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DEVELOP 1800F-400F FIBROUS-TYPE
INSULATION FOR RADIOISOTOPE POWER SYSTEMS

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VOLUME I

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OCTOBER 2, 1967

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CPL (Rockhaven)

by
J. O. Collins

JOHNS-MANVILLE RESEARCH & ENGINEERING CENTER
Manville, New Jersey

Prepared under
Contract AT(30-1)-3633

for the
Albuquerque Operations Office
U. S. ATOMIC ENERGY COMMISSION

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ABSTRACT

by

J. O. Collins

This is the Final Report for Phase I of AEC Contract AT(30-1)-3633.

Three MIN-K formulations were developed and evaluated for lead-telluride and silicon-germanium radioisotope thermoelectric generator service. Each formulation has certain optimum characteristics which govern its use, such as intricate service adjacent to lead-telluride elements, bulk load-bearing service to 1400F, or non-load-bearing service to 1800F. All three formulations were designed to have minimum outgassing characteristics.

ASTROQUARTZ, DYNAQUARTZ, Irish REFRASIL, and MICRO-QUARTZ refractory fibers were also found suitable for service adjacent to silicon-germanium thermoelectric elements. Similarly, GLASROCK No. 25, a silica foam, had the best combination of thermal conductivity and compression resistance characteristics of the materials evaluated for load-bearing service at 1800F.

The thermal conductivity evaluations and theoretical heat transfer study of the MIN-K formulations is still in progress, and will be reported in a supplement.

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1. INTRODUCTION

U. S. Atomic Energy Commission Contract AT(30-1)-3633 was initiated to develop and evaluate fibrous-type thermal insulation materials for use in radioisotope power systems in the temperature range of 1800-400F.

The undesirable characteristics of the currently used thermal insulations are:

1. Physically entrapped and/or chemically combined molecules in fibrous insulations are released as gases as a function of time and temperature into hermetically sealed systems. Adverse effects include chemical reaction with vital parts of the power generating system and/or increased heat losses through the insulation. Both of these effects result in reduced RTG efficiency.
2. Fibrous insulations exhibit a tendency to sinter at operating temperatures causing shrinkage of the insulation, and hence, unpredictable changes in the insulating characteristics.
3. Fibrous insulations also exhibit a tendency to creep under mechanical loads thereby complicating the design of the insulation system and reducing the load-carrying ability.

It was the intent of this program to:

1. Evaluate insulation outgassing, thermal instability, and dimensional change phenomena.
2. Improve, where possible, materials and processes for eliminating, minimizing, or controlling the water vapor/oxygen contamination phenomena.
3. Evaluate capability for intricate geometric shaping to meet system integration requirements.
4. Obtain as much lifetime test data at typical operating conditions as possible.

The execution of this effort not only included material development, but also evaluation of existing products. Those commercial products which were evaluated were not necessarily developed or manufactured to meet any Government specification, or designed to operate under the specific conditions pertinent to this study. Consequently, any failure to meet the objectives of this study, whether by test, previous experience, or engineering analysis prior to test is no reflection on any of the products or on the manufacturers. In certain instances, a material was chosen for consideration as representing a

class of materials, with availability representing the prime criteria for the choice.

This document constitutes the Phase I Final Report for Contract AT(30-1)-3633. Additional thermal conductivity data on the products developed under this contract, and the comparison of these data with theory will be presented in a supplement to this report.

II. THEORETICAL HEAT TRANSFER

A. THEORY VERSUS EXISTING DATA

In view of the interest in, and the development work on MIN-K type insulations, it was considered desirable to express mathematically the heat transfer characteristics of MIN-K so that its use under future operating conditions could be predicted with reasonable accuracy. The first step, therefore, was to test a mathematical model, utilizing not only published theories, but also theories developed at the Johns-Manville Research & Engineering Center, against existing data. The data chosen were for MIN-K 2000 containing 16 per cent TiO_2 at an average reported (by vendor) particle size of 4 microns, as obtained in air by the ASTM C-177-63 Refractory Guarded Hot Plate method.

Figure 1 compares the theoretical curve with average test data, and indicates excellent agreement between the two. The theoretical derivation used, and sample calculations were presented in Report No. AL0-3633-1 dated July 1, 1966 (First Quarterly Progress Report).

Further calculations indicated that the thermal conductivity could be reduced by reducing the opacifier particle size from 4 microns to 2 microns, and by increasing the opacifier content within the insulation. These effects are depicted in Figure 2. It was realized, however, that the effect of greater quantities of opacifier on the physical properties of the product must also be considered.

Subsequent investigations (see Section VI on Material Process and Development) showed that the 4 micron average particle size was actually closer to 2 microns, but that the size distribution pattern indicated that a large percentage of the particles was considerably larger and smaller than 2 microns. The net effect therefore could be approximated by a uniform 4 micron particle. A more refined TiO_2 product, having the same average particle size, but a considerably smaller size variation from the average, reduced the thermal conductivity approximately as depicted by Figure 2. Thus, the theory appeared to describe the thermal conductivity behavior of the MIN-K type products.

B. PRELIMINARY TESTS

Initial thermal conductivity tests in vacuum and argon of the MIN-K products developed under this contract indicated, however, that the existing theory referenced above did not adequately describe the heat transfer characteristics in these other atmospheres. (Although the theory allowed for changes in atmospheres, no data had been previously

FIGURE 1

COMPARISON OF THEORETICAL CONDUCTIVITY CURVE WITH
AVERAGE TEST POINTS FOR MIN-K 2000

FIGURE 2.

EFFECT OF TITANIA CONTENT AND PARTICLE SIZE
ON THEORETICAL THERMAL CONDUCTIVITY
OF MIN-K AT 1100F MEAN TEMPERATURE

available for correlation.) In each instance, it appeared that some interrelation between the basic modes of heat transfer existed, and that the alteration of one mode (such as gaseous conduction) may produce an opposite, although smaller, change in another mode (such as radiation).

The thermal conductivity evaluation phase of this program is still in progress. Consequently, new theoretical considerations will be developed and correlated with test data, and presented in a supplement to this Phase I Final Report.

III. CANDIDATE MATERIALS

Candidate materials for evaluation under this program were divided into two categories: thermal insulations for bulk and/or intricate service, and load-bearing materials. A summary of these candidates may be found in Tables 1 and 2, respectively.

In the selection of candidate materials, an extensive survey was made to determine which current products appeared most promising, and to determine the existence of new products. The efforts consisted of:

1. A technical literature search which included technical periodicals, industrial reports, reports by various Government agencies and reports of investigations conducted under Government contract such as those issued by Wright-Patterson Air Force Base.
2. A letter sent by the Atomic Energy Commission to nineteen of the leading insulation manufacturers requesting recommendations and data, particularly in the area of new products under development.
3. Suggestions from AEC and Sandia Corporation personnel.
4. Johns-Manville experience and contacts in the field.

MICROTHERM 20 Cr made by Boucher & Co., Kidderminster, England, was the only new product which warranted extensive evaluation as a candidate material. A discussion with representatives of Boucher & Co. revealed the product to be generally similar to the Johns-Manville MIN-K family of products.

Three products suggested by AEC and Sandia personnel, or which appeared promising as a result of the literature search, were not tested. TIPERSUL, a du Pont product, and FOAMSIL, a product of Pittsburgh Corning, were no longer being manufactured. Alumina whiskers, a product of Thermokinetic Fibers, could not be justified because it offered no advantage over conventional refractory fibers for applications in SNAP systems.

TABLE I.
THERMAL INSULATION CANDIDATE MATERIALS

<u>Product Name</u>	<u>Manufacturer</u>	<u>Type</u>	<u>Nominal Density, pcf*</u>	<u>General Description</u>
ASTROQUARTZ	J. P. Stevens	Fibrous	0.5	Pure quartz fiber.
DYNAFLEX	Johns-Manville	Fibrous	8	Silica-alumina-chromia fiber for 2700F service.
DYNAQUARTZ	Johns-Manville	Rigid Fibrous	10	Heat treated silica fiber for 2700F service.
FIBERFRAX	Carborundum	Fibrous	10	Silica-alumina fiber for 2200F service.
Irish REFRASIL	H. I. Thompson	Fibrous	6	Chrome treated silica fiber for +2000F service.
MICRO-QUARTZ	Johns-Manville	Fibrous	3.5	Leached silica fiber for 2000F service.
MICROTHERM 20 Cr	Boucher (England)	Rigid Particulate	20	Submicron particles and opacifier and fibrous reinforcement - compression molded.
MIN-K 1301 and MIN-K 2000	Johns-Manville	Rigid Particulate	20	Submicron particles and opacifier and fibrous reinforcement - compression molded.
THERMOFLEX	Johns-Manville	Fibrous	6, 12	Silica-alumina fiber for 2100F service.

*Product may or may not be available in other densities.

TABLE 2.
LOAD-BEARING CANDIDATE MATERIALS

<u>Product Name</u>	<u>Manufacturer</u>	<u>Type</u>	<u>Nominal Density, pcf*</u>	<u>General Description</u>
CERABOARD	Johns-Manville	Rigid Fibrous	45	Inorganic bonded silica-alumina fiber.
GH BOARD	Carborundum	Rigid Fibrous	35	Inorganic bonded silica-alumina fiber.
GLASROCK No. 25	Glasrock Products, Inc.	Foam	25	Open cell, fused silica.
GLASROCK No. 50	Glasrock Products, Inc.	Foam	50	Open cell, fused silica.
JM-23 INSULATING FIREBRICK	Johns-Manville	Brick	31	2300F refractory brick.
JM-3000 INSULATING FIREBRICK	Johns-Manville	Brick	65	3000F refractory brick.
T30LR LAMINATE	Carborundum	Rigid Fibrous	54	Inorganic bonded silica-alumina fiber.

*Product may or may not be available in other densities.

IV. EVALUATION OF THERMAL INSULATION CANDIDATES

A. GENERAL

This section is concerned exclusively with the evaluation of the candidate materials listed in Table 1, Section III. Not all of these candidates were subjected to all of the tests, since many of them were eliminated from further consideration for reasons detailed in the Quarterly Reports. Several products, however, were subjected to extensive testing both with respect to time and type of test because of their potential usefulness in a SNAP generator. These included ASTROQUARTZ, DYNAQUARTZ, MICRO-QUARTZ, Irish REFRASIL, and MICROTHERM 20 Cr.

The test procedures used in all evaluations were based, where possible, upon standard ASTM methods. Where special procedures were prepared, they were reported in the Quarterly Reports. Applicable report references are used herein.

B. THERMAL STABILITY

The candidate materials were isothermally exposed in air to 1400F, 1600F, 1800F, and 2000F for 24 hr. Maximum temperature variations in the electrically heated furnaces employed for thermal exposure were: $\pm 10.5^\circ\text{F}$ at 1400F, $\pm 6^\circ\text{F}$ at 1600F, $\pm 8^\circ\text{F}$ at 1800F, and $\pm 9^\circ\text{F}$ at 2000F. Table 3 summarizes the results. All values are based upon original dimensions.

Linear shrinkage of soft felt-type products such as ASTROQUARTZ, Irish REFRASIL, DYNAFLEX, MICRO-QUARTZ, and THERMOFLEX at a density of 6 pcf was difficult to determine with a high degree of precision. The soft nature of these products, particularly after combustion of the organic binder, made handling without deformation extremely difficult, and frequently caused the outlines of the sample to be poorly defined. Thickness was the most difficult of the three dimensions to determine. Since the thickness of the products as supplied ranged approximately from 1/8 to 5/8 in., a slight experimental error could indicate a significant change on a percentage basis. Linear shrinkage of rigid products such as DYNAQUARTZ, MIN-K 1301, and MIN-K 2000 or firm felt-type products such as 12 pcf THERMOFLEX were determined with a reasonable degree of precision. The densities shown in Table 3 for each product represent the average of the actual densities of three specimens prior to test.

ASTROQUARTZ, DYNAQUARTZ, Irish REFRASIL, and MICRO-QUARTZ were subjected to long-term thermal stabilities at 1600F (isothermal) in air in conjunction with the silicon-germanium chemical compatibility tests (see Section IV-E). These candidates were chosen because: (1) they are currently being used

TABLE 3.
THERMAL STABILITY OF CANDIDATE THERMAL INSULATIONS
AFTER 24 HR ISOTHERMAL EXPOSURE

Product	Test Density pcf	Dimensional Change, %		
		Length	Width	Thickness
ASTROQUARTZ	0.5			
1400F		0	0	---
1600F		0	0	+76
1800F		0	0	+86
2000F		0	-4	+44
DYNAFLEX	7.7			
1400F		---	---	---
1600F		0	0	+15
1800F		-2	-2	+11
2000F		-2	-2	+22
DYNAQUARTZ	10.1			
1400F				
1600F				
1800F				
2000F				
			no change	
FIBERFRAX	9.7, 8.4			
1400F		0	0	0, (0)
1600F		0	0	+2, (+7)
1800F		-2	-2	+6, (0)
2000F		-3	-3	+4, (0)
() = thickness change without binder.				
Irish REFRASIL	5.7			
1400F		0	-1	---
1600F		0	0	-4
1800F		0	-1	+21
2000F		-1	-2	+12
MICRO-QUARTZ	3.5			
1400F		-3	-3	-6
1600F		-5	-5	-5
1800F		-6	-6	-6
2000F		-10	-10	-8
MICROTHERM 20 Cr	18.8			
1400F		---	---	---
1600F		-2	-2	-2
1800F		-4	-5	-14
2000F		-35	-35	-45

TABLE 3. (Cont'd)

Product	Test Density pcf	Dimensional Change, %		
		Length	Width	Thickness
MIN-K 1301	21.1			
1400F		-2	-2	-3
1600F		-12	-12	-19
1800F		---	---	---
2000F		---	---	---
MIN-K 2000	22.2			
1400F		0	0	0
1600F		-1	-1	0
1800F		-2	-2	-5
2000F		-16	-16	-35
THERMOFLEX	5.1, 12.3			
1400F		0	0	+5
1600F		-1	-1	+8
1800F		-2	-2	+4
2000F		-2	-2	+3

in and around the silicon-germanium couples (MICRO-QUARTZ and DYNAQUARTZ), or (2) the candidates were similar to those in (1). Current usage of the candidates, however, dictated that they be compacted to 10-12 pcf density.

With the exception of DYNAQUARTZ, which was in the form of a rigid block at 10 pcf, the candidates were shredded and packed into 2-in. diameter straight-walled ceramic crucibles to a depth of approximately 5.5 in., and to a density of approximately 10 pcf. Although care was taken to randomize the fiber direction as much as possible, it is likely that the distribution tended toward a laminar structure across the crucible diameter.

