therefore, if for other reasons it is necessary to use rather large diameter tubes, the weight improvement will not be so striking. It is also to be noted, however, that use of two elements per tube instead of four, will, for sufficiently small inner tube diameters and thin tube walls, decrease the weight even further

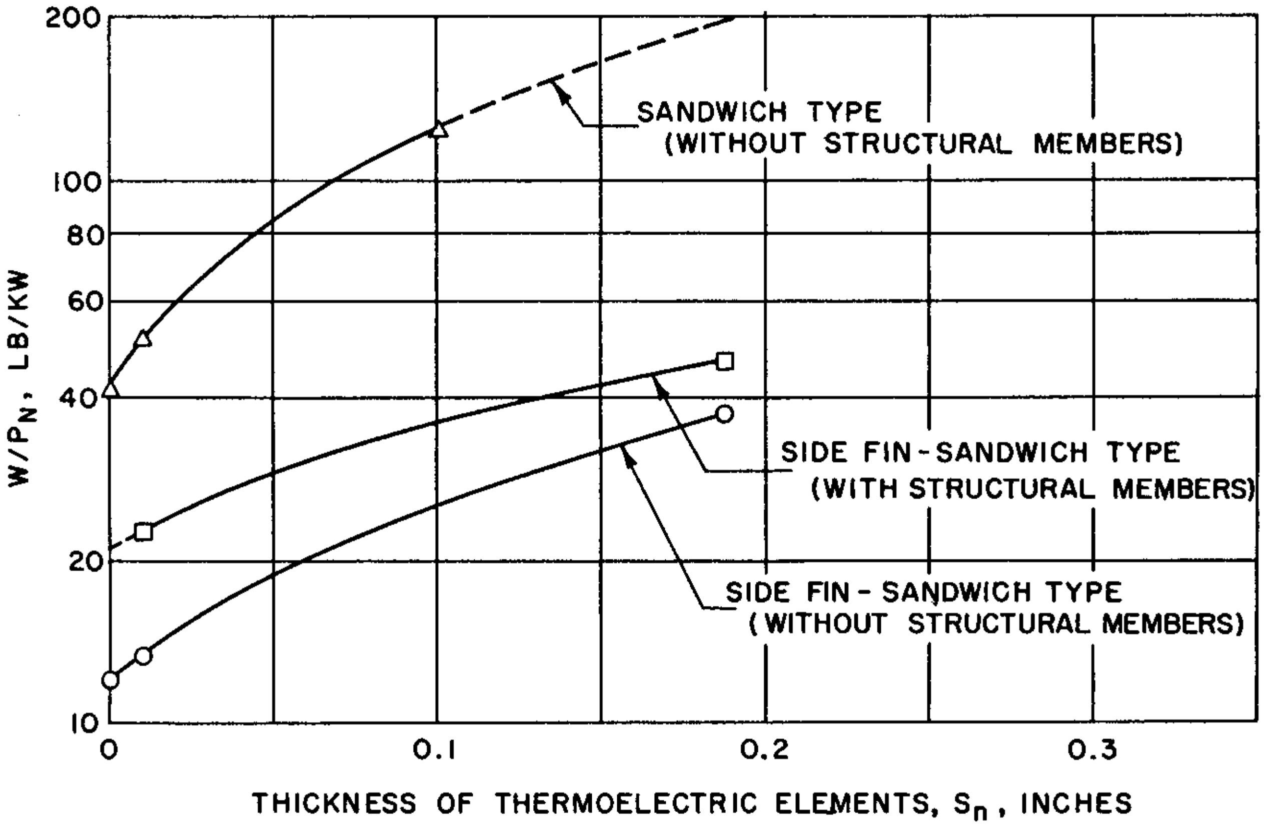

Figure 9: Minimum Generator-Radiator Weight — Lead Telluride.
$T_1 = 866$ K, $\eta_N = 3\%$

below that shown. The reason for this is that the heat input to the fin is thereby decreased, causing a significant reduction in fin weight which is sufficient to offset other factors working in the opposite direction. Finally, it is to be noted that use of beryllium fins instead of silver would result in a significant weight saving, since the weight of beryllium fins, to reject a given amount of heat, is roughly 50-60% of the weight of silver fins.

The preceding discussion shows that by careful attention to design, the weight of thermoelectric generators in space applications can be minimized to a significant extent. Specifically, these results indicate, for example, that it is theoretically possible, using presently available lead telluride thermoelectric materials, to achieve specific weights in the neighborhood of 20-30 lb/kw for the generator and radiator when the generator efficiency is 3-4%.

HEAT SOURCES

INTRODUCTION

Although the main effort applied to performance studies on this contract deals with the thermoelectric materials and generator irrespective of the source of heat, some studies were made of the various heat sources that might be used in order to gain perspective and assist in systems considerations. Heat sources considered include solar, chemical, radioisotopes, and nuclear reactors. In the last named category, two general types of reactors were treated: 1) Solid, homogeneous reactors, and 2) Forced circulation reactors.

These investigations are presented in some detail in Appendices O through T of Part III of this report. It is the purpose of this section of Part I of the report to summarize briefly these studies. This will be done by considering each heat source in turn and then making an over-all comparison.

SOLAR HEAT SOURCES

Appendix O of Part III contains details of the study made on Solar Heat Sources. The more important items covered in this appendix are summarized in what follows.

The power received by the sun just outside the earth's atmosphere is so low (about 130 watt/ft^2) that it is quite apparent that some means of concentrating this power is necessary if the sun is to be used to supply heat to devices such as thermoelectric generators which require hot side temperatures of 1000° F or more. To illustrate, the equilibrium temperature of a black body facing the sun and perfectly insulated on all other sides is only about 397° K (124° C, or 256°F).

Moreover, it can readily be shown that the degree of concentration required in order to obtain reasonably efficient operation at such temperatures must be quite large, and one is consequently immediately led to consideration of reflecting parabolic collectors such as have already found considerable use in solar furnace work. Two types of such collectors are generally considered. One can be termed the spherical collector, wherein the collector is circular in cross-section. The other can be termed the cylindrical collector, wherein the collector is parabolic only in one plane. In terms of performance, spherical collectors are basically capable of concentration ratios which are equal to the square of the concentration ratios obtainable from cylindrical collectors, assuming the same accuracy for the collectors and orientation systems. (Concentration ratio is here defined as the ratio of the flux density in the focal plane of the collector to the flux density impinging on the collector from the sun.) Thus, if a cylindrical collector has a concentration ratio of 40 (a typical value) an equivalent spherical collector would have a concentration ratio of 1600. This basic difference in concentration ratio capability has an extremely important effect on collection efficiencies at temperatures in the neighborhood of 1000° F or more. As a result, cylindrical collectors perform very poorly at these temperatures in comparison with spherical collectors.

The kind of absorber used to absorb the energy collected and focused by the collector has an important effect on performance. Two general types have been considered. One can be termed the aperture of cavity type. The other can be termed the selective surface type. In the aperture type, the absorber consists of a cavity in the side of which is an aperture. This aperture is placed at the focal point of the collector, and the energy from the collector passes through it and on into the cavity. For typical designs, this absorber essentially acts as a black body having an effective area equal to the aperture area.

In the selective surface type absorber, the energy reflected from the collector impinges directly on the wall of the absorber. This wall, in turn, is specially treated so that it has a high absorptivity to those frequencies in the sun's spectrum which contain the most energy and a low emissivity to the infra-red frequencies which are emitted by the absorbing surface.

