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SUBJECT: Thermoelectric Paper for the SP-100 Program Integration Meeting (June 13-15)

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Attached is a copy of the final version of the paper, "Application of Advanced Thermoelectric Materials to SP-100 Power Conversion System - Initial Considerations." For your information, I am returning your comments on the drafts which, in most cases, were incorporated into the paper. Thank you for your help and patience.

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"APPLICATION OF ADVANCED THERMOELECTRIC MATERIALS TO SP-100 POWER CONVERSION SYSTEM - INITIAL CONSIDERATIONS"

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ABSTRACT - Lanthanum sulfide and boron-carbide compositions have been selected as the thermoelectric materials in the thermoelectric power converter concept for the SP-100 Ground Engineering System Design Study. This paper presents the initial results of the incorporation of these advanced materials into the thermopile design. A sketch and description of the configuration are presented along with the designation of compositions for bonding the individual components of the assembly. The performance effects of various operating conditions and design parameters are also presented. The effect of alternative materials and/or property data for some of the ancillary components on the performance of the assembly is discussed. Design optimization studies are continuing and the technology needs are being assessed to identify tasks for the development program. The next activity is to develop a detailed design and resolve the selected critical technology items.

INTRODUCTION - In the system concept phase of the SP-100 Program the General Electric Company developed a thermopile design consisting of about 60,000 individual, all-bonded thermoelectric assemblies closely arrayed in a square pattern and bonded to fixed support panels. The assemblies are isolated electrically from each other and from the support panels, and are connected electrically in a series-parallel grid to produce desired voltage-current characteristics. Thermal energy is radiated to heat collectors attached to the hot junction of the thermoelectric elements while waste heat from the conversion process is conducted through the bonded interface to the support panels. These serve as fixed radiator panels and radiate a portion of the waste heat to space with the remaining waste heat being transported via liquid metal heat pipes to deployed radiator panels for rejection to space.

This design utilized silicon germanium modified with gallium phosphide additive as the thermoelectric material. An advanced material combination consisting of lanthanum sulfide as the "N" leg material and boron-carbide as the "P" leg material has been selected for the present design phase because of its superior performance potential. The overall configuration of the system remains the same as that described above, but the design of the individual thermocouple assemblies is modified to accommodate the property characteristics of the advanced materials. System parameters are being reoptimized and an early objective was to derive parametric interface data for system analysis and design. The starting point for the design investigations consisted of the thermoelectric material property data shown in Table 1. These material properties are projected to be achieved by July 1985 as a result of on-going development programs.

BASIC CONSIDERATIONS - Initial design activities concentrated on the compilation of property data (in addition to the transport data of Table 1) for the materials in the thermopile. Table 2 summarizes the data compiled for lanthanum sulfide and boron-carbide thermoelectric materials. These were assembled from a number of sources and include estimates based on the properties of related or similar materials where reliable physical property data were not available.

A scoping of the performance characteristics of the advanced thermoelectric materials was carried out to determine their range of probable operating conditions with the results as shown in Figure 1. Material conversion efficiencies versus couple output voltages were computed and compared to those for the previous baseline silicon germanium material. For similar temperature conditions, results showed the advanced thermoelectric materials would have higher conversion efficiencies. By taking advantage of the new materials' higher operating temperature potential, significant performance gains in conversion efficiency and voltage output could be achieved.

The coefficient of thermal expansion of lanthanum sulfide shown in Table 2 is a factor in selecting a material that can be successfully bonded to it. The bonded material will be suited for vacuum operation at elevated temperature, be chemically compatible with lanthanum sulfide, and have an appropriate combination of mechanical properties to avoid excessive stresses over the operational temperature range. Table 3 compares various candidate materials listed in order of increasing coefficient of thermal expansion. An idealized, one-dimensional model was used to calculate the induced stresses. It predicts that maximum stress occurs at room temperature after cooling from the bonding temperature. As the data shows, materials that are clearly compatible on a thermal stress basis are platinum felt and cobalt; the first by virtue of its compliance, the second because of a close matching of coefficient of thermal expansion. The actual thermal stresses in a bonded joint are complex and highly non-uniform. Therefore, a low safety margin design that relies on close matching of properties involves a high technical risk. For that reason, it was decided to incorporate a platinum felt pad, or a similarly compliant and ductile structured material in the couple assembly to avoid excessive stresses at the bonded interfaces of the lanthanum sulfide.