Table 4 summarizes the dimensional change of the candidates. All values are based on the original dimensions.

As one might expect, the felts tended to "spring back" due to the high packing density thus masking any potential shrinkage tendency in the depth direction. MICRO-QUARTZ, however, exhibited a significant diameter shrinkage, resulting in a looseness of the packed felt within the crucible. This was consistent with the 5 per cent shrinkage of the MICRO-QUARTZ felts after 24 hr at 1600F (see Table 3).

A similar test program was planned for these four candidates in vacuum at 1600F. The vacuum system, however, did not permit the evacuation of the Irish REFRASIL and MICRO-QUARTZ specimens without ejecting the specimens from the crucibles unless the packed density was reduced from 10 pcf to 6 pcf. Even then, there was no assurance that the depth of the specimens did not change as a result of the evacuation. The ASTROQUARTZ was less affected by the evacuation due to the coarser fiber and hence greater porosity of the packing. Under the circumstances, no thermal stability data were obtained in vacuum. In practice, the porosity of the packed bed of fibers should not present a problem provided the fibers are adequately contained on all sides prior to evacuation.

C. THERMOGRAVIMETRIC ANALYSES (TGA)

Thermogravimetric analyses were conducted to determine the weight loss of the candidate materials with respect to time to assist in establishing future outgassing procedures as necessary. The analyses determined the quantities of gases and vapors emitted rather than the composition of those gases.

Samples were preconditioned for 20 hr at room temperature and 54% RH prior to analysis. A temperature rise rate of 8C per min was used with

TABLE 4.

EFFECT OF TIME ON ISOTHERMAL STABILITY OF ASTROQUARTZ,
DYNAQUARTZ, IRISH REFRASIL, AND MICRO-QUARTZ AT 1600F IN AIR

	<u>500 hr</u>	<u>1000 hr</u>	<u>1500 hr</u>	<u>2000 hr</u>
	<u>Dimensional Change in Depth, Per Cent</u>			
ASTROQUARTZ	+0.2	+0.2	+0.2	+0.2
Irish REFRASIL	+0.6	+0.6	+0.6	+0.6
MICRO-QUARTZ	+0.8	+0.4	+0.2	+0.2
	<u>Dimensional Change in Diameter, Per Cent</u>			
ASTROQUARTZ	no change			
Irish REFRASIL	no change			
MICRO-QUARTZ	-5.3	-5.3	-5.3	-5.3
DYNAQUARTZ	<0.1 per cent on length, width, and thickness			

the standard TGA procedure. The analyses were conducted in air with the exception of MIN-K 1301 and THERMOFLEX. These were tested in both air and nitrogen since they contained components which oxidize at elevated temperatures and hence partially mask the loss of moisture and binder.

Table 5 is a summary of the TGA data. For ease of comparison, similar products were grouped together. THERMOFLEX was considered typical of the alumina-silica refractory fiber candidates containing binder, thus eliminating the need for the TGA evaluation of FIBERFRAX and DYNAFLEX.

The data for MICRO-QUARTZ, Irish REFRASIL, ASTROQUARTZ, and DYNAQUARTZ show the range of volatile content which could be encountered with fibrous silica materials. MICRO-QUARTZ, an acid-leached product, showed the greatest loss due to the high water content of the fibers. A large fraction of this water was adsorbed, and hence was readily removed at 300C. Adsorbed water is present primarily because of the presence of chemically combined water which results from the acid-leaching process. Consequently, water will re-adsorb with equal ease at room conditions unless the chemically combined water is also removed. This generally requires temperatures of 600C or higher, and is not reversible because of the sintering of the silica which results. This water removal and sintering process is believed to be the cause of the felt shrinkage.

Irish REFRASIL is also an acid-leached product, but is subsequently given a chrome treatment. From the low weight loss (0.3 per cent) and the relatively low temperature at which this loss took place, it appeared that this product had a thermal history during manufacture which was sufficient to remove most, if not all, of the chemically combined water. Lacking chemically combined water, the tendency to adsorb moisture from the air is practically eliminated. This also accounts in part for the greater thermal stability (see Table 3) of Irish REFRASIL over MICRO-QUARTZ in the 1400F-2000F temperature range.

ASTROQUARTZ is not an acid-leached product, but is fiberized directly from pure quartz. Consequently, one would anticipate only a very small amount of chemically combined and adsorbed moisture in the product. The relatively high weight loss of ASTROQUARTZ was attributed therefore entirely to its organic binder content. Typically, loss in weight due to binder occurs in the 200C to 500C temperature range. This is in contrast to adsorbed moisture which is generally driven off between 0C and 200C and chemically combined moisture which is driven off at 600C and above.

DYNAQUARTZ, being a heat-stabilized MICRO-QUARTZ fiber, contains essentially no chemically combined water and hence adsorbs very little moisture. This was borne out by the fact that DYNAQUARTZ had less than a 0.1 per cent weight loss up to 1000C.

TABLE 5.
THERMOGRAVIMETRIC ANALYSIS OF CANDIDATE THERMAL INSULATIONS
8C Temperature Rise/Minute - Weight Loss, Per Cent

<u>Product</u>	<u>0C</u> <u>32F</u>	<u>100C</u> <u>212F</u>	<u>200C</u> <u>392F</u>	<u>300C</u> <u>572F</u>	<u>400C</u> <u>752F</u>	<u>500C</u> <u>932F</u>	<u>600C</u> <u>1112F</u>	<u>700C</u> <u>1292F</u>	<u>800C</u> <u>1472F</u>	<u>900C</u> <u>1652F</u>	<u>1000C</u> <u>1832F</u>
MICRO-QUARTZ	0	3.0	5.6	6.0	6.3	6.7	7.1	7.4	7.6	7.7	7.6
Irish REFRASIL	0	0	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
ASTROQUARTZ	0	0	0	1.2	1.6	2.2	2.3	2.3	2.2	2.2	2.1
DYNAQUARTZ	Less than 0.1% loss to 1000C										
THERMOFLEX (Air)	0	0	0	0.1	0.8	2.4	2.7	2.7	2.6	2.5	2.4
THERMOFLEX (N ₂)	0	0	0	0.2	0.5	0.9	1.2	1.3	1.4	1.4	1.3
MIN-K 1301 (Air)	0	1.5	2.9	3.0	4.1	5.4	6.4	6.8	6.9	6.7	6.4
MIN-K 1301 (N ₂)	0	1.5	2.9	2.9	3.2	4.1	5.1	5.6	6.1	6.4	6.5
MIN-K 2000 (Air)	0	0.9	1.2	1.4	2.5	4.5	6.3	6.4	6.4	6.4	6.4
MICROTHERM 20 Cr (Air)	0	1.3	1.4	1.5	1.6	1.6	1.6	1.6	1.7	1.8	1.8

The weight loss of THERMOFLEX in air was attributed primarily to the organic binder content of the product. Above 700C, a weight gain was noted. This was probably due to the addition of oxygen to some of the silica-alumina bonds which had been left unsatisfied during fiberization. The loss of weight in nitrogen proceeded at a slower rate and to a lesser extent than in air. The difficulty of driving off high polymer compounds in a non-oxidizing medium was the apparent cause of this phenomenon.

Both MIN-K 1301 tests showed a greater weight loss in the 0C to 200C temperature range than the MIN-K 2000 test. This was indicative of the greater affinity of SANTOCEL A for adsorbed moisture than CAB-0-SIL M5. Both MIN-K 1301 tests also showed a weight loss due to the organic binder. As in the case of the THERMOFLEX tests, however, the MIN-K 1301 weight loss in nitrogen proceeded at a somewhat slower rate. Given sufficient time and/or temperature, MIN-K 1301 in air would continue to gain weight as a result of the oxidation of the opacifier. MIN-K 2000 does not have the oxidation tendencies of MIN-K 1301, and hence displays the characteristic steps of adsorbed moisture loss between 0C and 200C and binder loss between 300C and 600C.

MICROTHERM 20 Cr, which was reportedly free of organic binders, showed primarily an adsorbed moisture loss with a little chemically combined moisture loss above 700C. The relatively high adsorbed moisture content of the MICROTHERM 20 Cr compared with Irish REFRASIL (both of which contained only small amounts of chemically combined water) was probably indicative of the high surface area of MICROTHERM 20 Cr.

D. MICROTHERM 20 Cr

Because of the similarity between MICROTHERM 20 Cr and MIN-K, this product was subjected to closer scrutiny than the other candidate materials. MICROTHERM 20 Cr is one of several products developed by Boucher & Company, Kidderminster, England, to compete with MIN-K for application in RTG units developed by the U.K. Companion products, samples of which have neither been seen nor evaluated, are MICROTHERM 18 Si and MICROTHERM 15 C. After examination of MICROTHERM 20 Cr, it appeared that the number in the product name represented the density in pounds per cubic foot, while the letters were the chemical symbols for the opacifier.

MICROSCOPIC ANALYSIS

Petrographic examination of the 6-in. diameter by 1-in. thick specimens showed the following.

Bulky Silica	- Major
Chromic Oxide	- Minor
Amosite Fiber	- Approximately 5%
Glassy Fiber and Shot	- Approximately 5%

(Shot = unfiberized glassy material)

The amosite fiber showed a brown coloration, and an elevated refractive index typical of amosite which had been heated to 760C.

The ultimate particle size of the silica was approximately 0.03 microns as shown by the electron micrograph in Figure 3.

The chromic oxide had an average particle size of 1 micron with an approximate minimum of <0.3 microns and an approximate maximum of 6 microns. This oxide shows as black specks in Figures 4 and 5.

The amosite fiber ranged in diameter from <0.3 microns to 37 microns with an average of 2 microns. The length was from <10 microns to 1430 microns with an average of 200 microns. Figure 4 shows a typical example of an amosite fiber.

The glassy fibers ranged in diameter from 5.6 to 31 microns with an average of about 14 microns. A glassy fiber may be seen in Figure 5.

X-RAY DIFFRACTION

The X-ray diffractometer diagrams and the Debye-Scherrer films indicated a strong pattern of Cr_2O_3 . Additionally, the X-ray diagram of the dark brown fiber indicated it to be oxyamosite, or amosite which had been decomposed at temperatures between 500C and 800C.

SPECTROGRAPHIC ANALYSIS

The results of the spectrographic analysis are given in Table 6.

A spectrographic analysis of the glassy fiber and shot extracted from the MICROTHERM gave the qualitative analysis shown in Table 7.

FIGURE 3.

ELECTRON MICROGRAPH OF THE SILICA PARTICLES
IN MICROTHERM 20 Cr (36,000X MAGNIFICATION)

FIGURE 4.

MICROTHERM 20 Cr AT 500X MAGNIFICATION SHOWING CHROMIC OXIDE
(BLACK SPECKS) AND AMOSITE FIBER

FIGURE 5.

MICROTHERM 20 Cr AT 500X MAGNIFICATION SHOWING CHROMIC OXIDE
(BLACK SPECKS) AND GLASSY FIBER

TABLE 6.
SPECTROGRAPHIC ANALYSIS OF MICROTHERM 20 Cr*

SiO_2 (by difference)	62 $\pm$ 2 per cent
Cr_2O_3	32 $\pm$ 2
Al_2O_3	3.7
Fe_2O_3	1.8
TiO_2	0.26
MgO	0.24
Na_2O	0.1
Total ignition loss at 1800F -	1.9 per cent

*All elements expressed as oxides on the ignited basis.

TABLE 7.
SPECTROGRAPHIC ANALYSIS OF THE GLASSY FIBER
AND SHOT IN MICROTHERM 20 Cr

Al and Si	Major
Zr	Small
Ti	Trace
Fe	Not Detected
Na	Not Detected
B	Not Detected

MODULUS OF RUPTURE

The flexural strength of MICROTHERM 20 Cr was evaluated in accordance with the test procedure described in Report No. ALO-3633-3 (January 3, 1967). This evaluation was done on both the "as received" material, and on material which had been exposed to 1400F for 2 hr. Table 8 summarizes the results.

TABLE 8.

MODULUS OF RUPTURE OF MICROTHERM 20 Cr

<u>Thermal History</u>	<u>Number of Specimens</u>	<u>Average MR, psi</u>
None	4	16.5
1400F, 2 hr	4	20.7

Although the number of test specimens was limited, the effect of the firing cycle appeared evident. However, the low strengths verified pretest impressions that the material was relatively fragile, and could create handling problems during generator assembly.

STRESS-STRAIN

Eight specimens, 4 x 4 x 1 in., were evaluated for stress-strain characteristics. Four were tested "as received" and four after 2 hr at 1400F. The tests were conducted on a Riehle Hydraulic Model KA-60 at a loading rate of 60 psi per min, at room temperature and with a 0.001 in. deflection dial gauge. The load was applied over the entire area with no lateral restraint provided the specimens during test. A static preload of 0.34 psi was applied to each specimen.

Figure 6 is a plot of the average stress-strain data obtained at 0.005 in./in. strain increments. In each group of four specimens, there was very little variation from the average, indicating good uniformity within a given 12 x 12 x 1-in. block. The curves appeared to consist of three straight-line segments. The first encompassed the 0 to 0.02 in./in. strain range, while the third went from 0.12 to 0.15 in./in. The first range was probably a result of thickness regain after molding, while the third may signify an internal fracture. The middle portion of the curve was used to calculate the modulus of elasticity values of 1000 psi and 1140 psi for unfired and fired specimens, respectively.

FIGURE 6 .

STRESS-STRAIN RELATIONSHIP OF MICROTHERM 20 Cr

Loading Rate of 60 psi/min
Tested at Room Temperature

THERMAL CONDUCTIVITY

The thermal conductivity of MICROTHERM 20 Cr was evaluated in air using the Guarded Hot Plate apparatus (ASTM C-177). The results are given in Table 9.

(The third decimal place is used to plot the thermal conductivity versus mean temperature curve, but is generally not considered significant for normal quoting purposes.)

It will be noted that the published values describe essentially a straight line, whereas the test values describe a curvilinear function.

GENERAL COMMENTS

MICROTHERM 20 Cr is definitely similar to MIN-K and consists of very finely-divided silica opacified with about 32 per cent chromic oxide and reinforced with both amosite and alumina-silica fibers. It cannot be established definitely whether the amosite was fired prior to mixing with the other ingredients, or whether the MICROTHERM was fired after molding; the TGA curve would lead one to suspect the former due to the loss in weight above 120C.

The handleability appeared to be poor although no real test of its handleability was undertaken due to the relatively small amount of material available. Corners were easily chipped and broken even with careful handling. The low degree of integrity and handling strength may be due to any one or a combination of the following.

1. High opacifier content and hence lower silica.
2. Low fiber reinforcing efficiency per unit weight due to large fiber diameters.
3. A different silica material.