Appendix O of Part III shows some typical results of collection efficiency for spherical and cylindrical collectors using both aperture type and selective surface absorbers for various values of collector accuracy. Although results are for a rather restricted set of conditions, they point toward the use of a spherical collector with an aperture type absorber for temperatures in the current range of interest for thermoelectric applications (i.e. about 900° K for the absorber).

Appendix O also contains a discussion of the effects of collector geometric inaccuracies and orientation system inaccuracies on collector-absorber performance. It points out that there is an optimum collector rim angle which will minimize the aperture diameter required to pass all of the energy reflected from the collector. (Collector rim angle is defined as the angle between the axis of symmetry passing through the focus and a line drawn from the focus to the collector rim.) This angle is slightly less than 45° and is a function of collector and orientation angular errors. For a perfect collector and zero orientation angle error, this optimum rim angle is 44° 52' and results in a ratio of aperture diameter to collector diameter of 0.00934 as the minimum value which will pass all of the reflected energy. This is an area ratio of aperture to collector of about 1/11,500 for a spherical collector. Collector and orientation angular errors of only a few minutes of arc significantly affect this value.

The optimum design will not, however, usually be for the case where all of the reflected energy passes through the aperture, because the flux distribution across the aperture will generally be of such a nature that it is high in the center and low towards the outside. Thus, reduction of the aperture diameter, even though it cuts out part of the incoming flux energy, can increase overall collection efficiency because of a correspondingly greater decrease in the amount of energy re-radiated back out through the aperture. Study of the flux distribution for a perfect collector with zero orientation angle error indicates that as a consequence of this effect, the optimum collector rim angle will probably be somewhat greater than 45°. Its exact value, and the value of the corresponding optimum aperture diameter would, however, be a function of the exact inaccuracies involved and must be determined for any given case.

As far as weight of solar collectors is concerned, very little reliable data exists for light-weight, space applications. However, current estimates in the literature seem to range generally between 0.2 and 0.5 lb/ft^2 of surface. For a solar flux of 130 watt/ft^2, this in turn means a collector weight of approximately 1.5 to 4 lb/kw of incident thermal energy. In terms of useful energy delivered to a generator, this will be a function of absorber temperature, but for temperatures in the neighborhood of 900° K the above figures would probably increase anywhere from 30 to 100%.

The major problem areas involved with solar collectors seem to be: 1) The attainment of required geometrical accuracy with light-weight structures, and 2) Meteorite damage. The latter may be a problem because the uncertainty of 3 or 4 orders of magnitude in the density of meteorites completely covers the range from where meteorite damage is no problem at all to the point where it would make a collector useless after less than one year of operation due to pitting of the collector surface and essentially complete loss of specular reflectivity.

Some of the more significant tentative conclusions to be drawn are as follows:

1. Attainment of the required collector geometrical accuracy in a lightweight structure is believed to be the major problem area.

2. Meteorite damage could conceivably limit the useful life to much less than a year. More reliable data on meteorite density is needed.

3. It is doubtful if cylindrical collectors will find practical application at temperatures of interest for thermoelectric applications because of low collection efficiency. Spherical collectors will probably be required.

4. Cavity (i.e. aperture) type absorbers appear to have better performance than selective surface absorbers for absorber temperatures in the neighborhood of 900° K.

CHEMICAL HEAT SOURCES

Appendix P of Part III contains the results of the study of Chemical Heat Sources. The more important items covered in this appendix are summarized in what follows.

Conventional chemical sources of heat energy are derived from the reaction between a fuel and an oxidizer or the exothermic decomposition of chemical compounds. Unfortunately, in a space environment, the earth's atmosphere is not available as an abundant source of oxygen, so that an oxidizer as well as the fuel must be carried or stored. Now, the primary performance criterion in the selection of a self-contained chemical heat source in a space environment, assuming its practicability, is minimum weight of heat source per unit thermal energy output delivered to the generator proper. One of the major objectives of this study of chemical heat sources, therefore, was to obtain estimates of the weight of the chemical heat source per unit of energy delivered.for a wide variety of possibilities. A number of other physical properties of interest were also determined as well as information on such practical considerations as toxicity, stability on storage, etc.

Such information is tabulated in Part III, Appendix P. The following categories were investigated:

1. Fuels - Hydrogen, various metals, hydrides, hydrocarbons, unsymmetrical dimethyl hydrazine, and many others.

2. Oxidizers - Oxygen, fluorine, ozone, chlorine trifluoride, and others.

3. Fuel-oxygen combinations - Combination of oxygen with the fuels of item 1

4. Monopropellants - Normal propyl nitrate, ethylene oxide, hydrogen peroxide, and hydrazine.

5. Free radicals - Various species including hydrogen, oxygen, nitrogen, and many others.

In connection with item 3 above, some of the other oxidizers, such as fluorine, can achieve a somewhat greater heat release with the fuels than can oxygen. However, many of these oxidizers have serious application problems, such as stability, toxicity, and corrosivity. Consequently, oxygen was used for the combined calculations, particularly since it is felt that the other oxidizers do not have appreciably different performance in combination with the fuels.

Monopropellants have found extensive use in short-lived, self-contained missile and aircraft auxiliary power supplies. Use of free radicals, on the other hand, is not at all practicable as yet, and they are included only as an indication of future possibilities.

Table P-6 of Appendix P tabulates values of energy output from some of the better performing combinations investigated, and these are reproduced in the first column of Table 2 . These values include the weight of the chemicals only, and do not include any allowance for structure weight of the combustion system. They also assume 100% efficiency of conversion to heat energy.

For comparison with other heat sources, it is convenient to convert to units of lb/kw of thermal energy output. This requires assuming some length of mission time, however. Therefore, the last two columns of Table 2 give the chemical weight in lb/kw of thermal output for missions of 30 days and 1 year. Recalling that these figures do not include structure weight and that they assume 100% efficiency of conversion to heat energy, the use of chemicals as heat sources for long lived applications is not at all promising.

Table 2

Output of Typical Chemical Heat Sources

Fuel	Output Thermal Watt-Hr/lb.	Weight - lb/kw Thermal	
		30 day mission	1 year mission
Free Radicals (Atomic Hydrogen)	30,900	23.3	283
*Metals (Lithium)	2,514	286	3,480
*Hydrides (Pentaborane)	2,210	326	3,960
*Hydrocarbons (JP-4)	1,230	585	7,110
Monopropellants (Hydrazine)	381	1,890	22,900

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*Reaction with oxygen, stoichiometric mixture

RADIOISOTOPE HEAT SOURCES

Appendix R of Part III contains results of the study of radioisotopes as sources of heat. The more important items covered in this appendix are summarized in what follows.

Radioisotopes represent an interesting possibility for supplying thermal energy for space power applications. They represent a heat source that has relatively high values of power per unit mass and power per unit volume; one whose power variation with time is well known and which is static in that no moving parts are required to form or remove the heat generated. Disadvantages associated with the use of radioisotopes, on the other hand, consist of the problems associated with handling and storing them and the hazards associated with the launching of the vehicle and re-entry. The shielding problem in flight is an added complication. To date, these disadvantages seem to have outweighed the possible advantages insofar as actual use of isotopes for space applications is concerned, since no such system has been flown in spite of successful ground tests.