PRELIMINARY THERMOPILE DESIGNS - A number of material combinations and geometry/dimensional configurations were evaluated before the functional unicouple design arrangement shown in Figure 2 was selected. The primary considerations in the evolution of this configuration were the materials thermal expansion characteristics and large temperature gradients in the assembly, as mentioned previously.

The following description of the thermopile starts at the hot end of the assembly and proceeds through the various elements to the cold end. A split design of a graphite heat receiver is combined with flexible foils of platinum, which form the hot strap electrical path, to allow differential growth of the two thermolectric legs in the vertical direction of Figure 2. The graphite heat receivers are tapered toward the outer edges to minimize their weight for a given fin efficiency.

Below the hot strap are two platinum felt pads, one on each leg of the assembly. These pads function as transitional sections which have good thermal and electrical conductance and good structural strength while providing shear flexibility to accommodate thermal expansion differences between the hot strap and the thermoelectric materials.The next layer in the boron-carbide "P" leg is a thin membrane of graphite separating the platinum felt pad and the boron-carbide material which are chemically incompatible at elevated temperatures.

The thermoelectric materials in each leg form the next material layer. This is followed by another graphite membrane on the boron-carbide leg (again for compatibility purposes) and another platinum felt pad on the lanthanum sulfide leg. These are followed by separate sections of nickel-plated copper cold straps which are the electrical circuit between couple assemblies. The cold straps are in ribbon form having a width equal to the side dimension of the thermoelectric legs. The nickel plating on the cold strap protects the copper substrate at the operating temperatures on the "cold" side of the couple assembly.

An electrical insulating layer of tungsten-filled glass electrically isolates the electrical circuitry of the thermoelectric assembly from the support structure. Tungsten particles are added to the glass material to increase its thermal conductance characteristics. The glass layer is bonded to a structured copper component consisting of a close packed array of individual copper whiskers which structurally support the couple assembly while allowing differential lateral expansions between the beryllium support plate and the couple assembly.

Multi-foil thermal insulation (not shown in Figure 2) fills the volume between the graphite heat receiver and the copper cold straps. Alumina coatings are added to the lower surfaces of the graphite receivers to prevent thermal shorting to the multi-foil insulation. Also, several layers of quartz yarn are wound around the periphery of the thermoelectric legs to electrically isolate the legs from the multi-foils and to provide mechanical compliance between the legs and the multi-foil insulation. Quartz felt is packed in the gap between the two legs to lessen thermal bypass losses between the hot and cold sections of the assembly.

Figure 3 identifies the assembly sequence and the bonding processes to be used in the fabrication of the thermocouple assembly. The bonding procedure must consider the materials to be joined at each interface, their expected operating temperatures, and a fabrication sequence that is practical for the overall design of the assembly. The circled numbers indicate the order in which the four separate bonding operations would be performed. Also indicated are the selected braze alloys and corresponding brazing temperatures. Palco, Palcusil and Incusil are proven bonding processes but need to be verified for the particular material combinations at the designated interfaces.

PERFORMANCE CHARACTERISTICS - Analyses have been carried out to identify and quantify the design parameters such as conversion efficiency, thermopile weight, and junction temperatures that impact overall system performance. Geometry and other system configuration factors limit the fixed radiator panel area which is the area available for the heat receivers. Figures 4, 5, 6 and 7 summarize the results of some of the parametric studies made with a computer model of this functional design configuration. Figure 4 shows thermopile weight as a function of total parasitic electrical losses (straps and compliance pads) for several cold strap loss values. The locus of minimum weight is fairly flat with the lowest value being at about 15% total loss with a 6% cold strap loss. Figure 5 shows the impact of hot and cold junction temperatures on thermopile weight and efficiency. Concurrent total power system studies using this data resulted in the initial selection of hot and cold junction temperatures of 1000°C and 500°C respectively. Figure 6 shows the impact of the fixed radiator area and cold junction temperature on thermopile weight and efficiency. Decreasing this area results in higher weights and higher efficiencies. Figure 7 shows the impact of changing the number of couples and/or the length of the thermoelectric legs. Shorter leg lengths and greater number of couples provides lower thermopile weights and lower efficiencies. The lower efficiencies mean higher heat flows and larger radiators which counter these subsystem weight reductions. The true benefit can only be determined by incorporating this trade-off in an analysis of the total power system. Previous studies have also shown the weight benefit of larger numbers of couples and the use of a bicouple configuration. The trade-off with shorter leg lengths must also be made on a total system basis to determine the real weight benefit. Other factors such as thermal stresses (i.e larger thermal gradients) and manufacturing process control must also be considered in going to the shorter leg lengths.