MICROTHERM 20 Cr had a strong dusting tendency as noted by an inability to "clean" a cut edge of excess dust using a small fine hard brush.

Boucher appeared to have excellent control over the molded thickness and the thickness regain (after molding). The nominal 1-in. thick blocks ranged from 0.988 to 1.011 in. thick. The average density of the MICRO-THERM 20 Cr blocks, however, was slightly below 19 pcf.

TABLE 9.
THERMAL CONDUCTIVITY OF MICROTHERM 20 Cr IN AIR

<u>Mean Temperature, °F</u>	<u>Conductivity, Btu in./hr ft² °F</u>	
	<u>Actual</u>	<u>Published</u>
400	0.22(5)	0.20
500	0.23(0)	0.22
600	0.23(7)	0.23(5)
700	0.24(4)	0.25
800	0.25(1)	0.26(3)
900	0.26(3)	0.28
1000	0.27(7)	0.28
1100	0.29(5)	0.29(3)

Fiber distribution within the blocks also appeared excellent with only a few scattered minute clumps visible to the eye. There were, however, very small pockets of silica indicating incomplete mixing of the silica with the opacifier. Neither of these small inconsistencies in distribution should affect the thermal efficiency of the product.

A cloth or fine mesh screen pattern was evident on both faces of the blocks indicating that molding was not done directly against machined die surfaces as is the case with MIN-K.

E. CHEMICAL COMPATIBILITY OF FIBROUS INSULATIONS AND SILICON-GERMANIUM ELEMENTS

Four fibrous insulations, ASTROQUARTZ, DYNAQUARTZ, Irish REFRASIL, and MICRO-QUARTZ, were chosen as primary fibrous candidates for use adjacent to silicon-germanium thermoelectric elements, and a test procedure was devised to establish the extent of gross chemical incompatibility between N and P elements and these insulations.

The test involved packing the fibers into the 2-in. diameter by 6-in. high crucibles (as previously described under Section IV-B), and boring undersized holes into the fibrous mass to accept the 0.444-in. diameter by 0.271-in. long elements. In the case of the DYNAQUARTZ, a 3 x 6 x 1-in. block was drilled to accept the elements. A packing density of 10 pcf was attained for all fibrous candidates to be evaluated in air, whereas the density of the Irish REFRASIL and MICRO-QUARTZ was reduced to 6 pcf for the vacuum tests due to the ejection tendency of the fibers from the crucibles during pumpdown. One N and one P element were embedded into each candidate insulation for each of three exposure levels (500 hr, 1000 hr, and 1500 hr), whereas three N and three P elements were embedded for the 2000-hr level. No element was assigned more than one exposure level.

Approximately one-third of the silicon-germanium elements received from RCA, Harrison, New Jersey, were analyzed spectrographically prior to test to establish a sampling technique, and an average base impurity level. In all cases, no impurities were found in the elements. The sampling procedure consisted of mounting the cylindrical element in a lathe with a live center attachment, thus permitting full access to the cylindrical surface. The lathe was rotated at a speed of 365 rpm, and a 4 mm wide tungsten carbide cutting tool was used to remove the surface. The full width of the cutting tool was held in contact with the element surface. No transverse movement of the tool was permitted while it was in contact with the element. A 5 mg sample was collected for each analysis using all possible precautions to prevent external contamination. It has been estimated (using a 0.001-in. micrometer) that the diameter was reduced only by

approximately 0.0005 in. as a result of the sampling. Thus, it can be seen that the results are qualitative in nature, and apply only to the extreme surface of the element.

The element-insulation specimens which underwent air exposure were inserted into a glo-bar furnace operating at 1600F $\pm$ 20F (isothermal), and subsequently were air quenched at each time level. Thus, the 2000 hr specimens underwent four rapid heatups and cooldowns. The element-insulation specimens which were exposed to 1600F $\pm$ 20F (isothermal) in vacuum were heated to the test temperature in about 6 hr, and cooled in about 18 hr. Active vacuum was maintained (<2 microns) continuously throughout the entire test from room temperature to room temperature. These 2000-hr specimens also underwent four heating and cooling cycles.

The spectrographic analysis results of the chemical compatibility tests in air and vacuum are shown in Tables 10 and 11, respectively. It will be noted that the Irish REFRASIL and MICRO-QUARTZ specimens under vacuum exceeded 2000F for approximately 144 hr after 1800 hr at 1600F. This was caused by a malfunction of the electrical breaker contacts resulting in an uncontrollable temperature situation. The elements appeared to have reacted with the insulation as witnessed by the excessively "loose fit" of the elements in the insulation. (The three N and three P 2000-hr elements were initially stacked vertically within the same hole with a 1/4-in. clearance between them.) The hole into which the elements had been placed was over 1/2-in. in diameter after exposure except for the top 1/2 - 1 in. This top area with which the elements had not been in contact showed little or no change in size. Similarly, the holes from which previous elements had been removed appeared unchanged. Figure 7 shows successive layers of Irish REFRASIL (from top of picture, clockwise) beginning with the top layer and progressing downward to the area of element contact. Since the elements were in a vertical alignment, they dropped to the bottom of the cavity and fused together from the heat when the insulation no longer offered necessary support.

The MICRO-QUARTZ changed from white to gray immediately surrounding the hole, whereas the Irish REFRASIL changed from green to gray. Insulation not adjacent to the elements did not change color.

The elements were separated and analyzed in the same manner as the previous test elements. The major difference in the analyses occurred as a result of chromium from the Irish REFRASIL migrating to the surface of the elements. Slight amounts of other impurities not found previously were also detected. It is reasonable to assume, however, that the number and amount of impurities would have approximated those found at the earlier test levels had the test progressed to the 2000-hr level at 1600F.

TABLE 10.
CHEMICAL COMPATIBILITY BETWEEN SiGe ELEMENTS
AND SELECTED INSULATIONS AT 1600F IN AIR

Fibrous Product	Impurity in SiGe Elements									
	Chromium		Copper		Iron		Molybdenum		Nickel	
	N	P	N	P	N	P	N	P	N	P
Irish REFRASIL										
500 hr	v.s.	v.s.	†.	†.	†.	†.	ND	ND	ND	ND
1000 hr	†.	†.	†.	†.	†.	†.	ND	ND	ND	ND
1500 hr	†.	†.	†.	†.	†.	†.	ND	ND	ND	ND
2000 hr	†.	†.	†.	ND	†.	ND	ND	ND	ND	ND
	†.	†.	v.s.	†.	s.	s.	ND	ND	ND	ND
	†.	†.	v.s.	ND	†.	ND	ND	ND	ND	ND
MICRO-QUARTZ										
500 hr	ND	ND	†.	†.	ND	ND	ND	ND	ND	ND
1000 hr	ND	ND	†.	†.	ND	ND	ND	†.	ND	ND
1500 hr	ND	ND	†.	†.	v.s.	ND	ND	ND	†.	ND
2000 hr	ND	ND	v.s.	s.	ND	ND	ND	ND	ND	ND
	ND	ND	v.s.	†.	ND	ND	ND	ND	ND	ND
	ND	ND	v.s.	v.s.	ND	ND	ND	ND	ND	ND
ASTROQUARTZ										
500 hr	ND	ND	†.	s.	ND	ND	ND	ND	ND	ND
1000 hr	ND	ND	†.	v.s.	†.	†.	ND	ND	ND	ND
1500 hr	ND	ND	†.	v.s.	†.	ND	ND	ND	ND	†.
2000 hr	ND	ND	v.s.	s.	ND	ND	ND	ND	ND	ND
	ND	ND	v.s.	s.	†.	ND	ND	ND	ND	ND
	ND	ND	v.s.	s.	ND	ND	ND	ND	ND	ND
DYNAQUARTZ										
500 hr	ND	ND	†.	s.	ND	ND	ND	ND	ND	ND
1000 hr	ND	ND	†.	v.s.	†.	ND	ND	ND	ND	ND
1500 hr	ND	ND	v.s.	†.	†.	†.	ND	ND	ND	ND
2000 hr	ND	ND	v.s.	v.s.	†.	ND	ND	ND	ND	ND
	ND	ND	v.s.	v.s.	ND	†.	ND	ND	ND	ND
	ND	ND	v.s.	v.s.	v.s.	†.	ND	†.	ND	ND

ND - <0.001%
†. - <0.01%
v.s. - <0.1%
s. - <1.0%

TABLE II.

CHEMICAL COMPATIBILITY BETWEEN SiGe ELEMENTS AND SELECTED INSULATIONS AT 1600F IN VACUUM

Insulation	Chromium		Copper		Iron		Manganese		Molybdenum		Nickel		Titanium	
	N	P	N	P	N	P	N	P	N	P	N	P	N	P
ASTROQUARTZ														
500 hr	ND*	ND	v.s.	t.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1000 hr	ND	ND	v.s.	t.	t.	t.	ND	ND	ND	t.	ND	ND	ND	ND
1500 hr	v.s.	t.	s.	v.s.	t.	ND	ND	ND	ND	ND	ND	ND	ND	ND
2000 hr	t.	t.	v.s.	t.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	t.	t.	v.s.	t.	ND	t.	ND	ND	ND	ND	ND	t.	ND	ND
	t.	t.	s.	t.	ND	t.	ND	ND	ND	t.	ND	t.	ND	ND
DYNAQUARTZ														
500 hr	ND	ND	v.s.	v.s.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1000 hr	ND	ND	v.s.	t.	t.	ND	ND	ND	ND	ND	ND	ND	ND	ND
1500 hr	ND	ND	s.	t.	t.	t.	ND	ND	ND	ND	ND	ND	ND	ND
2000 hr	ND	ND	v.s.	t.	t.	t.	ND	ND	ND	ND	ND	ND	ND	ND
	ND	ND	v.s.	t.	t.	t.	ND	ND	ND	ND	ND	ND	ND	ND
	ND	ND	s.	t.	t.	t.	ND	ND	ND	t.	ND	ND	ND	ND
Irish REFRASIL														
500 hr	v.s.	v.s.	t.	t.	t.	t.	ND	ND	ND	ND	ND	ND	ND	ND
1000 hr	s.	s.	s.	t.	t.	t.	ND	ND	ND	ND	ND	ND	ND	ND
1500 hr	s.	s.	s.	v.s.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2000 hr**	m.h.	m.h.	m.l.	m.l.	s.	s.	t.	t.	ND	s.	s.	s.	s.	s.
	m.h.	m.h.	m.l.	m.l.	s.	s.	t.	t.	ND	t.	s.	s.	s.	s.
	m.h.	m.h.	m.l.	m.l.	s.	s.	t.	t.	ND	t.	s.	s.	s.	s.
MICRO-QUARTZ														
500 hr	ND	ND	v.s.	t.	ND	t.	ND	ND	ND	ND	ND	ND	ND	ND
1000 hr	ND	ND	s.	t.	ND	ND	ND	ND	ND	t.	t.	t.	ND	ND
1500 hr	ND	ND	s.	t.	ND	ND	ND	ND	ND	ND	t.	t.	ND	ND
2000 hr**	t.	t.	s.	m.l.	s.	s.	t.	t.	ND	t.	t.	t.	ND	ND
	t.	t.	v.s.	m.l.	s.	s.	t.	t.	ND	t.	t.	t.	ND	ND
	t.	t.	s.	m.l.	s.	s.	t.	t.	ND	t.	t.	t.	ND	ND

*ND - not detected - $<0.001\%$
 t. - trace - $<0.01\%$
 v.s. - very small - $<0.1\%$
 s. - small - $<1.0\%$
 m.l. - minor low - 1-5%
 m.h. - minor high - 5-10%

**Test ran for 1800 hr at 1600F plus 144 hr at over 2000F

FIGURE 7.

EFFECT OF SILICON-GERMANIUM ELEMENTS ON
IRISH REFRASIL AFTER 144 HR ABOVE 2000F IN VACUUM

Attempts were made to determine the source of copper as a contaminant in the analyses, and if the fibrous insulations were picking up chemical elements from the SiGe specimens after the 2000-hr exposure level in air.

With as much care as possible, fiber samples were taken from that portion of the mass which was in contact with the 2000-hr N and P elements, as well as from a section which was not in contact with the elements. Copper from the boring tool used to cut the holes in the fiber mass was the prime suspect. Table 12 summarizes the qualitative results which indicate that the boring tool could be suspect. However, the small amounts found in the SiGe elements, together with the fact that copper is a common contaminant in spectrographic analyses indicated that no further investigation was warranted. The analyses of the fibers also indicated the presence of no unusual impurities which could be ascribed to the SiGe elements.

F. SEEBECK COEFFICIENT AND RESISTIVITY COMPATIBILITY BETWEEN SiGe ELEMENTS AND IRISH REFRASIL

As a further check of the compatibility between the fibrous insulations and SiGe elements, a test was devised to establish the effect of intimate contact between SiGe elements and Irish REFRASIL on the Seebeck coefficient and resistivity of the elements. Irish REFRASIL was chosen since it represented the only one of the four selected insulations which contained a primary constituent other than silica, or which had not already undergone extended exposure in silicon-germanium thermocouple modules (other AEC-sponsored programs).

The test procedure approximated that for the chemical compatibility tests. Silicon-germanium bars 0.2 x 0.2 x 1.75 in. were embedded into the Irish REFRASIL fibrous mass contained within the 2-in. diameter by 6-in. high alumina crucibles. Rather than drill holes, however, the fibers were packed around the rectangular bars which were placed vertically within the crucibles. The packing density of the fibers slated for air exposure was 10 pcf, while that for the vacuum exposure was 6 pcf (to prevent "explosion" from the crucible during evacuation). Two N and two P elements were placed in each crucible.

Since the N elements are subject to fluctuations in Seebeck coefficient and resistivity depending upon the rate at which they are cooled, duplicate elements were also embedded into DYNAQUARTZ to act as "standards." These duplicates were paired at manufacture to insure, as nearly as possible, identical performance under identical exposure conditions. As in the case of the chemical compatibility tests, specimens given isothermal exposure at 1600F $\pm$ 20F in air were air quenched, whereas those specimens given isothermal exposure at 1600F $\pm$ 20F in vacuum ($\leq$ 2 microns) were cooled to room temperature under vacuum over an 18-hr period. (The one exception

TABLE 12.

COPPER CONTENT OF THE FIBROUS INSULATIONS IN
CONTACT WITH SIGe ELEMENTS AFTER 2000 HR AT 1600F IN AIR

	Qualitative Copper Content		
	<u>Adjacent to N</u>	<u>Adjacent to P</u>	<u>No Element Contact</u>
Irish REFRASIL	†.	†.	ND
MICRO-QUARTZ	†.	†.	†.
ASTROQUARTZ	†.	†.	ND
DYNAQUARTZ	ND	†.	ND

ND - not detected - $<0.001\%$

†. - trace - $<0.01\%$

to this routine was at the 1000-hr level in air where the furnace was turned off and allowed to cool slowly.) None of the elements were given a "burn-in" treatment prior to this test series.