In studying the applicability of radioisotopes, a general survey was made to select those isotopes having the most desirable characteristics for heat source application. The criteria considered most important are listed below:

1) Half life
2) Power density
3) Method of formation and decay schemes
4) Availability
5) Ability to withstand high temperature operation
6) Shielding requirements
7) Cost

For an isotope to be considered as a power source, desirable characteristics include large energy release per disintegration with the energy spectrum such that most of the energy is carried off by particles (beta or alpha) rather than by photons, a relatively long half-life, availability in a compound form that is stable at high temperatures, and availability in sufficient quantity.

A review of the nuclides indicates that several of the beta-emitting fission products qualify for further consideration on the basis of the above criteria. These are primarily cerium-144, strontium-90, cesium-137, and zirconium-95. Yttrium-91 is marginal because of half life, though in other specifications it is qualified. Two of the most favorable activation product isotopes are polonium-210 and curium-242, both alpha-emitters. Polonium was rejected because of temperature requirements, and the curium because it was not available in the required quantities at the time the study was made.

In order to achieve the high temperatures desired, it is generally necessary to consider the isotopes and elements in their oxide forms. Thus, the active isotope would be diluted with stable isotopes of the same element. In turn, the element would be combined with oxygen to form a high melting temperature oxide. Based on these dilutions, the heating values per unit weight and volume of the compounds may be determined. These values, together with those of production are presented in Table R-3 of Appendix R, Part III, and this table is reproduced here as Table 3.

Table 3

Isotope Production and Specific Power

Isotope	Isotope Annual Production grams	Isotope Specific Power watt/gm of parent isotope	Compound Specific Power watt/gm of compound	Compound Volumetric Power watt/cm^3 of compound	Annual Isotope Power watt
Ce-Pr-144	$3.68 \times 10^{4*}$	20.2	5.45	39.80	7.44×10^5
Sr-Y-90	3.46×10^4	0.785	0.463	2.18	2.72×10^4
Cs-Ba-137	5.05×10^4	0.150	0.060	0.34	7.60×10^3
Zr-Nb-95	5.88×10^3	34.2	1.13	6.21	2.01×10^5

* Assumed. Actual value is classified.

It will be noted that the above estimate indicates some very definite limitations on the amount of power available from these isotopes for the production rates used.

For purposes of comparison with other heat sources, it is convenient to convert some of the figures in Table 3 to lb/kw of thermal power output. This has been done and results are listed in Table 4.

Table 4

Isotope Weight per Unit Thermal Output

Isotope	Weight per Unit Thermal Output - lb/kw Parent Isotope	Compound
Ce-Pr-144	0.109	0.404
Sr-Y-90	2.8	4.75
Cs-Ba-137	14.7	36.7
Zr-Nb-95	0.0644	1.95

Another feature of significance is the variation of the isotope power with time. This is of most interest for the power production at the beginning and end of each operating period. If cerium-144 and zirconium-95 are operated for a period of 1 month, or if cesium-137 and strontium-90 are operated for a year, the thermal outputs change by less than 10%. If cerium-144 is operated for 1 year, however, the thermal output at the end of the period is only about 42% of the output at the beginning of the period.

Some estimates were made of the radiation environment associated with the use of the above radioisotopes assuming no shielding and are presented in Figure R-2 and Table R-6 of Appendix R, Part III.

Solid, Homogeneous Reactors

Appendix S of Part III summarizes the study of solid, homogeneous reactors. The more important features of this study are presented in what follows.

Solid, homogeneous reactors are of particular interest for space applications in that one can conceive of an extremely simple system containing essentially no moving parts wherein the reactor core is surrounded by thermoelectric elements or some other static energy converter. The heat generated in the core is transferred by conduction to the hot junctions of the thermoelectric generator and thence is either converted into electricity or radiated into space from the outer surface of the converter. Such is the sort of system on which this investigation was based.

Implicity in such a design concept are two points which should be kept in mind. First, such a system requires the use of thermoelectric materials whose performance is not unduly harmed by intense nuclear radiation, since the thermal insulating effect involved in putting a radiation shield between the reactor core and the thermoelectric material would be prohibitive. This means that not all thermoelectric materials are adaptable to this design concept, but there is reason to believe that there will be some materials capable of meeting this requirement. The Snap 10 program, for instance, is based on this design concept.

Second, if radiation shielding is required for protection of equipment or personnel, it will have to be of the shadow variety, since enclosure of the entire generator by a shield would introduce prohibitive temperature drops between the thermoelectric cold junctions and the radiator surface. However, since a shadow shield is desirable anyway from the standpoint of weight, this point is not of concern.

Four types of reactors were considered in some detail as follows:

1. U-metal, fully-enriched, sphere, unreflected
2. UO_2-ceramic, fully-enriched, sphere, unreflected
3. U-Be mixtures, fully-enriched, spheres, unreflected
4. UO_2-BeO mixtures, fully-enriched, spheres, unreflected

The geometries considered are rather idealized, but it was felt that this approach, in addition to its simplicity, would give a reasonably good comparison of the various reactors based on the inherent thermal and nuclear characteristics of the materials considered. On the other hand, only very preliminary consideration was given to the use of a reflector. Since it is possible that improved performance might be obtained by such means, investigation of this possibility would be of interest.

The four types of reactors investigated were selected over other possibilities for a number of reasons. First, the choice of solid, homogeneous reactors over liquid, homogeneous reactors was made because it is felt that liquid, homogeneous reactors are not desirable for space applications because of:

1. High pressure reached at high temperatures.
2. Chemical problems such as disassociation of the molecules.
3. The corrosive nature of uranium solutions and the possibility of leakage.

A gaseous moderated reactor, on the other hand, was not selected because of the difficulty of obtaining a compact reactor, and a large reactor could mean an extremely heavy shield weight. Hydrogenous moderated reactors obtained through the use of a metal hydride such as zirconium were not selected because release of hydrogen would be expected to limit the maximum core operating temperature to 1300-1500° F. For a reactor cooled only at the surface, these temperatures were not felt to allow sufficiently high surface temperatures with any reasonable amount of heat generation. Of other possible moderators, D_2O and carbon require large reactor sizes and were thus again not of interest.

On the other hand, a fast metal uranium metal reactor will be the smallest in size and is thus of considerable interest. Its melting point temperature is relatively low, however, and so one is lead to consideration of a fast UO_2 reactor, which has a very high melting point. Also, UO_2 is a proven reactor fuel. Since both of these reactors have very high fuel loadings, it was also of interest to investigate thermal reactors having relatively high temperature moderators. The choice of U-Be naturally followed, and in order to obtain higher temperatures again, the UO_2-BeO thermal reactor was also selected.

Table 5 gives estimated values of size and weight corresponding to the minimum critical mass of U-235 for each of these reactors.

Table 5

Size and Weight of Minimum Critical Mass, Unreflected, Spherical Reactors

Reactor Material	Reactor Diameter inches	U-235 Loading lb	Total Weight lb
U metal, fully enriched	6.9	106	113
UO_2-ceramic, fully enriched	11.3	229	279
U-Be mixture, fully enriched	36.4	4.6	1550
UO_2-BeO mixture, fully enriched	47.3	4.2	5570

From the above table, it is seen that although the thermal reactors require a much lower fuel loading than the fast reactors, they pay heavily for this in terms of size and weight. This effect will be compounded in an actual application, because the shielding size and weight also increases as the reactor core diameter increases. Moreover, the low fuel loading is not as much an advantage as might at first be thought, because one of the factors affecting reactor life is the percent of fuel burn-up. Consequently, life considerations might, for example, make it desirable to operate the thermal reactors at ratios of moderator to fuel which result in higher fuel loadings.