DESIGN VARIATIONS - The functional design of the thermoelectric couple assembly shown in Figure 2 is a reference point for continuing evaluation of the design configuration, materials and operating conditions. Analyses are being carried out to quantify the design parameters that impact the overall system performance and select values that optimize the system performance.

The platinum foil straps carrying electrical current between the hot junctions of the thermoelectric couple legs contribute 10-15% of the total weight and a much larger percentage of the material costs of the thermoelectric assembly. Alternate materials have been surveyed with the intent of reducing weight and/or cost with comparable performance characteristics. Table 4 identifies three potential alternate materials and compares their properties with those of the platinum baseline. Both palladium and a gold-palladium alloy have weight and cost advantages but also have relatively high vapor pressures at operating temperature, and so may require the use of a protective coating such as platinum or rhodium.

Rhodium has desirable properties of low density, low electrical resistivity and low vapor pressure, but it lacks sufficient ductility to be the principal element in a flexible strap. However, it would be valuable as a protective coating for both the palladium and the gold-palladium alloy, either in the sputtered or electroplated form.

The effect of substituting either palladium or gold-palladium alloy for platinum on the basis of equal electrical resistance in the thermoelectric assembly is shown in Table 5. Palladium provides a significant reduction in both cost and weight. The gold-palladium alloy would provide an even greater weight savings but a lesser reduction in cost. The additional weight and cost of a protective coating for these alternate strap materials would not be significant because of the very thin coatings required.

A bicouple design configuration has been developed and is shown in Figure 8. It provides subassemblies with double the output voltage of the unicouple arrangement shown in Figure 2. Prevous studies have shown that the bicouple provides system performance advantages so this configuration will be evaluated prior to freezing the conceptual design.

STATUS - At this functional design stage, the advanced thermoelectric materials have been incorporated into the conceptual system design and provide improved system performance (approximately a 25% improvement in area and a 10-20% relative improvement in mass). A bicouple configuration has been identified and its impact on system performance will be evaluated.

Activity is underway to develop a detailed design and assess the critical technology factors in the design. Development of the critical technology items will follow.

Table 1. Transport Properties of Thermoelectric Materials

	LANTHANUM SULFIDE				BORON CARBIDE			
TEMPERATURE (°C)	400	600	800	1000	400	600	800	1000
SEEBECK COEFFICIENT (μv/°C)	134	165	200	240	175	182	200	216
RESISTIVITY (mΩ cm)	1.2	1.6	2.0	2.4	3.1	2.2	2.1	2.2
THERMAL CONDUCTIVITY (mW/cm-°C)	20	20	20	20	20	20	20	20
FIGURE OF MERIT (10^3/°C)	.75	.85	1.0	1.2	.50	.75	.95	1.11

AS PROJECTED FOR JULY 1985

Table 2. Physical Properties of Thermoelectric Materials

PROPERTY	UNITS	LaS_x	B_xC
TENSILE STRENGTH	10^3psi	(5)	(73)
FLEXURAL STRENGTH	10^3psi		73
COMPRESSIVE STRENGTH	10^3psi		400
MODULUS OF ELASTICITY	10^6psi	(10)	65
COEF OF THERMAL EXPAN.	10^{-6}/°C	13	6.8
DENSITY	g/cc	4.9	2.5
MELTING POINT	°C	2000	2200
SUBLIMATION RATE	g/cm^2-hr	10^{-8}	–
SPECIFIC HEAT	cal/g°C	0.12	0.23
THERMAL CONDUCTIVITY	W/cm-°C		
550°C		0.02	0.02
1000°C		0.02	0.02
ELECTRICAL RESISTIVITY	milliohm-cm		
550°C		1.4	2.9
1000°C		2.4	2.2
BASIS			