All bars were tested for room temperature Seebeck coefficient and resistivity prior to exposure, after 1000 hr of exposure, and again after 2000 hr of exposure. Full identity of each bar was maintained throughout the test, and each was returned to its identical position following the 1000-hr Seebeck coefficient and resistivity tests.

Seebeck coefficient determinations were made by RCA, Harrison, New Jersey, using the Thermoelectric Power Probe, Model 112B, Cambridge Systems, Inc. and a DC Vacuum Tube Voltmeter, Model 412AR, Hewlett-Packard. Electrical resistivities were calculated from resistance values measured with a Vacuum Tube Voltmeter, Model 400DR, Hewlett-Packard in combination with current drawn from the line by means of a variac. The estimated precision and accuracy of the measurements was about ± 3 per cent for the Seebeck coefficient determinations and ± 2 per cent for electrical resistivity values.

Tables 13 and 14 show the Seebeck coefficient and resistivity data resulting from the isothermal exposure to $1600^{\circ}\text{F} \pm 20^{\circ}\text{F}$ in air and vacuum, respectively. It was found that the thermoelectric properties of the two silicon-germanium alloy samples in each pair were always within experimental uncertainty of each other, thus leading to the conclusion that the Irish REFRASIL was just as inert in combination with silicon-germanium alloys as DYNAQUARTZ. From previous experience, it is known that DYNAQUARTZ has no effect on the performance characteristics of silicon-germanium alloys.

Although both members of each pair of silicon-germanium bars behaved identically, it was noticed that in the case of the N-type alloys, the thermoelectric properties underwent slight modification. This consisted of increased or decreased values of both the electrical resistivity and the Seebeck coefficient. The P-type alloys did not exhibit such behavior, with the thermoelectric properties remaining at fixed values for the duration of all testing. The explanation of the observed effect in the N-type alloys is well known and has been extensively documented (i.e., "Silicon-Germanium Thermocouple Development" by V. Raag, Proceedings of the 17th Annual Power Sources Conference, May 1963, p 34, and also Final Report, Contract No. NAS 5-3410, December 1963.) Very briefly, the effect is due to the fact that N-type silicon-germanium alloys are doped to the solid solubility limit of the dopant, phosphorus. Because the solid solubility of phosphorus in silicon-germanium alloys is temperature dependent, generally increasing with increasing temperature, the amount of dopant in solid solution depends on the temperature at which

TABLE 13.

SEEBECK COEFFICIENT AND RESISTIVITY COMPATIBILITY
BETWEEN SiGe BARS AND IRISH REFRASIL IN AIR AT 1600F

Element Type	Exposure Time hr	IRISH REFRASIL				DYNAQUARTZ			
		Code No.	Manufacturer's I.D.	Seebeck Coefficient Microvolts/°C	Resistivity Milliohm Cent.	Code No.	Manufacturer's I.D.	Seebeck Coefficient Microvolts/°C	Resistivity Milliohm Cent.
N	0	N-1A	E483RN-1A	168	1.62	N-1B	E483RN-1B	171	1.69
	1000			126	1.07			120	0.97
	2000			168	1.61			171	1.59
	0	N-2A	E483RN-2A	169	1.71	N-2B	E483RN-2B	171	1.64
	1000			130	1.13			126	1.01
	2000			172	1.62			174	1.66
P	0	P-1A	E446RP-1A	95	0.87	P-1B	E446RP-1B	98	0.91
	1000			92	0.87			98	0.89
	2000			103	0.87			107	0.87
	0	P-2A	E446RP-2A	98	0.88	P-2B	E446RP-2B	97	0.92
	1000			100	0.87			100	0.87
	2000			105	0.86			106	0.88

TABLE 14.

SEEBECK COEFFICIENT AND RESISTIVITY COMPATIBILITY
BETWEEN SiGe BARS AND IRISH REFRASIL IN VACUUM AT 1600F

Element Type	Exposure Time hr	IRISH REFRASIL				DYNAQUARTZ			
		Code No.	Manufacturer's I.D.	Seebeck Coefficient Microvolts/°C	Resistivity Milliohm Cent.	Code No.	Manufacturer's I.D.	Seebeck Coefficient Microvolts/°C	Resistivity Milliohm Cent.
N	0	N-3A	E483RN-3A	167	1.69	N-3B	E483RN-3B	169	1.71
	1000			152	1.45			158	1.48
	2000			156	1.47			161	1.50
	0	N-4A	E483RN-4A	169	1.60	N-4B	E483RN-4B	169	1.62
	1000			156	1.51			159	1.49
	2000			155	1.51			161	1.49
P	0	P-3A	E446RP-3A	98	0.90	P-3B	E446RP-3B	97	0.91
	1000			102	0.88			103	0.87
	2000			107	0.90			104	0.91
	0	P-4A	E446RP-4A	98	0.93	P-4B	E446RP-4B	98	0.94
	1000			104	0.87			103	0.86
	2000			108	0.88			106	0.88

the elements are annealed. Upon cooling to room temperature for purposes of measurement, the N-type alloys are subjected to conditions of lower solid solubility of phosphorus. The elements attempt to adjust themselves to this new solubility condition by precipitating the excess dopant in solution. The extent to which they are able to do this depends on the rate of sample cooling since at very low temperatures, the precipitation process proceeds very slowly, while at relatively high temperatures, precipitation occurs at an appreciable rate. If such high temperatures are traversed rapidly during cooling, very little precipitation takes place. If they are traversed slowly, there is more time for precipitation to proceed. Thus, the amount of dopant in solid solution in the N-type silicon-germanium alloys at room temperature depends on the previous thermal history of the alloys. Because the Seebeck coefficient and electrical sensitivity directly depend on the amount of dopant in solid solution (each dopant atom contributes one carrier to the conduction process), these properties also depend on the previous thermal history of the alloys. Observed changes in the thermoelectric properties of the N-type silicon-germanium elements are therefore completely predictable in terms of the amounts of dopant in solid solution.

The agreement between predicted and measured values of the test elements indicated that the silicon-germanium alloy had not basically changed, even though the properties may have been modified as a result of changed solid solubility conditions of dopant. If, however, there had been disagreement between the measured and predicted property values, the indication would have been that the alloys had basically changed, and the probable reason for such change would have been an interaction with the insulation surrounding the test samples. All of the data were subjected to this consideration, and it was found that in all instances the observed changes in the thermoelectric properties of the N-type silicon-germanium alloys were completely predictable, thus further enhancing the conclusion that Irish REFRASIL had no adverse effect on the properties of silicon-germanium alloys within the limits of the test method.

G. THERMAL CONDUCTIVITY OF SELECTED FIBROUS INSULATIONS

The thermal conductivity in air of 10 pcf (nominal) ASTROQUARTZ, DYNAQUARTZ, Irish REFRASIL, and MICRO-QUARTZ is presented in Figure 8. These tests were conducted in the ASTM C-177-63 Refractory Guarded Hot Plate apparatus with an approximate 200F ΔT , and 1-in. thick specimens. Since all of these products except DYNAQUARTZ are typically low density products (less than 4 pcf), the felts were cut, stacked, and compressed to achieve the desired density. The resiliency of the ASTROQUARTZ was such that over 100 lb of weight atop the test apparatus was necessary to maintain the required density during test. (Although the ASTM procedure does not cover this situation, the weights were sufficiently isolated from the test apparatus, so as not to effect the results.)

FIGURE 8.

THERMAL CONDUCTIVITY IN AIR OF SELECTED FIBROUS INSULATIONS

10 pcf Nominal Density

The three flexible felts, ASTROQUARTZ, Irish REFRASIL, and MICRO-QUARTZ displayed the typical relationship of varying fiber diameters. For example, ASTROQUARTZ had an average fiber diameter of 4.5 microns, Irish REFRASIL was 2.6 microns, and MICRO-QUARTZ was 1.2 microns. At the lower mean temperatures where radiation is a less important mode of heat transfer, they all had essentially the same thermal conductivity. As the mean temperature increased, and radiation became more and more predominant, the number of interruptions or "roadblocks" in the path of the radiation became increasingly important. Thus, the finer the fiber diameter, the more fibers per unit volume, and hence, the more interruptions. Although one would not consider silica to be an efficient opacifier, it can be seen that its presence does provide some degree of radiation scattering.

Irish REFRASIL was different from the other two fibrous insulations in that it had been given a chrome treatment. Although chrome (or Cr_2O_3) is considered to be a reasonably efficient opacifier, the simple comparison between products given above is not sufficient to speculate into the extent of improvement in thermal conductivity afforded by the chrome.

DYNAQUARTZ is made from 1.2 micron diameter MICRO-QUARTZ fiber. However, the high temperature firing treatment to which the DYNAQUARTZ is subjected as a part of its manufacture results in a considerable amount of fiber-to-fiber fusion, and hence, in a rigid product. The fused fibers probably were the cause for the higher thermal conductivity at the lower temperatures. However, since it is essentially a straight line regression, a distinct fibrous structure must still be present, and acting as radiation blockers.

H. SPECTROGRAPHIC ANALYSES OF SELECTED FIBROUS INSULATIONS

The four selected fibrous insulations were analyzed for impurities (and Cr_2O_3 content in the case of the Irish REFRASIL). The results are shown in Table 15 in terms of the cation, although most probably they occur as an oxide.

As previously discussed in Section IV-C, ASTROQUARTZ is fiberized from pure quartz, and hence, contains only trace amounts of impurities. Irish REFRASIL and MICRO-QUARTZ are acid-leached fibers, and hence, are prone to contain additional amounts of impurities which could not be economically removed by this process. DYNAQUARTZ is made from MICRO-QUARTZ fiber, and hence, contains similar quantities of impurities.

TABLE 15.
SPECTROGRAPHIC ANALYSIS OF ASTROQUARTZ, DYNAQUARTZ,
IRISH REFRASIL AND MICRO-QUARTZ

<u>Impurity</u>	<u>ASTROQUARTZ</u>	<u>DYNAQUARTZ AND MICRO-QUARTZ</u>	<u>IRISH REFRASIL</u>
Aluminum	<0.01%	0.042%	0.22
Boron	<0.01	<0.01	0.093
Calcium	<0.01	0.27	0.28
Copper	---	---	0.001
Iron	<0.01	0.011	0.077
Magnesium	<0.01	0.22	0.17
Nickel	---	---	0.0086
Sodium*	<0.05	<0.05	0.18
Titanium	<0.01	<0.01	0.30
Zirconium	<0.01	<0.01	0.037
Chromium	---	---	8.2
Silicon	balance	balance	balance

*0.05 per cent represents the minimum level to which a definite percentage can be assigned. Quantities below 0.05 can, however, be detected.

I. CONCLUSIONS - EVALUATION OF THERMAL INSULATION CANDIDATES

1. ASTROQUARTZ, DYNAQUARTZ, Irish REFRASIL, and MICRO-QUARTZ were considered prime candidates for use in SiGe generators because of one or more of the following: temperature stability, cleanliness (absence of unfiberized material), purity, thermal efficiency, and previous generator application.
2. ASTROQUARTZ, DYNAQUARTZ, and Irish REFRASIL showed no shrinkage under isothermal conditions of 1600F for 2000 hr, and 1800F for 24 hr at the test densities. MICRO-QUARTZ showed 5 per cent shrinkage, although experience in SiGe modules under ΔT conditions indicated no shrinkage problems.
3. MICRO-QUARTZ had the greatest weight loss of the prime fibrous candidates as determined by TGA. This loss was adsorbed and chemically combined water only. The weight loss of ASTROQUARTZ was attributed to an organic binder, while Irish REFRASIL and DYNAQUARTZ showed little or no loss in weight.
4. ASTROQUARTZ, DYNAQUARTZ, Irish REFRASIL, and MICRO-QUARTZ were found to be chemically compatible with N and P SiGe elements after 2000 hr at 1600F (isothermal) in both air and vacuum environments.
5. Irish REFRASIL was considered compatible with N and P SiGe bars after 2000 hr at 1600F (isothermal) in air and vacuum based upon room temperature Seebeck coefficient and resistivity measurements before and after exposure.
6. Of the three flexible insulations, MICRO-QUARTZ ranked first, Irish REFRASIL second, and ASTROQUARTZ third based on thermal efficiency at all mean temperatures above 500F. DYNAQUARTZ was the least efficient at the low mean temperatures, but was second to MICRO-QUARTZ above 1000F mean temperature.
7. Physical testing for up to 2000 hr indicates that ASTROQUARTZ, DYNAQUARTZ, Irish REFRASIL, and MICRO-QUARTZ should be satisfactory for service in SiGe generators.
8. MICROTHERM 20 Cr is similar to the MIN-K products with respect to thermal efficiency. It utilizes 32 per cent Cr_2O_3 as the opacifier and contains no binder. Other physical properties (strength, handleability, etc.) were poor and considered inadequate for current module

and generator assembly techniques. Thickness shrinkages of 14 per cent at 1600F (isothermal) indicated its application would be limited to PbTe service.

9. Further consideration of MICROTHERM 20 Cr for thermoelectric generator service is not recommended.

V. EVALUATION OF LOAD-BEARING CANDIDATES

A. GENERAL

The load-bearing candidates discussed in this section are listed in Table 2, Section III. One product which showed considerable potential was subjected to tests beyond those originally planned. Other materials (not listed in Table 2) were rejected at the outset because of very high densities, and/or high thermal conductivities. The purpose of this portion of the program was to establish which of the known products best combined the attributes of resistance to permanent set (creep, or load-relaxation) and thermal insulation effectiveness at a maximum hot face service temperature of 1800F. A load of 200 psi was considered to be the maximum typical load.

Figures 9 and 10 show photographically and schematically the compression-relaxation units used to conduct all hot face load-relaxation evaluations. It will be noted that the thermocouple directly below the resistance-wound heater plate was connected to the indicator-controller. A second couple, placed in a small groove cut into the test specimen, indicated the hot face temperature of the specimen. Adjustments in the hot face temperature of the specimen were accomplished by adjusting the controller, and hence, the temperature at the heater plate. This technique reduced the hot face temperature fluctuation to approximately ± 5 F. A similar thermocouple-groove arrangement is used to measure the cold face temperature.

Each specimen was measured to 0.001 in., and installed into the unit with hot and cold face thermocouples. The heater plate was turned on, the hot face temperature stabilized at the desired level, and the load applied. Constant vigilance was maintained, particularly during the first 8 hr of test to insure that pressure remained constant.