Turning now to calculation results, the basic approach was to set, as a limiting condition, central temperatures in the core which are equal to the melting points of the materials used and then determine the allowable thermal heat output as a function of surface temperature of the reactor when the reactor is just large enough to be critical. The melting point criteria is used to establish an upper temperature limit since upon melting, fuels lose their ability to retain gaseous fission products, and large pressures can subsequently crack or otherwise deform the fuel elements beyond predictable use.

Results of these calculations are presented on Figures S-11 and S-12 of Appendix, S, Part III, which give, respectively, output in thermal watt/lb and output in kw as functions of reactor surface temperature for the four reactors considered. From these figures, the following information is obtained.

1. The maximum specific thermal output, in watt/lb is given by the U and U-Be reactors, both of which have about 220 watt/lb (or, alternatively, about 4.5 lb/kw) at a reactor surface temperature of 1100° F. The allowable output of these reactors drops to zero, however, at surface temperatures of 2000 to 2300° F.

2. The UO_2 and UO_2-BeO reactors have specific thermal outputs of 50 watt/lb or less (20 or more lb/kw thermal) at surface temperatures of 1100° F, but can operate as high as 4000 to 5000° F, although with very small output at these temperatures.

3. The U-Be and UO_2-BeO reactors have the greatest thermal output at surface temperatures of 1100° F, being about 335 kw and 310 kw respectively, while the U metal and UO_2 reactors can put out only about 25 and 10 kw respectively at this temperature.

All of the above calculations were made for a cosine power distribution in the reactor. If the power distribution were flat instead of cosine, the reactor power output would be approximately doubled. Since the amount of uranium in the U-Be and the UO_2-BeO reactors is almost insignificant in comparison to the moderator, such a flat distribution should be quite possible in these reactors by preferentially loading the uranium. This should have little effect on size and weight. Consequently, for these reactors, it should be possible to essentially double the power output shown by Figures S-11 and S-12, resulting in a maximum output for the U-Be reactor at a surface temperature of 1100° F of about 440 watt/lb or, alternatively, about 2.3 lb/kw, and a corresponding total output of about 670 kw.

Of the reactors investigated, the U-Be reactor is thus seen to give the best performance at surface temperatures (about 1100°F) suitable for thermoelectric generators. However, it is generally apparent also that the requirement of removing heat solely by conduction through the reactor core severely limits the heat output obtainable from the reactor. Comparison with more complex reactors using heat removal by means of forced circulation is therefore desirable.

Forced Circulation Reactors

Appendix T of Part III summarizes the study of forced circulation reactors. The more important features of this study are presented in what follows.

As indicated above, one of the reasons that reactors using forced circulation to accomplish cooling are of interest is because of the possibility of their being much lighter in weight per unit power output than solid, homogeneous reactors. Another reason is that they are more flexible in that, they allow removal of the generator to a position beyond the shielding. Thus, generators incapable of operating in a region of high radiation can be used with such reactors.

In considering these reactors, one of the first choices to be made is the coolant to be used. In this study, water cooling was eliminated because of the high pressures and heavy equipment needed to contain the coolant at temperatures of interest. Organic cooled reactors were eliminated because of concern over chemical stability for long periods of time at 1000° F or greater. This left liquid metals and gases for consideration. A brief study then led to the choice of liquid metals, in particular sodium or potassium. The basic reasons for this selection are as follows:

1) Although gases should allow operation at higher temperatures than liquid metals because material problems will be less, it is not felt that these temperatures are sufficiently high at present to compensate for the relatively poor heat transfer and pressure drop characteristics of gases as compared with liquid metals.

2) Much experience has been gained with sodium and potassium liquid metals, and a considerable amount of information is known concerning their properties.

3) With liquid metals, the possibility exists of using an electromagnetic pump requiring no moving parts, thus maintaining the basic advantages of a static system.

The study made here consisted in the main of a compilation of material previously prepared for other purposes and hence is not as general as would be expected otherwise. It is restricted to fast reactors using UC or UO_2 as fuel, and the coolant temperatures of about 1700° F are somewhat higher than presently required for thermoelectric materials. Nevertheless the results are considered useful in terms of providing some performance estimates.

In the study, a particular design concept was selected (Figure T-6 of Appendix T, Part III), and rather detailed performance calculations were carried out for various fuels and power levels. Results are given in Table T-3 of Appendix T, Part III. These will not be repeated here except to note that specific weight values, not including shielding, range from 0.11 to 1.23 lb/kw of thermal output.

These weight values are believed to be predominantly functions of power level and output power per unit weight of U-235 fuel, both of which were varied over wide ranges. In particular, it is to be noted that power output per unit weight of U-235 fuel provides a direct measure of fuel burn-up for any given time. Since percent fuel burn-up appears to be one of the important factors affecting life, it is apparent that weight comparisons based on widely different values of output per unit fuel weight must be made with caution, since they may represent reactors having widely different life capabilities. As a frame of reference in this connection, 1% fuel burn-up is a figure which generally appears to be quite permissible, and this corresponds to about 36.5 KW/KG of U-235 over a period of one year. The results in Table T-3 bracket this figure.

From these results and similar studies made in another connection after completion of this investigation, it seems quite reasonable to believe that forced circulation nuclear reactors which can operate for periods on the order of a year or more should be capable of achieving weights appreciably less than 1 lb/kw thermal (probably 0.3 lb/kw or even lower) although not necessarily at low power levels. These weights neglect shielding. It can be concluded therefore that forced circulation reactors can be significantly lighter in weight than solid, homogeneous reactors. This is as anticipated.

Appendix T of Part III also considers shielding weights in an approximate manner, both for shielding against typical transistor equipment and for biological shielding. These results are given in Figures T-7 and T-8 in terms of lb/ft^2 of shielding required for various distances from the reactor of the item being shielded.

COMPARISON OF VARIOUS HEAT SOURCES

From the information just discussed, a brief comparison of the various heat sources considered may be of interest. First, consider the various indications of weight that have been determined. These are given in Table 6 for operating periods of 30 days and one year, assuming hot junction temperatures on the order of 1100° F. It should be emphasized that these estimates are very tentative, and serve only to indicate rough bench marks of performance.

Table 6

Approximate Weights of Various Heat Sources

Heat Source	Approximate Weight - lb/kw of Thermal Output	
	30 day life	1 year life
Solar Collectors [1]	2 - 8	2 - 8
Chemicals [2]	300 - 1900	3500 - 23,000
Radioisotopes [3]	0.4 - 2	1 - 5
Reactor, solid, homogeneous [4]	2 - 5	2 - 5
Reactor, forced convection [5]	0.3	0.3 - 1

Notes:
1) Includes absorber losses.
2) Depending upon chemicals used. 100% combustion efficiency assumed. Structure weight not included.
3) Depending upon isotope used. Container and shielding weight not included.
4) Shielding weight not included.
5) Shielding weight not included. Probably higher for thermal output less than a few hundred kw.

From the above tabulation, chemical sources are not of interest for long lived applications. The others run surprisingly close, particularly when one considers that the isotope and reactor sources do not include shielding weights. It is apparent that more detailed study than it was possible to apply here is necessary in order to get really definitive comparisons. Such studies must not only include life and operating temperature but also power level and many other details concerning the mission. For example, the amount of time spent in the shade is critical for a solar collector system because of the weight required for energy storage. The type of mission, manned or unmanned, is critical for the radioisotope and reactor heat sources because of the drastic effect on required shielding weight.