( ) DATA ESTIMATED FROM PROPERTIES OF RELATED OR SIMILAR MATERIALS

Table 3. Thermal Expansion Compatibility of Various Materials With Lanthanum Sulfide

MATERIAL BONDED TO LANTHANUM SULFIDE	THERMAL EXPANSION COEFFICIENT (/°C)	ELASTIC MODULUS (10^6 PSI)	MAXIMUM STRAIN AT INTERFACE IN/IN	STRESS IN BONDED MATERIAL (10^3 PSI)	MAX STRESS IN LaS$_x$ (10^3 PSI)	ASSESSMENT
GRAPHITE	8.3×10^{-6}	1.6	.0069	-10.9 (10)	0.7 (5.0)	MARGINAL
PLATINUM	9×10^{-6}	25	.0049	-104 (2)	6.9 (5.0)	NOT ACCEPTABLE
PLATINUM FELT	9×10^{-6}	1	.0049	-0.5 (2)	0.03 (5.0)	ACCEPTABLE
TITANIUM	9.2×10^{-6}	15	.0046	-63 (25)	4.2 (5.0)	MARGINAL
COBALT	12.2×10^{-6}	30	.0010	-24 (48)	1.6 (5.0)	ACCEPTABLE
NICKEL	15.5×10^{-6}	30	.0030	76 (16)	-5.1 (5.0)	MARGINAL

NOTES:
- STRESSES AT ROOM TEMPERATURE AFTER BONDING AT 1235°C (WORST CASE)
- TENSION STRESS POSITIVE
- MATERIAL PROPERTIES PER PRECEEDING CHART
- ( ) ALLOWABLE STRESS

Table 4. Properties of Various Alternate Electric Strap Materials

MATERIAL	DENSITY g/cc)	MELTING POINT (°C)	VAPOR PRESSURE AT 1100°C (torr)	ELECTRICAL RESISTIVITY (microhm-cm)		THERMAL EXPANSION COEFFICIENT (/°C)	THERMAL CONDUCTIVITY (w/cm-°C)	RELATIVE COST PER UNIT WEIGHT
				20°C	1100°C			
PLATINUM	21.4	1769	4×10^{-11}	9.8	46	8.8×10^{-6}	.74	1.0
PALLADIUM	19.3	1554	2×10^{-5} ▷1	10.8	45	11.7×10^{-6}	.76	.56
88Au-12Pd	18.4	1300	4×10^{-5} ▷1	3.2 ▷3	18 ▷3	13.9×10^{-6}	2.86	.86
RHODIUM ▷2	12.4	1966	6×10^{-11}	4.5	32	8.3×10^{-6}	1.51	2.0

NOTES
- ▷1 MATERIALS WITH VAPOR PRESSURE GREATER THAN 10^{-8} TORR WILL REQUIRE PROTECTIVE COATING.
- ▷2 RHODIUM HAS POOR DUCTILITY AND IS NOT SUITABLE FOR COMPLIANT STRAP, BUT IS SUITABLE FOR PLATING OVER GOLD AND PALLADIUM.
- ▷3 ELECTRICAL RESISTIVITY FOR GOLD-PALLADIUM ESTIMATED.

Table 5. Effect of Substitution of Alternate Strap Materials For Platinum

MATERIAL	STRAP WEIGHT ① RELATIVE TO PLATINUM	STRAP COST RELATIVE TO PLATINUM
PLATINUM	1.0	1.0
PALLADIUM	.88	.49
88Au-12Pd	.34	.29

① BASED ON EQUAL ELECTRICAL RESISTANCE.