Pressure was held constant for 168 hr (1 week) after which it was released, the heater plate cooled to about 500F (overnight), and the sample removed and re-measured. Although this test did not represent service conditions (if the specimen yielded, it would not be under the same stress), it represented a simple and somewhat more severe test, thus permitting better differentiation between materials. The sole measure of a material's performance was the change in thickness.

The specimens were, for the most part, approximately 1 in. thick, and 4 x 4 in. square. However, multiple layers of GH Board and T30LR were required to attain the desired test thickness. The T30LR product required sanding to remove surface irregularities prior to test.

FIGURE 9.
COMPRESSION-RELAXATION TEST UNITS

FIGURE 10.

TYPICAL COMPRESSION-RELAXATION APPARATUS

Several tests did not attain 1800F hot face, probably due to the high heat loss through the sample, plus the power input limitations to the heater plates.

B. LOAD-BEARING RESULTS

Table 16 summarizes the results of the load-bearing material evaluations. Due to a ± 0.002 -in. measurement accuracy, it can be stated that essentially no permanent set occurred with either the GLASROCK 25 or GLASROCK 50 products. Since it was assumed that permanent set would be an indication of load-relaxation in a generator configuration, it follows that the load-relaxation would be minimal, if not zero, with the Glasrock products.

C. OTHER GLASROCK 25 EVALUATIONS

SHEAR STRENGTH

GLASROCK 25 was subjected to shear evaluations normal to its thickness direction. The test utilized 1 x 2 x 3/4-in. specimens which were placed on their 2 x 3/4-in. edge within a confining fixture. The fixture was so constructed as to prevent any movement of half of the projected area or 2 x 3/8-in., while the remaining half was subjected to a guillotine action over its 2 x 3/8-in. area. The loading rate was 50 lb/min or 37.5 psi/min.

Twelve specimens averaged 210 psi shear strength with a maximum of 225 psi and a minimum of 186 psi. All tests were conducted at room temperature.

MODULUS OF RUPTURE

Four specimens of GLASROCK 25 were tested for modulus of rupture (bend strength) at room temperature. The test specimens were 8 x 4-1/2 x 1 in. nominal size, and were tested across a 7-in. span. The range of values was from 150 psi to 195 psi with an average of 172 psi.

THERMAL CONDUCTIVITY

A 12 x 12 x 1-in. GLASROCK 25 specimen was tested for thermal conductivity in the Johns-Manville Rapid Heat Meter apparatus. This apparatus represents a rapid measuring technique as compared with the ASTM Guarded Hot Plate method. It is calibrated regularly with the Guarded Hot Plate, and

TABLE 16.
PERMANENT STRAIN OF LOAD-BEARING CANDIDATES AFTER 168 HR

<u>Material</u>	<u>Density pcf</u>	<u>Test Pressure psi</u>	<u>Hot Face °F</u>	<u>Permanent Strain in./in.</u>
GLASROCK 25	24	150	1790	0.001
	24	200	1800	0.002
	24	200	1680	0.001
	24	200	1650	0.002
	24	200	1680	none
GLASROCK 50	50	200	1690	0.002
	50	200	1680	-0.002*
	50	200	1650	0.001
	50	200	1670	0.001
JM-3000	67	50	1780	0.005
JM-23	34	50	1800	0.017
	34	300	1800	Crushed (24 hr)**
CERABOARD	45	100	1800	0.041
	45	200	1800	0.041 (96 hr)**
GH BOARD (3 pcs)	36	150	1800	0.321
	31	200	1790	0.277
GH BOARD (4 pcs)	31	200	1800	0.424 (120 hr)**
T30LR	55	200	1725	0.034
	53	200	1695	0.029
	54	200	1710	0.035
	54	200	1670	0.037

* Measured thicker after test than before test.

**Tests aborted due to heater failure.

has a proven maximum error of +8 per cent. It is also reproducible to below +3 per cent. The Heat Meter, therefore, is a valuable tool for rapid, accurate test values.

The thermal conductivity of GLASROCK 25 was 0.8 and 1.4 Btu in./hr ft² °F at 73F and 800F mean temperatures, respectively. As expected, this material was not comparable in insulation value to the other insulations evaluated under the overall program. However, considering the strength, weight, and conductivity factors together, the product was considered to have excellent merit.

D. CONCLUSIONS - LOAD-BEARING CANDIDATES

1. GLASROCK 25 has the best combination of load-bearing and thermal insulation capabilities of the load-bearing candidates investigated.
2. There is sufficient reason to believe that the thermal conductivity of GLASROCK 25 could be reduced through the addition of opacifiers. A development program to this effect has been proposed.

VI. MATERIAL AND PROCESS DEVELOPMENT

A. GENERAL

Standard MIN-K consists primarily of very finely divided silica particles combined with minor percentages of an opacifier, asbestos fibers, and binder. In this program to improve the characteristics of MIN-K, the first and most direct approach was to eliminate and/or replace those ingredients which were considered detrimental and expendable. The silica particles, although possessing small amounts of chemically bound water, represented the major source of MIN-K's efficiency by providing extremely fine pores (in the approximate size range of the mean free path of the gas molecule), and thus could not be eliminated. The opacifier (primarily silicon or titanium dioxide) contained little or no water or other volatiles, and hence, would not present an outgassing problem. Asbestos fiber could be replaced with a vitreous fiber which would not only minimize the outgassing (although some vitreous fibers also contain considerable amounts of combined water), but which also would reduce the potential poisoning of the generator elements due to impurities in the asbestos. Finally, previous experience had indicated that the combination of silica, opacifier, and fiber may have sufficient integrity after pressing without the use of a binder.

The investigation, therefore, included the following:

1. An evaluation of several silica materials considering purity, weight loss due to combined water, resistance to sintering (shrinking) with temperature, and integrity of the molded block without binder.
2. The replacement of asbestos fiber with various vitreous fibers.
3. The elimination of the binder.

In addition, the effect of opacifier particle size and content on the thermal conductivity as predicted by the theoretical analysis was also evaluated.

The development program centered around two main types of insulations: one serviceable to 1400F (PbTe systems), and one serviceable to 1800F (SiGe systems). Within each category, however, there existed the potential for two different insulations: one for bulk and possibly load-bearing service around the heat source, and one for intricate shaping around the thermoelectrics. In the case of the PbTe systems, the bulk insulation should be capable of 1400F service, while the intricate insulation required a temperature limit of only about 1200F. Similar potential requirements

existed for the SiGe systems with temperature limits of 1800F and 1600F, respectively. Obviously, it would be advantageous to develop the least number of insulations compatible with the general requirements.

The following sections describe the development phase by areas of investigation such as Raw Materials, Formulations, Process, etc., rather than chronologically by time.

B. RAW MATERIALS

SILICAS

Six silica materials were evaluated (some to a greater degree than others) for potential application. Table 17 gives the manufacturer's data for each.

SANTOCEL A, CAB-O-SIL M5, and ARC SILICA 800 were subsequently analyzed spectrographically to determine their impurity content. These results are shown in Table 18.

SANTOCEL A was eliminated from further consideration because of its impurities which not only tended to lower its temperature resistance, but also provided a source of contamination for generator components such as the elements, bonds, shoes, straps, etc. It also was somewhat inferior to CAB-O-SIL M5 with respect to integrity after molding without binder.

Similarly, ARC SILICA 800 had no integrity after molding (without binder) unless the density was increased to 24 pcf or higher. Owing to the sensitivity of the thermal conductivity of MIN-K products in general to densities above 20 pcf (rapid increase with increased density), ARC SILICA 800 was not considered further.

The AEROSIL products, which were evaluated primarily for 1800F service, had good molding characteristics and the resultant blocks had similar thermal conductivity values of approximately 0.24 Btu in./hr ft² °F at 1000F mean temperature. AEROSIL Uncompressed, however, had half the linear and thickness shrinkage of the other two after 24 hr of isothermal exposure to 1800F. Additional evaluations of AEROSIL Uncompressed were conducted in conjunction with the 1800F insulation program (see "H", this section).

TABLE 17.

MANUFACTURERS' TYPICAL PROPERTIES OF SILICA MATERIALS*

Property	SANTOCEL A (Monsanto)	CAB-O-SIL M5 (G. L. Cabot)	ARC SILICA 800 (Pittsburgh Plate Glass)	Uncompressed	AEROSIL 2491-380 (Degussa Inc.)	
					2491	2491
Particle Size, $m\mu$	25	15 - 20	15	10 - 40	3 - 15	5 - 20
Surface, m^2/g	---	175 - 200	185	175 - 225	340 - 420	270 - 330
Bulk Density, lb/ft^3	5	3	5	3	3	3
Ignition Loss, % (Excluding moisture)	3 - 4	0.2 - 1.0	1.0 - 3.8	---	---	---
SiO_2 , % (Moisture-free)	97 - 98	99.0 - 99.7	99.6	>99.8	>99.8	>99.8
Na_2SO_4 , %	2 - 3	---	---	---	---	---
HCl, %	---	---	---	< 0.025	< 0.025	< 0.025
Al_2O_3 , %	---	0.01	0.15	< 0.05	< 0.05	< 0.05
Fe_2O_3 , %	---	---	0.02	< 0.003	< 0.003	< 0.003
SiC, %	---	---	0.20	---	---	---
TiO_2 , %	---	---	0.002	< 0.03	< 0.03	< 0.03

*Blank spaces indicate not reported.

TABLE 18.
SPECTROGRAPHIC ANALYSIS OF SANTOCEL A,
CAB-0-SIL M5, AND ARC SILICA 800

	<u>SANTOCEL A</u>	<u>CAB-0-SIL M5</u>	<u>ARC SILICA 800</u>
Aluminum	0.048%	< 0.01%	0.025%
Boron	< 0.01	< 0.01	< 0.01
Calcium	< 0.01	< 0.01	< 0.01
Iron	0.014	< 0.01	< 0.01
Magnesium	< 0.01	< 0.01	< 0.01
Sodium*	0.31	< 0.05	< 0.05
Titanium	0.020	< 0.01	< 0.01
Zirconium	< 0.01	< 0.01	< 0.01

*0.05 per cent represents the minimum estimate possible by this analysis.

CAB-O-SIL M5 appeared to have the best combination of insulating ability, molded integrity, and purity, and was therefore chosen as the prime silica candidate for the experimental insulations. A thermogravimetric analysis of CAB-O-SIL M5 (see Figure 11) indicated that more than half of its weight loss was a result of adsorbed moisture (preconditioned at room temperature and 54 per cent relative humidity). Thus, a product made with CAB-O-SIL M5 might be expected to give off only 0.25 to 0.50 per cent moisture, if properly dried (not necessarily fired) prior to testing.

REINFORCING FIBERS

The candidate reinforcing fibers comprised those listed in Table 1 (Section III), together with ASTROQUARTZ staple fiber chopped to 1/4 and 1/2 in. lengths. Fibers such as THERMOFLEX, FIBERFRAX, and DYNAFLEX were eliminated immediately because of the presence of shot, or unfiberized particles mixed with or sometimes attached to the fibers. These particles could be a detriment to the thermal performance of the MIN-K, as well as a hinderance to machining operations. DYNAQUARTZ was considered briefly (see "H", this section), but was found to be unsatisfactory. Irish REFRASIL, because of its good thermal stability and low ignition loss, appeared to be an excellent candidate. However, fear of contamination of generator parts with chromium dictated that only the pure silica fibers such as ASTROQUARTZ and MICRO-QUARTZ be considered. Subsequently, however, the compatibility tests between silicon-germanium elements and Irish REFRASIL indicated that this fear was ungrounded.

The prime candidates for fiber reinforcement therefore were narrowed to ASTROQUARTZ and MICRO-QUARTZ. Exotic reinforcements such as whiskers were considered unnecessary for this application.

OPACIFIERS

Past experience, reinforced by a brief theoretical study under this contract indicated that silicon and titanium dioxide were probably the most efficient particulate opacifiers for MIN-K. Silicon, however, has two basic disadvantages:

1. It begins to oxidize in air above 1200F, making it transparent to radiation.
2. Its high solid conductivity limits the amount per unit volume of products that can be used without adversely affecting the thermal conductivity of the product.

FIGURE 11.

THERMOGRAVIMETRIC ANALYSIS OF CAB-O-SIL M5
Heating Rate: 8C per min

Titanium dioxide, however, has neither of these characteristics and hence, can be used in greater amounts to obtain improved thermal efficiency. For these reasons, and because the use of TiO_2 for all applications would reduce the potential number of different formulations for ultimate use in the RTG's, TiO_2 was given prime consideration.

The TiO_2 opacifier presently used in one of the standard MIN-K products is designated -325 mesh H.G. by its manufacturer, TAM Division of National Lead. This material was reported to have an average particle size of 4 microns. Additional refinement of this material by the manufacturer led to the -5 micron H.G. product, having a reported average particle size of 2 microns. In theory (see Section II), the 2-micron particle should be a more efficient opacifier. Similarly, greater quantities of opacifier should reduce the thermal conductivity.

Experimental blocks of MIN-K containing 16 per cent and 32 per cent of the -325 mesh H.G. and the -5 micron H.G. TiO_2 opacifiers, were evaluated for thermal conductivity on the Johns-Manville Rapid Heat Meter apparatus at 1000F mean temperature. The results, as shown in Table 19, essentially verified the predictions.

Each grade of TiO_2 was then subjected to a particle size determination by an air permeability technique (to yield an average particle size), and by a sedimentation technique to yield a breakdown according to size ranges. Table 20 summarizes the results.

Although the average particle sizes were essentially the same by this measurement technique, the -5 micron H.G. material had a greater concentration of particles in the 1 to 4 micron range. It could therefore be assumed that there also was a greater concentration within the 1.5 to 2.5 micron range considered optimum by the theoretical analysis. Thus, although the average of the -325 mesh H.G. TiO_2 was 1.7 microns, the large percentage of particles above and below the 1 to 4 micron range reduced its effectiveness as an opacifier.

A spectrographic analysis of the -5 micron H.G. TiO_2 is shown in Table 21.

Thus, -5 micron H.G. TiO_2 was chosen as the opacifier for the experimental formulations. Its per cent content by weight in the formulations was maintained at 16 per cent. This represented a tradeoff between thermal efficiency and mechanical properties.

TABLE 19.