TOLERANCE LEVELS AND SHIELDING REQUIREMENTS FOR COMPONENTS SUBJECTED TO NUCLEAR RADIATION

Appendix Q of Part III contains results of a brief investigation made in this connection. Components considered include thermoelectric materials, transistor type semiconductors, and various electronic components. No conclusions are drawn for thermoelectric materials, but some quantitative information is given on the others.

PRACTICAL WEAPON SYSTEMS APPLICATIONS

It has become strikingly apparent over the past two years that the greatest need for weapon systems development by the Air Force lies in what can be termed space applications, i.e. various missile, satellite, and maneuverable vehicle systems, both manned and unmanned, which operate outside the earth's atmosphere for major portions of their flight time. Moreover, in keeping with the fact that the need for and experience with space operation is so new, the major problems in connection with these applications seem to lie in the space portions of the mission. Many of these problems are unconventional, and they appear in many instances to require unconventional solutions. This appears to be the situation in electrical power supplies, for it has also become apparent in recent months that one of the major problems in these applications is the source of electrical power. Lack of a really satisfactory solution is becoming a key drawback in advancing both manned and unmanned space vehicles.

The foregoing is in marked contrast to the situation in air weapon systems where, even though significant future developments can be expected, it would appear that in the region of auxiliary power supplies an extension of conventional methods will not only adequately satisfy the requirements but will probably do it best.

Based on such considerations, the performance and applications studies carried out on this contract have concentrated on space applications. In keeping with this, the discussion of practical weapon systems applications will also be restricted essentially to space applications. That is where the need lies, and that is where the problems are.

The question of what constitutes a practical application of a piece of equipment warrants brief attention. One definition might be that it is an application where the equipment is known to work for the required period time. If this definition were applied to space power supplies, it would mean that the only systems which have been shown to be practical are those involving either primary batteries or silicon solar cells using secondary batteries for energy storage. Even in the latter case, there may be some question regarding life time. On the other hand, there are many suggested power supply systems for space applications whose proponents say that they should be practical and that it is just a matter of proving it by developing them and showing that they will work. If this is true, then the question of whether a system is practical or not is not nearly of as much interest as the question of which of the various practical systems will work the best; that is, have the lightest weight, the fewest hazards, the least cost, etc.

In discussing practical weapon systems applications for thermoelectric generators it is useful, therefore, to consider not just power systems employing such generators but also to make comparisons with other power systems which are being considered and developed. These considerations should be, moreover, from two standpoints. The first is concerned with the prospects for any given system being practical in the sense first suggested here. That is, "Will it work long enough in space?". The second standpoint is concerned with considerations of which systems should work the best.

It is of interest first to list the possible systems, after which they will be discussed from these two standpoints.

POWER SYSTEMS TO BE CONSIDERED FOR SPACE WEAPON SYSTEMS APPLICATIONS

The following electrical power supply systems deserve consideration for space applications.

1. Batteries - single discharge
2. Fuel Cells - single discharge
3. Solar-photovoltaic with battery or fuel cell energy storage for operation in the sun's shadow and possibly for peak load conditions.
4. Concentration solar collectors driving any of the following:
    a. Thermoelectric generator
    b. Thermionic converter
    c. Turbine-generator
    d. Reciprocating engine-generator

    These systems will also need energy storage in the form of thermal energy, batteries, or fuel cells for operation in the sun's shadow. Battery or fuel cell energy storage might also be used for peak load conditions.
5. Chemically fueled systems driving any of the following:
    a. Thermoelectric generator
    b. Thermionic converter
    c. Turbine-generator
    d. Reciprocating engine-generator
6. Radioisotopes driving any of the following:
    a. Thermoelectric generator
    b. Thermionic converter
    c. Turbine-generator
    d. Reciprocating engine-generator

    These systems might also use battery or fuel cell energy storage for peak load conditions.
7. Nuclear reactors driving any of the following:
    a. Thermoelectric generator
    b. Thermionic converter
    c. Turbine-generator
    d. Reciprocating engine-generator

    Battery or fuel cell energy storage might also be used in the nuclear reactor systems for peak load conditions.

PRACTICALITY CONSIDERATIONS OF VARIOUS POWER SYSTEMS

Consider now the above systems and their components strictly from the standpoint of whether they will or will not be expected to work long enough in space. For systems 1. and 3. the question is, of course, already partially answered in the affirmative, since they are being used in many applications. In all of the other systems, the answer must be based on conjecture, since they have either not been operated in space at all, or not long enough to be of significance. Many of them have not even been operated on the ground as systems, only as components and then often for limited periods of time.

Therefore, in endeavoring to rate these components and systems as to their practicality for space applications, one immediately gets into the realm where violent differences of opinion can exist, and reasonably so, because there are simply not enough facts available. Consequently it is not considered appropriate to endeavor to make a detailed rating of these components as to their practicality. However, it is appropriate to make some general comments as to the relative standing of thermoelectric generators with respect to the others.

Basically, it is believed that, viewed strictly in terms of their potential ability to operate reliably in space for extended periods of time, thermoelectric generators rank very near the top, if not at the top, of the energy conversion devices that might be considered. For example, they should not be as vulnerable to meteorite damage as solar cells or tubes filled with circulation fluids, such as are required for turbine or reciprocating engine generators. They should not be as vulnerable to ionizing radiation damage as solar cells. Their relatively lower temperature of operation, as compared with the thermionic converter, is a favorable factor for long life. In this connection, n-type lead telluride elements manufactured by the Baso Company of Milwaukee, Wisconsin and more recently by the Minnesota Mining and Manufacturing Company have been used for a number of years as control elements in oil burners. Much operating experience has been gained which indicates no apparent deterioration in performance for continuous periods of operation of five years or more and with essentially no need for attention during this time. Significant data on other materials are lacking, but this serves as an indication.

Thermoelectric generators do not have the problems of requiring long lived, maintenance free, bearings and seals. They do not have the freezing problems associated with some liquid metal systems if a start-up in space is required after a prolonged shut-down. Zero gravity, moreover, should have no effect on thermoelectric generator performance, although it can constitute a problem in systems where gas and liquid are both present in the same circuit.

On the negative side, vacuum conditions will increase sublimation problems, and vibration during launch will require careful design.

Taken together, the above considerations certainly justify rating thermoelectric generators very high in terms of their ability of operating satisfactorily in space for long periods of time.

PERFORMANCE OF VARIOUS POWER SYSTEMS

Assume for the moment that all of the systems previously listed have been found to work satisfactorily for the required period of time. The question as to which system is then most "practical" in terms of weight, cost, hazards, etc. becomes important.

The chief hazards exist with the use of radioisotope or nuclear heat sources. Proper evaluation of this problem is a complex one which is outside the scope of this report. Moreover, since such sources may be used with any number of types of energy converters, it is not particularly germane to an evaluation of thermoelectric generators with respect to other types.

Cost is also an area felt to be outside the scope of this report, although there seems to be no basic reason why thermoelectric generator costs should not compare favorably with other possible conversion methods once effective production techniques were established and quantity production initiated.

The remainder of the discussion, then, will concern itself with the important parameter of weight. Unfortunately, here too available facts are insufficient to be very definitive. First of all, the lack of operating experience and data make many component weight estimates open to considerable question. Solar collector weight, as previously discussed, is an example. Secondly, the weight of any system is highly dependent upon the specific mission requirements and must really be determined for each individual case. To illustrate, the amount of energy storage required can completely shift the balance from one system to another. A solar collector system operating continuously in the sun might look very favorable with respect to a nuclear system, whereas just the reverse could be true if there are considerable periods of operation in the shade.