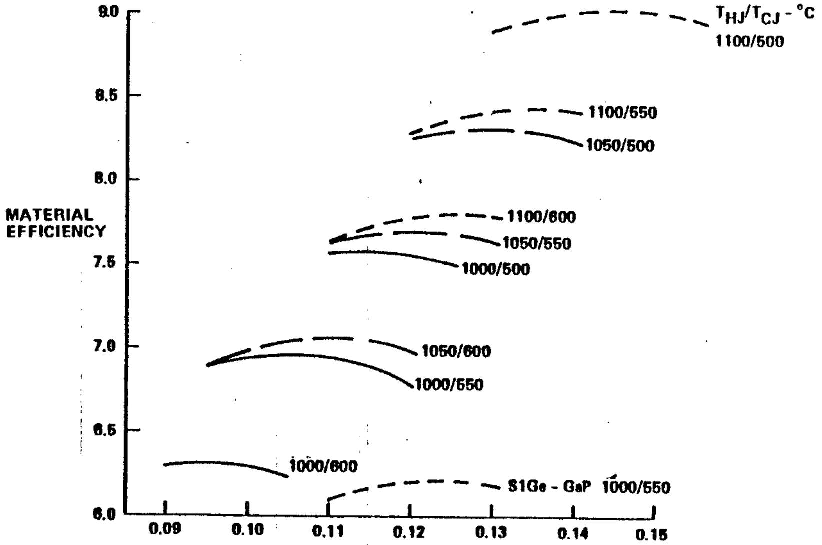

Figure 1. Thermoelectric Material Efficiency

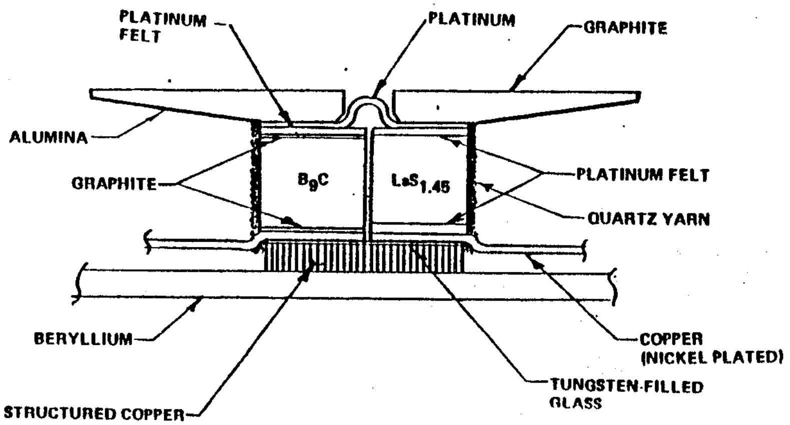

Figure 2. Preliminary Functional Design of Unicouple

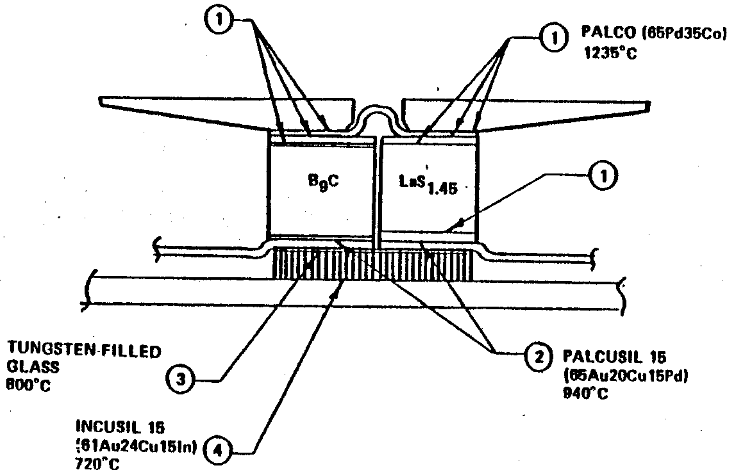

Figure 3. Bonding Processes