EFFECT OF TiO_2 PARTICLE SIZE AND CONTENT ON THE
THERMAL CONDUCTIVITY OF EXPERIMENTAL FORMULATIONS
AT 1000F MEAN TEMPERATURE

<u>TiO_2 Designation</u>	<u>TiO_2 Content, Wt. %</u>	<u>Conductivity Btu in./hr ft² °F</u>
-325 mesh H.G.	16	0.25
-325 mesh H.G.	32	0.22
-5 micron H.G.	16	0.24
-5 micron H.G.	32	0.21

TABLE 20.
PARTICLE SIZE DETERMINATION OF TAM TiO_2

Blaine Method

-325 mesh H.G.	1.70 microns
-5 micron H.G.	1.82 microns

Sedimentation Method

<u>Size Range</u>	<u>Weight, %</u>	
	<u>-325 mesh H.G.</u>	<u>-5 micron H.G.</u>
>20 microns	0.8	---
10-20 microns	5.6	---
8-10 microns	4.4	---
6-8 microns	6.1	0.3
4-6 microns	12.8	2.5
2-4 microns	9.6	35.7
1-2 microns	41.5	49.5
<1 micron	19.2	12.0

TABLE 21.
SPECTROGRAPHIC ANALYSIS OF -5 MICRON H.G. TiO_2

<u>Metal</u>	<u>Content, per cent</u>
Aluminum	0.14
Antimony	0.21
Barium	0.014
Iron	0.018
Lead	0.01
Magnesium	0.01
Silicon	0.23
Zirconium	0.03

C. FORMULATIONS

Table 22 lists all of the experimental formulations investigated during this effort. Although many of the formulations appear identical with respect to the amounts and types of ingredients, a new number was assigned whenever anything about the formulation was changed such as pretreatment of an ingredient (prefiring or premilling), type of mixing equipment, mixing time, etc. In general, the first 25 or 30 formulations involved the investigation of the mixing procedure, whereas the remaining formulations attempted to optimize the physical and thermal properties. Although silicon was discarded as an opacifier early in the program, the resulting dark color of the experimental blocks facilitated the observation of mixing uniformity and fiber openness within the block. A full description of each formulation may be found in the pertinent quarterly report.

D. PROCESS

Standard MIN-K ingredients have been, and still are, mixed in a ribbon mixer, and subsequently passed through a comminuting machine for final opening and dispersion. Conversion to the vitreous fibers as reinforcement resulted in unopened fiber bundles or clumps, which in turn significantly reduced the reinforcing efficiency of the fibers. Multiple passes through the comminuting machine only served to pulverize the fine fibers (such as MICRO-QUARTZ) and shorten the staple fiber (such as ASTROQUARTZ).

In contrast, a Waring blender-type mixer called Henschel (distributed by Prodex Products Corporation) provided good opening action on the staple fiber bundles, with little or no apparent shortening, and good dispersion of the finer fibers which were introduced into the mix in felt form. A similar type of mixer called the Papenmeier (distributed by Welding Engineers) was also evaluated, but found to provide less opening action on the fine fiber clumps. The Henschel was chosen therefore as the process mixer. This conclusion should in no way be construed to indicate the relative merits of these two machines when used for the purpose for which they were designed, that of blending fiber and resin compounds.

Mixing variables which were investigated included mixing time, blade speed, blade position, and blade design. A mixing time of 6 min was found sufficient to open the fiber clumps, but not enough to begin shortening the fibers. Similarly, the low speed (700 rpm) was preferred over the high speed (1400 rpm).

The blade position and design affected primarily the amount of fiber hangup which occurred. For example, a blade close to the bottom of the mixer (0 - 1/4 in.) would retain a clump, which in turn would pick up

TABLE 22.
EXPERIMENTAL MIN-K FORMULATIONS

Formulation No.	Silica		Fiber				Opacifier	
	Code	Per Cent	Code	Per Cent	Code	Per Cent	Code	Per Cent
1953	(1)	75	(1)	9			(1)	16
1954	(1)	75	(1)	9			(1)	16
1955	(1)	75	(1)	9			(1)	16
1956	(1)	75	(3)	9			(1)	16
1957	(1)	75	(2)	9*			(1)	16
1958	(1)	75	(2)	9*			(1)	16
1959	(1)	75	(3)	9			(1)	16
1960	(2)	75	(3)	9			(1)	16
1961	(1)	75	(4)	9			(1)	16
1962	(1)	79	(4)	5			(1)	16
1963	(1)	79	(3)	5			(1)	16
1964	(1)	75	(4)	9			(1)	16
1965	(1)	75	(4)	9			(1)	16
1966	(1)	75	(4)	9			(1)	16
1967	(1)	75	(4)	9			(1)	16
1968	(1)	75	(4)	9			(1)	16
1969	(1)	75	(4)	9			(1)	16
1970	(1)	76	(4)	8			(1)	16
1971	(1)	77	(4)	7			(1)	16
1972	(1)	78	(4)	6			(1)	16
1973	(1)	79	(4)	5			(1)	16
1974	(1)	74	(4)	10			(1)	16
1975	(1)	75	(5)	9			(1)	16
1976	(1)	79	(5)	5			(1)	16
1977	(2)	75	(4)	9			(1)	16
1978	(1)	77	(3)	2	(5)	5	(1)	16
1979	(1)	75	(3)	4	(5)	5	(1)	16
1980	(1)	78	(3)	1	(5)	5	(1)	16
1981	(1)	76	(3)	3	(5)	5	(1)	16
1982	(1)	79	(4)	5			(2)	16
1983	(1)	63	(4)	5			(2)	32
1984	(1)	79	(5)	5*			(1)	16
1985	(1)	79	(4)	5			(3)	16
1986	(1)	63	(4)	5			(3)	32
1987	(1)	75	(4)	4	(5)	5	(1)	16
1988	(1)	75	(3)	4*	(5)	5	(1)	16
1989	(1)	75	(3)	9			(1)	16

TABLE 22. (CONTINUED)

Formulation No.	Silica		Fiber				Opacifier	
	Code	Per Cent	Code	Per Cent	Code	Per Cent	Code	Per Cent
1990	(1)	75	(3)	9*			(1)	16
1991	(1)	75	(3)	9			(1)	16
1992	(1)	75	(3)	9*			(1)	16
1993	(1)	75	(3)	4*	(5)	5	(1)	16
1994	(1)	75	(3)	9			(1)	16
1995	(1)	75	(3)	9*			(1)	16
1996	(1)	79	(4)	5			(1)	16
1997	(1)	75	(3)	4	(5)	5	(1)	16
1999	(1)	75	(3)	8	(4)	1	(3)	16
2000	(1)	75	(3)	7	(4)	2	(3)	16
2001	(1)	75	(3)	6	(4)	3	(3)	16
2002	(1)	75	(3)	4	(5)	5	(3)	16
2003	(1)	67	(3)	4	(5)	5	(3)	24
2004	(3)	75	(3)	4	(5)	5	(3)	16
2005	(4)	75	(3)	4	(5)	5	(3)	16
2006	(5)	75	(3)	4	(5)	5	(3)	16
2007	(1)	75*	(3)	4	(5)	5	(3)	16
2008	(1)	75*	(3)	4	(5)	5	(3)	16
2009	(1)	75*	(3)	4	(5)	5	(3)	16
2010	(1)	75*	(3)	8	(4)	1	(3)	16
2011**	(1)	73*	(3)	8	(4)	1	(3)	16
2012	(3)	75*	(3)	8	(4)	1	(3)	16
2013**	(3)	73*	(3)	8	(4)	1	(3)	16
2014**	(3)	73*	(3)	4	(5)	5	(3)	16
2015**	(3)	73*	(3)	4	(5)	5	(3)	16
2016**	(1)	73*	(3)	4	(5)	5	(3)	16
2017**	(1)	73*	(3)	4*	(5)	5	(3)	16
2018**	(1)	73*	(3)	4*	(5)	5	(3)	16
2019***	(1)	80					(3)	17
2020	(1)	75	(3)	4*	(5)	5	(3)	16
2021	(1)	75	(5)	5			(3)	16
2022	(1)	75	(4)	4	(5)	5	(3)	16
2023	(1)	75	(3)	4*	(5)	5	(3)	16
2024	(1)	75	(3)	4*	(5)	5	(3)	16
2025	(1)	75	(5)	5	(6)	4	(3)	16

CODES FOR TABLE 22

Silica:	(1)	CAB-O-SIL M5
	(2)	ARC SILICA 800
	(3)	AEROSIL Uncompressed
	(4)	AEROSIL 2491-380
	(5)	AEROSIL 2491
Fiber:	(1)	475 GLASS A Fiber
	(2)	CHOPPED G SILICA
	(3)	MICRO-QUARTZ AA Fiber
	(4)	ASTROQUARTZ 1/4-in. Staple
	(5)	ASTROQUARTZ 1/2-in. Staple
	(6)	DYNAQUARTZ
Opacifier:	(1)	Silicon
	(2)	TAM -325 Mesh H.G. TiO_2
	(3)	TAM -5 Micron H.G. TiO_2

* Heat treated.

** Plus 2 per cent BRP 5095 powdered phenolic resin.

***Plus 3 per cent BRP 5095 powdered phenolic resin.

additional fibers. Likewise, a blade with a circular rim either midway, or at the tip of the blade, would also attract fiber clumps. The most satisfactory arrangement was two propeller-type units, each with two blades, with one unit mounted above and at right angles to the other. The bottom unit was kept about 1/2 in. above the floor of the mixer.

The basis for comparison between the numerous process conditions was visual and strength. Each formulation was molded and subjected to a simple bend test (modulus of rupture), plus a visual examination of the fractured cross-section after test. Inadequate mixing resulted in a low modulus of rupture, and small fiber clumps within the interior of the block. Although excessive mixing generally did not produce fiber clumps, the modulus of rupture was again low due to fiber shortening. The MR generally peaked at some intermediate mixing condition which was then considered optimum. Process scaleup will require a similar evaluation to insure that the size factor has not altered the desired optimum mixing conditions.

E. MOLDING PROCEDURE

No distinctly new molding techniques were devised as a result of this program. As in all MIN-K molding, matched steel dies were used. Although no binder was employed, an adequate coating of a mold release agent was used.

All molding was done at room temperature (except for the several formulations which contained binder), and pressure was maintained for a minimum of 1 hr. Although this was probably longer than necessary, the program intent did not require that this variable be investigated. It is known, however, that mold times of less than 15 min will result in excessive thickness regain, and hence, low densities and poor block strengths.

Since the formulations have a bulk density of 3 - 4 pcf before molding (as compared with a 20 pcf product density), and contain no binder, some regain in dimension parallel to the direction of compression was expected. Experience indicated that the unbonded formulations regained approximately 10 - 12 per cent. Therefore, compensating spacers in the flat 12 x 12 and 9 x 9 molds were added to yield a mold cavity below the nominal finished thickness of the part. Generally, the regain was consistent, and finished thicknesses within ± 0.015 in. of nominal were possible.

F. BULK INSULATION FOR LEAD-TELLURIDE SYSTEMS

Bulk insulation (insulation around the heat source) for a lead-telluride system should be capable of 1400F temperature service, load resistance,

handling strength in reasonably large pieces, cutting and fitting, etc., as well as the other requirements for low thermal conductivity, minimum outgassing, and compatibility with generator materials.

The concept of bulk insulation, molded into flat or simple contoured shapes, permitted the use of 1/2-in. ASTROQUARTZ staple fiber for added reinforcement. This fiber alone, however, was not adequate since it appeared to be only in "suspension" with the other ingredients of the mix, and gave the impression that it could separate (prior to molding) from the mix. This fiber did not appear to contain or reduce the highly flowing and dusting characteristics of the CAB-O-SIL M5. The addition of MICRO-QUARTZ fiber to the batch, however, significantly altered these characteristics for the better. In addition, the MICRO-QUARTZ fibers, which are much shorter and somewhat smaller in diameter than the ASTROQUARTZ fibers, imparted further reinforcement to the molded product. Formulation 2002 containing 5 per cent 1/2-in. ASTROQUARTZ staple, and 4 per cent MICRO-QUARTZ, was considered optimum for the bulk insulation service.

G. INTRICATE INSULATION FOR LEAD-TELLURIDE SERVICE

The concept of an intricate molded insulation in direct contact with the energy conversion units presented a somewhat different combination of properties. Although the conductivity, outgassing, and compatibility requirements were the same, the intricate insulation need only operate at 1200F, and be capable of molding into smaller, but more complex shapes. The moldability requirement was the major factor for changing the formulation.

Long staple fibers provided excellent reinforcement. However, they did not "flow" into small and intricate contours within the mold cavity, and also hindered the flow of the other ingredients into these areas as well. The result was soft, easily broken edges, lips, etc. The substitution of 1/4-in. ASTROQUARTZ staple for the 1/2-in. staple helped somewhat, but still did not provide for a satisfactory intricate molding. (A small SNAP 19 T/E module configuration was used for evaluating moldability.) The substitution of MICRO-QUARTZ for 1/4-in. ASTROQUARTZ staple significantly improved the moldability of the formulation due to the greater mobility of the mix. An optimum combination of 8 per cent MICRO-QUARTZ and 1 per cent 1/4-in. ASTROQUARTZ staple was subsequently achieved in Formulation 1999.

H. INSULATION FOR SILICON-GERMANIUM SYSTEMS

Requirements for silicon-germanium insulation(s) differed from those of the lead-telluride insulations in that the bulk insulation should be capable of 1800F. Additionally, the method of assembly of the T/E module and insulation package required the use of an insulation which could be packed in and around the elements following their assembly. This precluded the use of a molded insulation in this area. (Recent designs, however, are attempting to utilize the molded insulation rather than fibrous insulation.) The effort therefore centered upon the bulk insulation development.

Linear shrinkage was the main problem in the development of an 1800F insulation. Various techniques were attempted to overcome this problem. They included: evaluation of other silica materials, prefiring the silica to 1800F prior to formulation, and prefiring the MICRO-QUARTZ to 1800F prior to formulation. CAB-O-SIL M5 was found to be the best of the silicas evaluated. Prefiring of either the silica or the MICRO-QUARTZ fiber improved the resistance to shrinkage of the product. However, prefired silica resulted in relatively weak moldings, which in some instances required binder for handling integrity. Thus, by prefiring the silica and the subsequent addition of binder, the requirement for minimizing outgassing could not be met. DYNAQUARTZ was substituted for MICRO-QUARTZ and was pulverized by the mixing process, thus affording no reinforcement to the block. This was probably a result of the high degree of fiber to fiber sintering which had taken place during the manufacture of the DYNAQUARTZ. Therefore, Formulation 2020, containing 4 per cent prefired MICRO-QUARTZ and 5 per cent 1/2-in. ASTROQUARTZ was selected for use as bulk insulation in silicon-germanium systems.

It will be shown later that Formulation 2020 does not have the temperature stability of Formulation 2002 at their respective design temperatures. Further improvement in Formulation 2020 would require a complete change in basic ingredients, together with a detailed study of the sintering phenomenon inherent with extremely fine particles. This study was beyond the scope of the present effort, but will be conducted in a follow-on program.