This situation has been well summarized by Dr. W. C. Cooley* who concludes that in the power level range of a few kilowatts, for example, it is impossible to find rational grounds for excluding any number of possible combinations due to the early state of development of them all.

Consequently, it is again possible to make only some fairly general statements regarding the weight of thermoelectric systems with respect to others. These are as follows:

1. Based on presently available materials properties and fabrication techniques, the weight of thermoelectric generators does not look very promising when compared with weight predictions for thermionic or turbine-generator systems, for example.- This occurs in two ways. First, the generator weight itself is relatively high. See, for instance, in this report the value of 200 lb/kw specified in the specifications for the 100 watt Solar Thermoelectric Generator. Second, the efficiency is low, which in turn means that the heat source weight will tend to be high. See, for example, the 2% generator efficiency also specified in the specifications for the 100 watt Solar Thermoelectric Generator. Applying such a figure to the rough estimates of specific weight of various heat sources as given in Table 6 , this efficiency results in heat source weights covering the range from 15 to 400 lb/kw of electrical energy output for one year's operation. (Chemical heat sources have been excluded from these figures since they are obviously unsuitable.)

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*Cooley, Dr. W. C., A Comparison of Nuclear and Solar Power Systems for Manned Space Stations, Paper presented at the Manned Space Stations Symposium, Los Angeles, California, April 20-22, 1960 (Sponsored by IAS, NASA, and Rand Corp.)

It should also be emphasized that these heat source weights do not include shielding for the radioisotope and nuclear sources.

2. Solution of the junction and sublimation problems would result in significant improvements in performance, but even more is needed. Again referring to the specifications for the 100 watt Solar Thermoelectric Generator, studies made in connection with their preparation indicate that if the junction and sublimation problems could be solved satisfactorily, the generator weight could be decreased to about 35 lb/kw for a generator efficiency of about 3%. The range of correpond-ing weights for possible heat sources now becomes 10 lb/kw to 270 lb/kw of electrical energy, the low figure being the forced circulation nuclear reactor without shielding. These figures begin to look much more interesting. However, it is still apparent that more improvement is desirable and probably necessary.

3. Significantly improved thermoelectric materials are, therefore, believed to be necessary before space systems employing thermoelectric generators can be competitive on a weight basis with predictions for other systems.- In this connection, one direction to go is in terms of increased temperature with no change or even some decrease in materials properties. However, it is believed that this can be overdone, and care should be exercised. Going too far in this direction can lead to life problems, reduced collection efficiency when used with solar collectors, and materials problems when used with nuclear reactors. The other direction to go is to improve materials properties without increasing the temperature. A combination of the two is probably best.

It is also of interest to note from 2) above and Table 6 that, except for the forced circulation nuclear reactor heat source, the heat source weight appreciably exceeds the generator weight. This is particularly true for the solar collector and indicates that improvement in generator efficiency will pay off much more than a further reduction in the generator weight.

CONCLUSION

In conclusion, it can be stated that Thermoelectric Generator Systems, like a number of other possible systems, warrant continued consideration for any space weapon systems applications having mission durations longer than a few hours. It does not appear possible at this time, however, to make generalizations as to areas where thermoelectric generators might be most applicable, either in terms of power level or mission life. Thermoelectric generators are believed to rate at or near the top in terms of ability to operate reliably for long periods of time with no maintenance. On the other hand, weight estimates based on presently available materials and production techniques do not compare very favorably with many other systems. A considerable improvement in material properties would, however, make the situation look much more favorable. In the meantime, the degree of effort that should be applied to thermoelectric development for space weapon systems applications would seem to depend upon one's answer to three questions:

1. How good are the chances for obtaining significant improvements in material properties?

2. How realistic are the performance estimates of the various systems with respect to one another?

3. How serious, really, are some of the previously mentioned development problems which other energy converters seem to have and which thermoelectric generators don't seem to have to the same degree? That is, will they be overcome and, if so, how long will it take and how much will it cost?

There is considerable room for differences of opinion in answers to the above questions. Nevertheless, the need for improved power supply systems is so great and the uncertainties involved in the prospects for all systems are so large that it would seem prudent to maintain a continued active interest in and development of thermoelectric generators for space weapon systems applications.

SECTION IV

GENERATOR DESIGN

INTRODUCTION

The work performed in this phase of the contract had two major objectives: 1) The preparation of specifications for a 100 watt thermoelectric generator suitable for use in space applications using currently available materials, 2) The construction of a small (approximately 5 watts net power output) model generator also using currently available materials. The purpose of this section is to summarize the work done toward the attainment of these objectives. This material is presented in much greater detail in Part IV of this report.

The intent of the preparation of the 100 watt generator specifications was to write them in such a manner that, in the opinion of the contractor, the specifications can be met: 1) By the use of materials currently available, 2) Without requiring major developments in fabrication and construction techniques.

The intent of the model generator construction program was to utilize the best design concepts developed under this contract to build a model of a design consistent with that required for space applications. However, it was also recognized that should these concepts require extensive development of fabrication techniques, it would be necessary to revert to a more conventional design since such extensive developments were beyond the scope of this contract. A simulated heat source in the form of an electric resistance heater was to be used.

The efforts to build a model generator can be divided into two general categories, the initial attempt based on the sandwich type configuration using bonded contacts, and a more conventional design using the side fin-sandwich configuration with pressure contacts. Efforts to build the more conventional model using pressure contacts were initiated when it became apparent that the fabrication technique developments required for the bonded contact design were too extensive to be completed under this contract. Both designs used p- and n-type lead telluride thermoelectric materials.

The sandwich type design using bonded contacts is discussed under two headings, Design Concepts, and Fabrication Problems. Some discussion pertinent to the pressure contact design using the side fin-sandwich configuration is also found in the material headed Design Concepts, but the majority of the information regarding this design is found under the heading, Model Thermoelectric Generator.

DESIGN CONCEPTS

Two types of configuration have been considered, the sandwich type and the side fin type. A combination of the two, the side fin-sandwich type has been shown (see Part III, Appendix N) to have the lowest specific weight. Both of these configurations have the generator and radiator as an integral unit and do not require circulating fluids for waste heat rejection. Both are also flexible as to the source of heat used.

The sandwich type configuration is shown in Part I, Section III, Figure 3 and in Part IV, Figure 1. The thermoelectric elements, rectangular in shape, are sandwiched between two adjacent segmented plates which serve as electrical conductors. The hot plate also serves to collect and distribute the heat from the heat source, and the cold plate also serves as the radiator. The reason for the space between adjacent elements is to provide increased radiator area. This space may be filled with insulation to minimize heat leakage.

The initial work of the generator design phase of the contract was directed toward the construction of a model generator of the sandwich type configuration. Preliminary performance estimates for this design indicated a specific weight of 52 lb/kw, a thermal efficiency of 2.5% and a power output of 5.7 watts. The preliminary design of this model is illustrated in Part IV, Figures 2 and 3. A more detailed performance estimate is given in Table 1, Part IV.

Construction of a model generator of this type requires solutions to the fabrication problems listed below by the titles under which they are discussed in the material headed, Fabrication Problems.