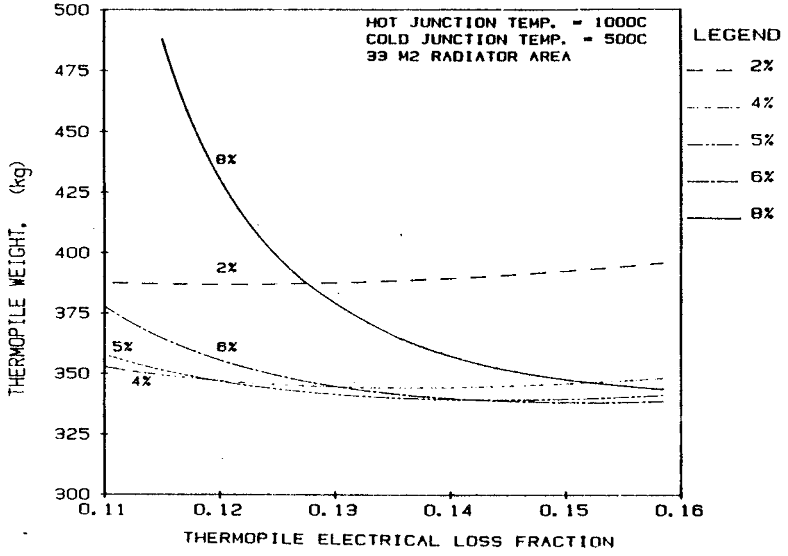

Figure 4. Thermopile Weight Vs. Total Electrical Loss

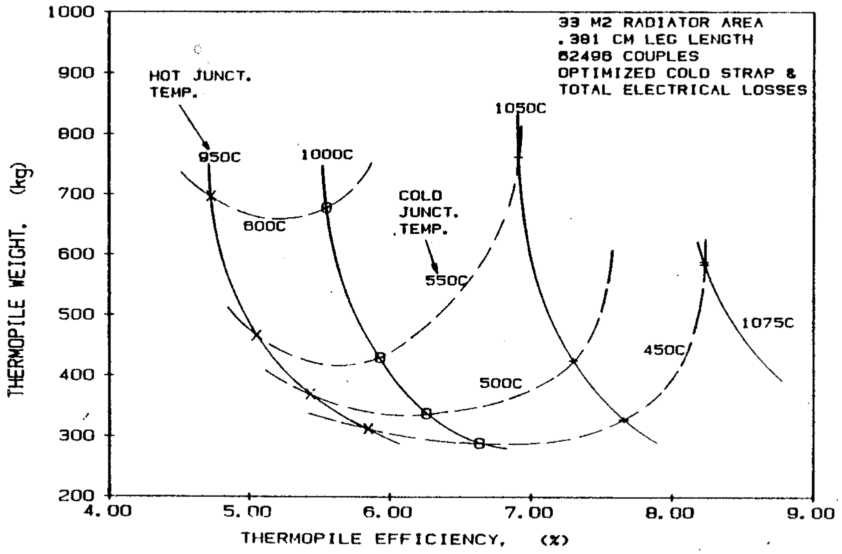

Figure 5. Thermopile Weight and Efficiency For Various Junction Temperatures

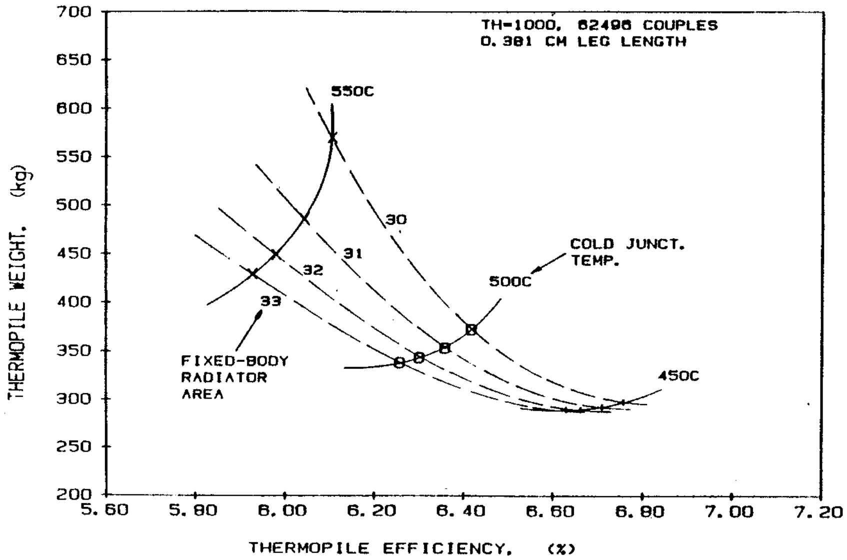