I. FIRING

Since none of the three formulations contained binder, they were weaker in the as-molded state than the standard MIN-K products. It was found, however, that post-firing of the formulations (after molding) to 1300 - 1400F for 2 hr initiated the particle-to-particle sintering process, and resulted in a 50 per cent increase in strength (per the modulus of rupture

test). It is believed that this sintering is an incipient state which, when allowed to proceed at higher temperatures, results in measurable shrinkage of the product. The short-term exposure, however, did not produce such evidence, provided the temperature did not exceed 1400F. At temperatures slightly above 1400F, Formulation 1999, which contained the highest per cent of unfired (prior to formulating) MICRO-QUARTZ, did show evidence of dimensional shrinkage.

J. CONCLUSIONS - MATERIAL AND PROCESS DEVELOPMENT

1. CAB-O-SIL M5, MICRO-QUARTZ, ASTROQUARTZ staple, and TAM -5 micron H.G. TiO_2 were selected as the best ingredients for the experimental MIN-K formulations.
2. The use of a Henschel mixer provided excellent fiber opening and mixing with a minimum of fiber breakdown.
3. Formulation 2002 was selected for bulk insulation service in lead-telluride units.
4. Formulation 1999 was selected for intricate insulation service in lead-telluride units.
5. Formulation 2020 was selected for bulk insulation service in silicon-germanium units.

VII. EVALUATION OF EXPERIMENTAL MIN-K FORMULATIONS

A. MODULUS OF RUPTURE

One of the basic tests used throughout the program to evaluate the various experimental formulations was the modulus of rupture (MR) test. A 4-1/2-in. square, 1/2 to 1-in. thick specimen, was placed over parallel supports 4 in. apart, and a load applied slowly across the width of the specimen. The MR was then calculated from the formula:

$$MR = \frac{3}{2} \frac{wl}{bt^2}$$

where: w = maximum load, lb

 l = span, in.

 b = width of specimen, in.

 t = thickness of specimen, in.

Table 23 summarizes the MR results of Formulations 1999, 2002, and 2020. All tests were conducted at room temperature. The low staple fiber content of Formulation 1999 (1 per cent) resulted in a significantly lower MR than Formulation 2002. This, however, did not effect the handleability of the product, primarily because it was designed for relatively small moldings. The effect of prefiring the MICRO-QUARTZ was also significant in Formulation 2020. It is speculated that since the prefiring probably resulted in incipient sintering of the fibers themselves, as well as fiber to fiber, the Henschel mixer tended to break the fibers rather than separate them. This would then yield fibers of lower length-to-diameter ratios having less reinforcing capability.

The MR test, and in particular the span, width, and thickness ratios of the specimens, was intended primarily as a comparative test. The values obtained from this test, however, are reasonably indicative of the strength of the material.

B. SHEAR STRENGTH OF FORMULATION 2002

All MIN-K products are known to be weak in the laminar direction (normal to the pressed direction). In order to confirm this fact, a shear test

TABLE 23.
ROOM TEMPERATURE MODULUS OF RUPTURE OF
FORMULATIONS 1999, 2002, AND 2020

<u>Formulation</u>	<u>No. of Tests</u>	<u>MR, psi</u>
1999	8	62
2002	44	80
2020	20	68

was devised and conducted at room temperature. The test utilized 1 x 2 x 3/4-in. thick specimens which were placed on their 2 x 3/4-in. edge within a confining fixture. The fixture was so constructed as to prevent any movement of half of the projected area, or 2 x 3/8-in., while the remaining half was subjected to a guillotine action over its entire area at a loading rate of 50 lb/min (or approximately 37.5 psi/min).

An average value of 22.1 psi was obtained for the 12 specimens, with an approximate spread of ± 25 per cent for the individual values. Previous work on MIN-K 1301 containing binder resulted in an average of 44 psi, with a higher spread of values. Although no data existed for a direct comparison, it was assumed that MIN-K 1301 with the binder removed would have a shear strength approximating that of Formulation 2002. Thus, none of the MIN-K formulations should be required to sustain excessive shear forces during service.

C. THERMAL STABILITY

The thermal stability of Formulation 1999 was evaluated for 1 wk (168 hr) in air at an isothermal temperature of 1200F. In all cases (4 specimens), the measured change in dimension was within the estimated reproducibility of the measuring gauge (± 0.002 in.). This was not unexpected since the specimens had already undergone a 2-hr firing at 1400F.

Formulation 2002 was subjected to considerably more thermal stability evaluations, both isothermal and hot face, for up to 2000 hr. The shrinkage in air under isothermal conditions of 1400F, 1500F, and 1600F is summarized in Table 24. Twelve specimens were tested for 2000 hr at 1400F, plus 100 hr at 1500F, plus 48 hr at 1600F. Four of the twelve were continued on test for a total of 1000 hr at 1600F. Essentially all of the shrinkage at each temperature level took place within the first week of exposure. The estimated accuracy of the values in Table 24 is: length, ± 0.03 per cent; width, ± 0.07 per cent; and thickness, ± 0.2 per cent.

To establish more meaningful shrinkage data under conditions of thermal gradient, two 4 x 4 x 1-in. specimens of Formulation 2002 were inserted into hot face test units, with less than 1 psi load applied. The specimens were heated to 1400F hot face for 500 hr, removed, measured, re-inserted, and heated to 1600F hot face for an additional total exposure of 1548 hr. Table 25 summarizes the data. Note that the "shrinkage" is presented in terms of dimensional change, rather than per cent shrinkage as has been done previously.

TABLE 24.
THERMAL STABILITY OF FORMULATION 2002 IN AIR
UNDER ISOTHERMAL CONDITIONS

<u>Exposure Conditions</u>	<u>Shrinkage*, per cent</u>		
	<u>Length</u>	<u>Width</u>	<u>Thickness</u>
2000 hr at 1400F +	0.4	0.8	0.8
100 hr at 1500F +	0.4	0.9	0.8
48 hr at 1600F +	0.5	0.9	0.9
475 hr at 1600F +	0.6	0.6	1.2
1000 hr at 1600F	0.6	0.7	1.4

*All values are based on specimen dimensions prior to test.

TABLE 25.

THERMAL STABILITY OF FORMULATION 2002 IN AIR
AT 1400F AND 1600F HOT FACE

Specimen No.	Exposure Time hr	Average Hot Face °F	Average Cold Face °F	Total Dimensional Change, Inches		
				Length	Width	Thickness
1	500	1398	283	none	-0.001	+0.002
2	500	1403	274	-0.002	-0.002	-0.004
1	425	1598	671*	-0.004	-0.005	-0.002
2	425	1597	666*	-0.008	-0.005	-0.005
1	1000	1599	672*	-0.006	-0.011	-0.006
2	1000	1597	666*	-0.008	-0.002	-0.009
1	1548	1597	671*	-0.005	-0.007	-0.005
2	1548	1598	665*	-0.010	-0.007	-0.010

*Fibrous insulation was used to cover the cold face of each specimen to increase the mean temperature of the specimen.

It can be seen that at 1400F hot face, no length and width shrinkage could be detected within the limits of measuring accuracy. Similarly, the measured thickness shrinkage was considerably below that for the isothermal exposure (0.001 in. represents approximately 0.1 per cent of the original thickness).

The 1600F hot face tests were conducted such that both the hot face and the cold face (and hence, the mean temperature) exceeded normal design operating limits. Despite these exaggerated conditions, the shrinkage remained below 1 per cent. The comparison between isothermal and hot face stability testing (comparing Table 24 with Table 25) was most evident in the thickness dimension as anticipated, with the hot face tests representing the more realistic stability values. All dimensions in Table 25 represent changes from the original dimensions prior to any hot face exposure.

Formulation 2020 was also subjected to isothermal and hot face shrinkage tests. The isothermal tests, however, were conducted in air and vacuum. Table 26 gives the results of the isothermal tests. It can be seen that the isothermal shrinkage in vacuum was approaching 50 per cent of that in air as the period of exposure increased. A review of the literature confirmed this phenomenon. It further showed that, contrary to most other refractory materials, the sintering rate of silica is increased when moisture is present. Based on these findings, the general conclusion can be drawn that all of the experimental formulations will shrink less at a given temperature when the formulation and the surrounding atmosphere are free from moisture. Since both the lead-telluride and the silicon-germanium systems operate in a moisture-free environment, all of the long-term shrinkage tests run in air could probably be reduced by approximately 50 per cent to describe more realistically service capabilities.

Since the isothermal shrinkage of Formulation 2020 was so high, even in vacuum, hot face tests in air were also conducted. Table 27 summarizes these results. During the development phase of this high temperature formulation, major emphasis was given to the minimizing of the length and width shrinkage (as determined by short-term, isothermal tests). This would then insure that, under temperature gradient conditions, the insulation would not shrink sufficiently to open gaps between joints and allow a direct thermal radiation path through to the cold side. The net result was that the ratio of thickness to length or width shrinkage was considerably greater for Formulation 2020 than for Formulation 2002 at their respective service temperatures. It can be seen, however, that 1800F hot face is about the maximum safe operating temperature for Formulation 2020.

TABLE 26.
ISOTHERMAL STABILITY OF FORMULATION 2020
AT 1800F IN AIR AND VACUUM

<u>Time, hr</u>	<u>Environment at 1800F</u>	<u>Shrinkage, %</u>		
		<u>Length</u>	<u>Width</u>	<u>Thickness</u>
476	air	1.0	1.2	9.6
	vacuum	0.9	1.1	7.5
1027	air	1.7	2.0	13.2
	vacuum	1.3	1.5	9.1
1500	air	2.6	3.0	17.9
	vacuum	1.6	1.9	10.5
2000	air	3.6	4.1	20.5
	vacuum	1.8	2.2	11.4

TABLE 27.
THERMAL SHRINKAGE OF FORMULATION 2020
IN AIR AT 1800F HOT FACE TEMPERATURE

<u>Time, hr</u>	<u>Shrinkage, per cent</u>		
	<u>Length</u>	<u>Width</u>	<u>Thickness</u>
500	0.1	0.1	0.6
1000	0.1	0.1	1.4
1500	0.1	0.1	1.7
2000	0.2	0.2	2.1

D. STRESS-STRAIN CHARACTERISTICS

Formulation 1999, having been developed solely for intricate service where no stresses would be imparted to the insulation, was not evaluated for stress-strain characteristics. However, 35 Formulation 2002 specimens, 4-1/2 x 4-1/2 x 1 in. and unconfined, were given a stress-strain evaluation at room temperature. Thirty of these were loaded at a rate of 60 psi/min, while five were loaded at a rate of 180 psi/min. Additionally, 5 specimens were tested at 1400F hot face and 60 psi/min loading rate up to 200 psi total stress.

All room temperature test specimens had an initial static preload of 0.3 psi, whereas the hot face test specimens had an initial static preload of 3 psi. Although the lower preload (0.3 psi) would have been preferred, a 3 psi preload on the hot face compression units was necessary to insure proper nesting of the heater plate, thermocouple, and specimen assembly within the body of the furnace.

Figure 12 represents the average stress-strain curve for the thirty specimens tested at room temperature and at a loading rate of 60 psi/min. The dash lines represent the standard deviation (68 per cent limits), while the dotted lines represent twice the standard deviation (95 per cent limits).

The equation for the stress-strain curve between 0.02 and 0.15 in./in. strain was:

$$\text{Stress} = -11.04 + (2002)(\text{strain})$$

The non-linear portion of the curve (below 0.02 in./in.) was not considered in the calculations, and hence, a negative stress intercept was obtained. The 95 per cent confidence limits were calculated to be ± 3.7 psi at 0.02 in./in., ± 13.4 psi at 0.08 in./in., and ± 26.8 psi at 0.14 in./in. Previous data on MIN-K 1301 by Martin Company resulted in 90 per cent confidence limits of ± 16 psi at 0.02 in./in.

Five specimens were subjected to room temperature loading at a rate of 180 psi/min. The equation for these data was:

$$\text{Stress} = -11.84 + (2052)(\text{strain})$$

FIGURE 12.

ROOM TEMPERATURE STRESS-STRAIN CHARACTERISTICS OF
FORMULATION 2002 PARALLEL TO THE DIRECTION OF MOLDING

It will be noted that this equation does not significantly differ (on a practical basis) from that derived from the previous data taken at the lower loading rate.

Likewise, five specimens were subjected to 1400F hot face, and 60 psi/min loading rate. The equation derived from these data was:

$$\text{Stress} = 8.33 + (2116)(\text{strain})$$

As previously noted, the preload for the hot face tests was greater than that for the room temperature tests, and thus the apparent positive stress intercept. This curve is plotted in Figure 13. The 68 per cent and 95 per cent confidence limits are also plotted.

The adjustment of the stress intercept of the hot face curve, the combination of all room temperature data, and the rounding off of the equation constants in keeping with practical engineering and design requirements resulted in the following equations:

$$\begin{array}{l} \text{Room Temperature} \\ \text{Stress} = -11 + (2000)(\text{strain}) \end{array}$$

$$\begin{array}{l} \text{Hot Face} \\ \text{Stress} = -11 + (2100)(\text{strain}) \end{array}$$

These equations are plotted in Figure 14.

Similar tests were conducted normal to the direction of molding (parallel to the "laminar planes" of the insulation) at room temperature with no lateral support. As the stress increased, cracks along the "laminar planes" developed, and became progressively worse. The plot of the data yielded a non-linear function, and confirmed suspicions that the material had considerably poorer load-carrying capability (unrestrained) in this direction.

Twenty specimens of Formulation 2020 were evaluated at room temperature and a loading rate of 60 psi/min parallel to the direction of molding. The resulting equation was:

$$\text{Stress} = -13 + (1950)(\text{strain})$$

FIGURE 13.

STRESS-STRAIN CHARACTERISTICS OF FORMULATION 2002
AT 1400F HOT FACE PARALLEL TO THE DIRECTION OF MOLDING

FIGURE 14.

COMBINED STRESS-STRAIN CHARACTERISTICS FOR FORMULATION 2002
PARALLEL TO THE DIRECTION OF MOLDING

A comparison between this equation and the equation for Formulation 2002 will show that the two have very similar stress-strain characteristics.

Formulation 2020 was not evaluated at 1800F hot face because of its high rate of sintering under the combined effect of temperature and load (see "E", Load Relaxation).

E. LOAD-RELAXATION OF FORMULATION 2002

A load-relaxation test was devised to simulate the effect of a generator assembly preload on an insulation adjacent to the heat source, and to determine the fall-off rate of this initial preload with time due to insulation relaxation. This test was conducted at a 1400F hot face temperature.