1. Diffusion Barrier
2. Junction Formation
3. Sublimation and Oxidation
4. High Temperature "Glue"
5. High Emissivity Coating
6. Conductor Joining
7. Materials Fabrication

The side fin type of construction is one in which the heat discharged on the cold side is conducted to fins extending outward from the thermoelectric elements and is then rejected to space by thermal radiation. An example of the side fin configuration is shown in Part IV, Figure 4, part (a). Here the generator elements are placed around a tube in the form of segmented annular discs or wafers. The internal tube contains the heat source. In the axial direction, these discs are stacked one against another with adjacent discs consisting alternately of n- and p-type thermoelectric material. The axial separation between each disc is just sufficient to provide for a thin layer of electrical insulation. Cylindrical rings on the inner and outer radii of the discs are connected in the proper order to function as current carrying conductors. Appropriate electrical insulation is required at the inner and outer radii.

In the side fin configuration the axial spacing between adjacent thermoelectric elements is very small, being just large enough to accommodate electrical insulation. Actually, the principle used in the sandwich type construction to obtain increased radiator area could be used here by increasing the axial spacing between the thermoelectric elements and filling the resulting gap with thermal insulation. This combination is the side fin-sandwich type.

The side fin-sandwich type configuration is utilized in the design of the model generator using pressure contacts as described under the heading, Model Thermoelectric Generator.

MATERIALS SELECTION

The selection of thermoelectric materials for the 100 watt thermoelectric generator specifications and the 5 watt model generator is discussed here.

Figure of Merit and temperature capability are the two most important performance criteria for thermoelectric materials in space applications. Two other factors of importance in selecting materials are availability and the extent to which the technology of their use has been developed. On the basis of these considerations, p- and n-type lead telluride materials were selected.

FABRICATION PROBLEMS

DIFFUSION BARRIER

Most materials normally considered suitable for conductors are not generally compatible with lead telluride at high temperatures because they cause deterioration of the thermoelectric elements in various ways. To protect the elements against the harmful effects of direct contact with the conductors, a diffusion barrier of a material suitable for direct contact with lead telluride at high temperatures is required. Iron or low carbon steel have both been established as compatible and have been recommended as suitable barriers. The thickness of iron required to adequately protect the thermoelements for one year against diffusion of silver was estimated. On the basis of this estimate 5 mils was selected as a reasonable thickness for the diffusion barrier.

JUNCTION FORMATION

The necessity for a diffusion barrier poses the problem in bonded contact construction of depositing a nonporous layer of iron on the ends of the thermoelements. Efforts to develop a technique for affecting such a deposit of iron on p- and n-type lead telluride are described below.

Electrodeposition - Iron

The initial attempts to apply the iron diffusion barrier were by conventional electroplating techniques. It was found that conventional iron plating baths were generally far too acid. A bath of iron sulfate and potassium sulfate was used with better results. However, the adherence of the plate was still inadequate. Further attempts were made using nickel as a flash to protect the lead telluride from the iron bath. Again, significant improvement in adherence was observed but the results were still not promising.

Electrodeposition - Nickel

Nickel was also believed to have promise as a diffusion barrier so experiments were conducted to evaluate this possibility. Samples of lead telluride were successfully plated by very careful control of the plating process in which a Watts Bath was employed. However, the surfaces turned out to be porous when examined under a microscope. Changing the plating solution to a sulphamate solution resulted in the attainment of non-porous surfaces rather consistently.

The nickel plated samples were then soldered to copper cylinders and junction resistance measurements were made. Junction resistances of less than 10 micro-ohm-cm^2 were observed for both the p- and n-type samples.

Experimental attempts to evaluate the stability of the nickel plated junctions at 1200 F resulted in varying degrees of degradation. It was concluded that nickel plated lead telluride junctions are suitable at low temperatures but will not survive at temperatures in the vicinity of 1200 F. The maximum temperature limit for this type of junction has not been definitely established, but is believed to be in the vicinity of 800 - 900 F.

Vacuum Deposition

Attempts to deposit iron on lead telluride by this technique resulted in the successful deposition of a very thin film. Efforts to build up the thickness of this film by electrodeposition were unsuccessful. The behavior of the sample during the latter process indicated the vacuum-deposited film was quite porous. The fact that the film was porous and thinner than required led to the termination of this investigation.

Diffusion Bonding

Samples of n-type lead telluride were sufficiently well bonded by this technique to yield contact resistances of between 14 and 25 micro-ohm-cm^2. However, no p-type samples were bonded in a manner that would permit the handling necessary for electrical and mechanical testing.

Flame Spraying

With the use of conventional flame spraying techniques it was possible to apply iron to n-type lead telluride. Bond strength obtained was apparently adequate and the electrical resistance of the junction was approximately 10 micro-ohms-cm^2. However, all attempts using conventional flame spraying techniques to deposit iron on the p-type were unsuccessful. The lead telluride cracked, apparently due to thermal shock. Linde Company succeeded in applying a coating of low carbon steel to the p-type using their Flame Plating process. However, there is some doubt whether this coating of itself would serve as an effective diffusion barrier because it may be porous. This method appeared to have some promise but was not completely evaluated because of the necessity to change to a pressure contact design.

Iron Carbonyl

This process resulted in the adherent deposition of iron on lead telluride but the deposits were spoiled by dendritic aggregates of small iron cubes which grew perpendicular to the iron surface as the deposition proceeded. Several attempts to eliminate this condition were unsuccessful. It was concluded that this method was not sufficiently promising for immediate application.

SUBLIMATION AND OXIDATION

At high temperatures lead telluride will oxidize rapidly causing the electrical properties to deteriorate and the material's effectiveness as a thermoelement is destroyed. In addition, at temperatures of about 1100 F lead telluride sublimes at a rate that would tend to limit the service life of the generator particularly when elements of small dimensions are used.

The purpose of this effort was to provide a thin protective coating that would prevent deterioration of the elements due to either oxidation or sublimation. A number of glassy and vitrified coatings were tried but were generally unsuccessful. A number of other coatings and cements were also tried without success.

Two coatings investigated late in the course of the program indicated some promise. These were, 1) mixture of magnesium oxide and sodium silicate and 2) commercial cement (Eccoceram - CS). Evaluation of these coatings was not completed because a protective coating was no longer required when the decision was made to revert to a pressure contact design.

HIGH TEMPERATURE GLUE

A high temperature adhesive is required to bond a structural member to the hot side of the sandwich type generator. A barium sulphate cement with a sodium silicate binder which met the requirements regarding weight, strength and electrical resistivity was prepared. This adhesive is believed to be an adequate solution to the problem but it has not been completely evaluated.

HIGH EMISSIVITY COATING

For maximum performance the surface of the radiator must have high thermal emissivity. A coating of black cobalt oxide mixed with a 50% Ludox, 50% water solution was found to adhere well to the radiating surface material (silver) and to have an emissivity of approximately 0.97. This coating is believed to be satisfactory for its intended purpose.

CONDUCTOR JOINING

Some method of bonding the conductor to the diffusion barrier and to the thermal insulation is required. Attempts to solder or flame spray silver to the insulation were unsuccessful. However, a silver paint adhered quite well to the insulation when it was coated with colloidal silica. This paint has approximately 80% of the conductivity on an equal weight of pure silver. It would also bond to the iron diffusion barrier but would adhere well only in an oxidizing atmosphere which could not be tolerated by lead telluride. Work on this problem was discontinued when the decision was made to use a pressure contact design.