Figure 6. Thermopile Weight and Efficiency For Various Radiator Areas

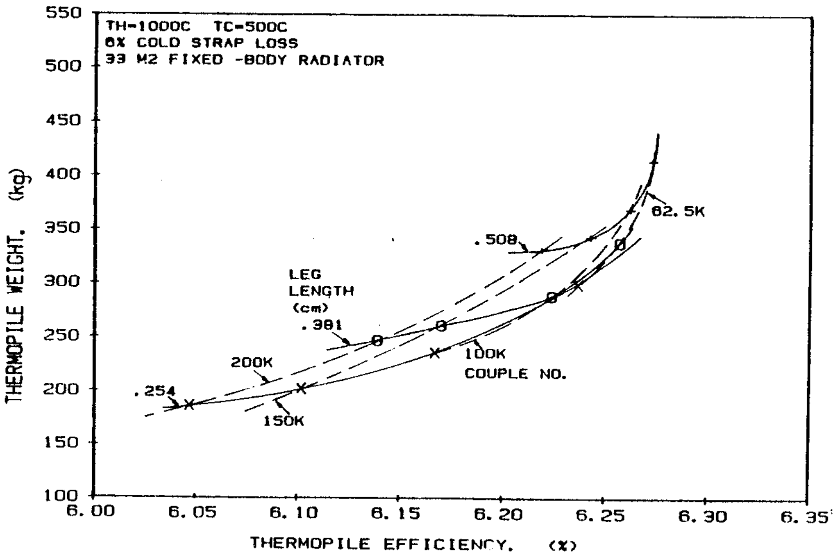

Figure 7. Thermopile Weight Vs. System Efficiency

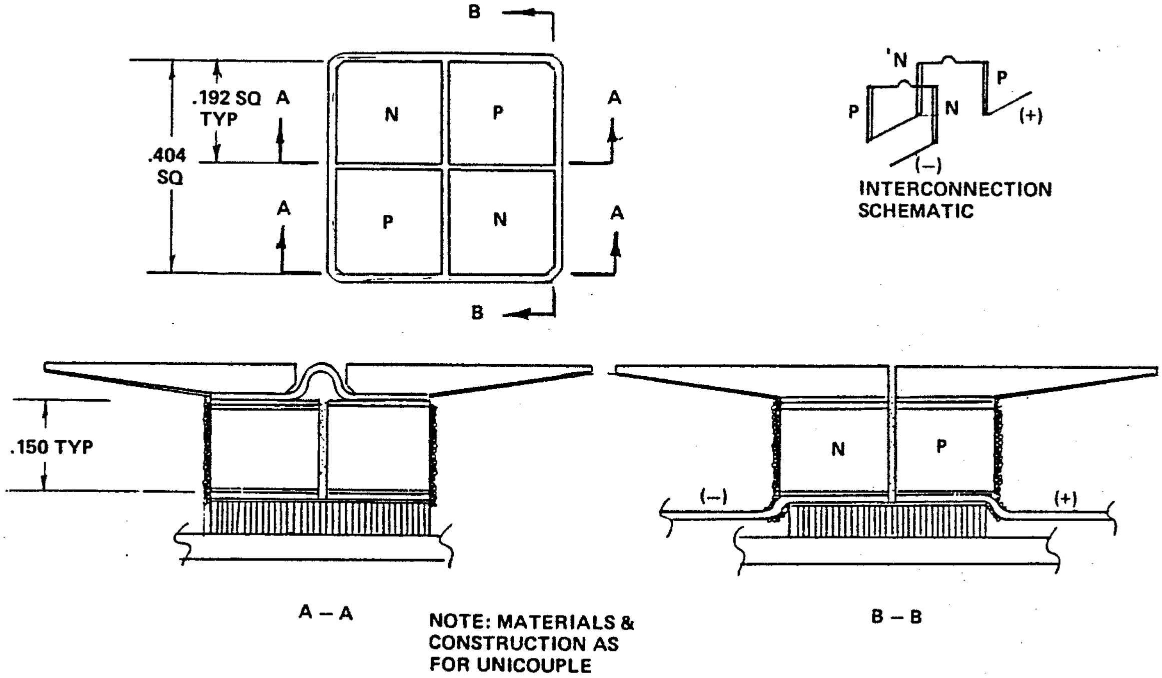

Figure 8. Design Concept For Bicouple