MATERIAL FABRICATION

Construction of the sandwich type model generator requires thermoelectric elements in the form of small rectangular wafers approximately 0.25 inch by 0.15 inch by 0.010 and 0.017 inch thick. A number of techniques were investigated with the result that two methods were found for obtaining the n-type samples of the proper dimensions and one method for obtaining the p-type elements. The vendor, utilizing a proprietary process, prepared rectangular wafers of both the p- and n-type samples. Elements of the n-type were also successfully prepared by slicing thin wafers from round bar stock using a diamond sawing process. These wafers were then diced ultrasonically to the rectangular shape required. It appears that the problem of obtaining elements of the proper dimensions and properties has been solved satisfactorily.

MODEL THERMOELECTRIC GENERATOR

DESIGN CONSIDERATIONS

Failure to achieve timely solutions to all of the fabrication problems involved in construction of a model generator of the sandwich type using bonded contacts necessitated a change in design concept to a more conventional type. Specifically, the lack of a technique for depositing iron on p-type lead telluride required the use of pressure contacts. Also, the fact that a coating suitable for protection of the thermoelements against sublimation and oxidation was unavailable necessitated the use of mica sleeves for sublimation protection and the provision of an inert or reducing atmosphere in a sealed enclosure surrounding the elements.

The side fin-sandwich type of construction was selected for this design because it offered several opportunities for applying the spring forces needed for pressure contacts. After consideration of several methods of applying said forces a C ring design was selected. In this design the contact pressure is applied by spreading the jaws of the C ring slightly and inserting the lead telluride element and conductor assemblies. The design of the model generator using the C ring is illustrated in Part IV, Figures 15, 16, 17 and 18.

DESIGN POINT SELECTION

The design was approximately optimized by making a series of calculations in which various design parameters were successively varied one or two at a time. This procedure was followed because the procedure presented in Part III, Appendix N was not completely developed when the selection was made. Later comparison of the design with the results shown in Appendix N indicates, that considering the compromises made for practical reasons (particularly the heavy containment structure required for pressure contacts), the design may not be too far from optimum.

The model generator as designed was expected to have a specific weight of 70 lb/kw at a thermal efficiency of about 3.4%.

DESIGN DETAILS

The design details of this model generator are best understood by referring to the material under this heading in Part IV and Figures 15, 16, 17 and 18 of Part IV. This material is summarized very briefly below.

The generator consists of two rows of 21 alternate p- and n-type elements arranged on opposite sides of a square tube that contains the electrical resistance heater. The elements are connected in electrical series by means of hot and cold conductor assemblies consisting of the iron caps or diffusion barriers and connecting links of copper. Each pair of diametrically opposed elements is held in place by the clamping action of an Inconel X C ring. Mica is inserted between the hot conductor assemblies and the center tube and between the C rings and the cold conductors to provide electrical insulation.

A cylindrical envelope of 0.001 inch thick stainless steel is provided to enclose the generator. This envelope is bonded to the C rings and the interior of the casing is packed with potassium titanate insulation. Ceramic to metal end shields are provided to complete the generator casing. The radiator, consisting of silver coated with a high emissivity material, is attached to the outer surface of the casing utilizing a diffusion bonding technique.

It should be noted at this point that this model generator has not been completed. Technical difficulties with regard to single ring model tests and high junction resistances slowed progress to the point where the model could not be completed within the time or funding available. Some fabrication difficulties with regard to assembly of the complete 21 ring model were also encountered.

TESTS

Resistance Measurements

Measurements of junction resistance and element resistivity were made on single elements in a resistance profiling device primarily to evaluate the performance of the pressure contact junctions. The resistance profiling equipment used is described in some detail in Part IV. The results, although erratic, indicated junction resistances much higher than the approximately 30×10^{-6} ohm-cm^2 anticipated.

A surprising result found during the course of these measurements was that the p-type resistivity apparently increased with time at high temperatures. However, it now appears possible that the increase observed was due solely to oxidation caused by trace impurities present in the atmosphere used or evolved from parts of the test equipment.

Single Ring Models

To evaluate the pressure contact generator design a program of single ring model testing was inaugurated. These models (for the C ring design) consisted of a pair of p- and n-type elements assembled in a single C ring about a shortened version of the center tube. They were tested in a chamber in which various inert and reducing atmospheres could be provided.

The first models tested were four element per ring models that utilized differential thermal expansion to provide the pressure contact forces. These models were of the first pressure contact design considered as discussed in Part IV, DESIGN CONSIDERATIONS. They are referred to as the solid ring design in Part IV, Table 6. The last five models tested were of the C ring design.

In the course of this single ring model assembly and testing program various difficulties as noted in Part IV, Table 6 were encountered and the performance of the earlier models was most disappointing. As these difficulties were eliminated in subsequent models the performance gradually improved, but only to about 60% of design power output. The failure to achieve design power output is attributed primarily to high junction resistance.

On the basis of these tests, the power output of the generator is expected to be 3 watts as opposed to the design objective of 5 watts. Neglecting end effects, a specific weight of approximately 120 lb/kw at a thermal efficiency of about 2% is now anticipated instead of the design values of 70 lb/kw and 3.4%.

SPECIFICATIONS - 100 WATT SOLAR THERMOELECTRIC GENERATOR

INTRODUCTION

Based on the experience gained on this contract, specifications were prepared for a 100 watt solar thermoelectric generator. These specifications are contained in an appendix of Part IV of this report. They cover the design, construction, and ground feasibility test of a generator whose ultimate application would be as a source of power for space applications having a lifetime of at least one year.

In addition to the generator, a complete system for this purpose would involve a solar collector, an orientation sub-system, a voltage regulation sub-system, and an energy storage sub-system. The specifications do not cover these other sub-systems, however, but deal solely with the generator itself, except insofar as they define certain requirements that the collector and orientation sub-systems can be assumed to meet, since such information is necessary in order to design the generator.

Although the specifications stipulate particular values of weight, volume, and generator efficiency, they have in most instances been left as general as possible in order to allow design flexibility. However, they do stipulate that the design be based on use of a circular, parabolic collector, since such a collector as contrasted with a cylindrical collector, is felt to be necessary for achieving reasonable performance. They also require that the heat transfer between the cold junctions and the radiator does not involve moving parts or the circulation of heat transfer fluids. This latter requirement is felt to be desirable from the standpoint of simplicity.

DESIGN CONSIDERATIONS

In order to arrive at numerical values for weight, volume, and efficiency requirements, it was necessary to select a specific design concept and carry out design studies based on it. The design concept selected is basically the same as that used for the 5 watt generator, wherein the thermoelectric elements are mounted in the annular space between two concentric circular tubes, and side fins extend outward to radiate the waste heat. The energy of the sun is reflected from a circular, parabolic collector through an aperture in the end of this tube. This collector-generator configuration is indicated in Figure 29 of Part IV of this report.

Performance estimates are based on the use of lead telluride as the thermoelectric material. They also contemplate use of pressure contacts and include an allowance for the high junction contact resistances encountered in efforts to build the 5 watt generator. Consequently, if this junction problem could be wholly or partially solved, it would be possible to specify better performance.

SUMMARY OF ANTICIPATED PERFORMANCE

Based on the above design considerations, the following performance requirements are believed to be realistic and were therefore incorporated into the specifications.

Minimum power output - 100 watts

Maximum weight of generator - 20 pounds

Maximum envelope volume of generator - 3400 cubic inches

Minimum generator efficiency - 2%

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