After insertion of the specimen into the furnace, and temperature equilibrium was achieved, the intended initial preload was applied to the specimen and the specimen deflection determined. This deflection was then maintained throughout the entire test, while the load required to maintain the deflection was reduced as the specimen relaxed. Since the furnace itself had specific stress-strain characteristics, calibration data taken before test were used as correction factors in the calculation of the specimen deflection at any given time.

Initial loads of 50, 100, and 150 psi were investigated with three specimens tested at each load. Figure 15 is a log-log plot of fraction of initial stress versus time. The cross-hatched area represents the data span for all specimens. Thus, after 2000 hr, the average load sustained by Formulation 2002 was 50 per cent of the initial load for a constant specimen deflection.

For comparison purposes, two specimens were subjected to the same test except at room temperature, one specimen at 100 psi preload, and one specimen at 150 psi preload. These results are also plotted in Figure 15. Since only two specimens were run, no conclusion can be drawn as to whether the effect of initial preload was a dependent or independent variable at room temperature.

A similar test was conducted on Formulation 2020 specimens at 1800F hot face. The rate of load-relaxation was very rapid, approaching 50 per cent of initial load within several days. The tests were not continued. Formulation 2020 should not be required to sustain external loads when operating at 1800F hot face.

FIGURE 15.
LOAD RELAXATION OF FORMULATION 2002

F. MOISTURE ADSORPTION/DESORPTION OF FORMULATION 2002

It has been common knowledge that the MIN-K products rapidly adsorb atmospheric moisture. The rate of adsorption and subsequent desorption was determined for Formulation 2002. Similar results can be ascribed to Formulations 1999 and 2020, also.

The test specimens were 4 x 4 x 1/4-in., 1/2-in., and 1-in. in size. The moisture adsorption tests were conducted in a sealed chamber into which the desired humidities were achieved through the use of the following super-saturated salt solutions.

22% RH	-	CH ₃ COOK
51% RH	-	Ca (NO ₃) ₂ · 4H ₂ O
91% RH	-	(CH ₃ COO) ₂ Ca

These solutions, contained in a small dish, were placed in the chamber, and a blower was provided to circulate the air within the chamber. The humidity was measured by a humidistat using the proper sensing elements for each humidity range, and a recording humidistat for record-keeping purposes. A chainomatic balance was mounted directly above the humidity chamber. The sample holder within the chamber was suspended by a fine diameter wire from the balance arm through a small hole in the chamber. Access to the chamber for the insertion of the samples was provided by a hole fitted with a plastic sleeve, each end of which (one end inside the chamber, and one end outside the chamber) could be sealed. To insert the dry (at 230F to constant weight) sample into the chamber, the operator's arm was placed into the sleeve and sealed around the upper portion of the arm. The seal inside the chamber was then opened, permitting the operator to place the dry specimen on the balance pan and to initiate weighings.

The desorption tests were run by placing the same balance above a drying oven (operating at 230F), and suspending the balance pan into the oven. There was no air circulation within the oven, thus providing not only reproducible conditions, but also the slowest drying conditions. The specimens were preconditioned in their respective relative humidity conditions until an equilibrium weight was attained.

The results of the moisture adsorption tests are plotted in Figures 16, 17, and 18 for 22% RH, 51% RH, and 91% RH, respectively. The curves do not necessarily include the equilibrium points, since the significant portion of the curves occurred in the early stages of adsorption.

FIGURE 16.

MOISTURE ADSORPTION OF FORMULATION 2002 IN 22% RH

FIGURE 17.

MOISTURE ADSORPTION OF FORMULATION 2002 IN 51% RH

FIGURE 18.

MOISTURE ADSORPTION OF FORMULATION 2002 IN 91% RH

Similarly, Figures 19, 20, and 21 represent the moisture desorption or drying rates. In all cases, the per cent weight change was based upon the initial weight of the sample. Thus, on a per cent basis, the moisture pickup during adsorption may appear to be greater than the amount of moisture driven off at 230F during desorption.

Prior to the desorption tests, all specimens were placed in a desiccator containing the proper salt solution until equilibrium was attained. In two instances, 91% RH equilibrium appeared difficult to achieve in the 1/4-in. and 1-in. thick specimens. Consequently, these two specimens were placed in 100% RH conditions for 3 and 5 days (1/4-in. and 1-in., respectively), and subsequently returned to the 91% RH condition. Equilibrium was subsequently achieved in 5 and 6 days, respectively. Table 28 summarizes the equilibrium moisture contents for each thickness and at each humidity level.

G. THERMAL CONDUCTIVITY

The thermal conductivity evaluation of Formulations 1999, 2002, and 2020 is still in progress. Available results are reported here, and the balance of the program will be reported in a supplement.

The program will include the evaluation of Formulations 1999 and 2002 between the approximate mean temperatures of 500F and 1200F in air, vacuum ($<10^{-4}$ mm Hg), argon (760 mm Hg), and a 50-50 mixture of argon and helium (760 mm Hg). These materials will then be subjected to long-term exposures to 1000F in argon, and re-evaluated to determine if the thermal conductivity changes with time. Similarly, Formulation 2020 will be evaluated in air and vacuum, exposed to 1600F in vacuum for prolonged periods, and re-evaluated.

Figures 22, 23, and 24 present the thermal conductivity of Formulations 1999, 2002, and 2020, respectively. The argon and vacuum curves for Formulation 1999 and 2002 did not follow the anticipated path predicted by earlier theoretical derivations. Thus, in a MIN-K type material, the advantage gained in a vacuum or heavy gas over air is apparently reduced significantly as the mean temperature is increased. Further attempts to define this phenomenon will be presented in the supplement report.

FIGURE 19.

MOISTURE DESORPTION OF FORMULATION 2002
AFTER CONDITIONING AT 22% RH

FIGURE 20.

MOISTURE DESORPTION OF FORMULATION 2002
AFTER CONDITIONING AT 51% RH

FIGURE 21.

MOISTURE DESORPTION OF FORMULATION 2002
AFTER CONDITIONING AT 91% RH

TABLE 28.
EQUILIBRIUM MOISTURE CONTENT OF FORMULATION 2002 AT
VARIOUS HUMIDITY LEVELS

Sample Thickness in.	Relative Humidity %	Time to Reach Equilibrium Days	Equilibrium Moisture Content %
1/4	22	4.0	0.60
1/2	22	7.5	0.64
1	22	1.0	0.69
1/4	51	5.0	1.53
1/2	51	7.0	1.52
1	51	7.5	1.48
1/4	91	---	7.1*
1/2	91	19.0	7.3
1	91	---	6.8*

*These values were obtained by subjecting the specimens to 100% RH and subsequent exposure to 91% RH for 5 and 6 days for the 1/4-in. and 1-in. specimens, respectively. Values obtained in the conventional manner were:

1/4-in. - 5.8 per cent after 11.0 days

1-in. - 6.0 per cent after 13.0 days

FIGURE 22.

THERMAL CONDUCTIVITY OF FORMULATION 1999
IN AIR, ARGON, AND VACUUM

FIGURE 23.

THERMAL CONDUCTIVITY OF FORMULATION 2002 IN AIR,
ARGON, AND VACUUM

FIGURE 24.

THERMAL CONDUCTIVITY OF FORMULATION 2020 IN AIR

H. MACHINABILITY

The machining of MIN-K has become increasingly more important, not only for prototype units (thus eliminating expensive tooling), but also on production units where certain finishing and fitting operations must be done during generator fabrication. Consequently, it was important that the new formulations have good machining characteristics.

The following machining operations were conducted on Formulations 1999, 2002, and 2020: drilling and counterboring, sawing, turning on a lathe, routing, shaving, milling, and sanding. Typical machining data on MIN-K 1301 showed a reject rate of between 25 and 75 per cent, with the major cause for rejection being the presence of fiber clumps. In general, these clumps would pull out of the MIN-K, leaving a small hole.

Figure 25 is a photograph of Formulation 2002 after undergoing the machining operations. In all categories, the three formulations were equal, and all were far superior to MIN-K 1301. Most significant was the fact that none of the twelve parts (encompassing all three formulations) would have been "rejected," had they been slated for service. This evaluation was considered the best measure of the uniformity of the formulations since the machining compared very small, localized areas.

The successful machining of MIN-K still relies heavily upon the care and skill of the operator. Supporting jigs and mounting fixtures must be used in most cases. Additionally, hole spacings or rim thicknesses should not be less than 1/4 in. unless adequate backup support is provided during machining.

I. OUTGASSING OF FORMULATION 2002

One of the major areas of investigation was the evaluation of the outgassing characteristics of the experimental formulations slated for lead-telluride service. Formulation 2002 was chosen for this test so that the test could be conducted at 1400F. The test was designed to permit water and residual gas analyses periodically after the specimens had attained 1400F (isothermal) in an argon atmosphere. However, analyses were also conducted at the various stages of preconditioning (evacuations and argon backfills at various temperatures).

The equipment consisted of 4-in. diameter by 3-ft long ceramic tubes (closed at one end), recessed vertically into a kiln with approximately 10 in. of the tube extending above the top of the kiln. The tube was

FIGURE 25.
TYPICAL MACHINED PARTS OF FORMULATION 2002

sealed with a metal flange and Viton gasket assembly. The flange was adapted to accommodate a vacuum line, and argon backfill line, a 0-3 atmosphere pressure gauge, and an exhaust port for gas sampling. The temperature at the Viton gasket was held to about 150F-200F by the use of a radiation shield inserted into the top third of the tube. This shield consisted of ten 2-mil Inconel discs, fastened together with small Inconel tabs welded from foil to foil in accordion fashion. A 1-1/2-in. diameter hole was cut off center in each disc, and each disc rotated slightly at assembly. This allowed a through path for evacuation purposes, but prevented a through path for radiation.

Each test specimen consisted of two pieces of Formulation 2002, 6 x 3 x 1 in. One specimen was preconditioned to 1050F for 30 min in air followed by 30 min at 1050F under active vacuum. The other specimens were preconditioned to 90% RH, 90F, and 30% RH, 75F, respectively. After preconditioning, each specimen (each in a separate tube) plus an empty tube was subjected to a series of 15 min pumpdown and 15 min outgassing cycles at room temperature, 400F, 600F, and 1000F. At the 600F and 1000F temperature levels, the tubes were backfilled with argon to 1030 mm Hg, and a water and residual gas analysis conducted on each tube.

The temperature was subsequently increased to 1400F and held constant for 2000 hr. Water and gas analyses were made every 500 hr. The argon pressure was increased to 1030 mm Hg following each analysis. A detailed description of the individual steps of the procedure may be found in the Fourth Quarterly Report, AL0-3633-4, dated April 3, 1967.

The plots of the pumpdown and outgassing cycles in terms of time versus pressure for each tube up to the 600F temperature level followed a predictable pattern. The specimens having the higher initial moisture contents pumped down slower, and outgassed faster than those with lower initial moisture contents. Once the specimens were backfilled with argon, however, the difference in pumpdown rates disappeared. This may have been due to the larger, less mobile argon molecule dominating the evacuation rate of the insulation.

After backfilling each tube with argon at 600F, a water and residual gas analysis was conducted. The water content was then converted to per cent by weight of the test specimen at STP. The results are shown in Table 29.

The pumpdown and outgassing cycles were repeated at 600F for the two tubes showing the higher water contents. However, after each cycle, the tubes were pressurized with argon for a minimum of 5 min to investigate the effect of repetitive backfills. Following a 96-hr time period to achieve equilibrium within the tubes, the water content was rechecked.

TABLE 29.
WATER AND RESIDUAL GAS CONTENT AT 600F

Specimen No.*	Water		Residual Gas, ppm					
	ppm	% by Weight	<u>N₂</u>	<u>O₂</u>	<u>CO₂</u>	<u>CO</u>	<u>H₂</u>	<u>CH₄</u>
1	500	0.0010	65	ND	47	ND	ND	25
2	900	0.0018	60	ND	37	ND	ND	10
3	6	nil	85	ND	32	ND	ND	ND
4	20	---	80	6	20	ND	ND	ND

*Specimen No. 1 - 33% RH, 75F

Specimen No. 2 - 90% RH, 90F

Specimen No. 3 - Evacuated at 1050F

Specimen No. 4 - Empty tube

The tube containing the 33% RH specimen then contained 78 ppm water, while the tube containing the 90% RH specimen still contained 620 ppm water.

The tubes were then heated to 1000 $\pm$ 20F (argon pressure held at approximately 1030 mm Hg) and allowed to come to equilibrium for a minimum of 96 hr. The water content and residual gas analyses determined at 1000F are given in Table 30.

Each tube was again pumped down, allowed to outgas, and backfilled with argon for a total of three cycles at 1050F. The times were changed, however, to 30 min for the first pumpdown, and 5 min for each subsequent outgas and pumpdown to coincide with current generator procedures at 1050F hot face. The tubes were then heated to 1400 $\pm$ 20F at 1030 mm Hg argon and held for 96 hr. The water content and residual gas analyses at 1400F are given in Table 31.

It was apparent that the effect of preconditioning of the specimens no longer was significant. All three specimens showed similar levels of moisture outgassing as compared with the empty tube.

The tubes could not be placed on extended test at 1400F, however, since the water contents were already above the limit of the measuring device. Consequently, the three tubes containing the specimens were again pumped, outgassed, and backfilled three times. The pumpdown and outgassing times were 5 min each. Water and residual gas analysis results after 96 hr at 1030 mm Hg are shown in Table 32. Although one specimen continued to show a relatively high level of water content, the system was placed on long-term status.

The water and residual gas analyses after 500, 1000, 1500, and 2000 hr at 1400F and 1030 mm Hg argon are shown in Table 33. The excessive hydrogen content was traced to the Inconel radiation shields. The shields over specimen Nos. 2 and 3 were slightly lower in the tubes, and thus a greater number of layers became hot and released the hydrogen. (Inconel normally has a relatively high hydrogen content which is released upon heating. This fact was not realized until after the test, and thus constituted a poor choice of material.) The sudden increase in nitrogen and oxygen over specimen No. 3 at the 500-hr level probably was a result of molecular diffusion into the system. It will be recalled that specimen No. 3 underwent more heating and evacuation than the other two (preconditioned at 1050F and evacuated for 30 min). Thus, it is not likely that this amount of gas remained adsorbed within the specimen.

TABLE 30.
WATER AND RESIDUAL GAS CONTENT AT 1000F

Specimen No.*	Water		Residual Gas, ppm					
	ppm	% by weight	<u>N₂</u>	<u>O₂</u>	<u>CO₂</u>	<u>CO</u>	<u>H₂</u>	<u>CH₄</u>
1	>1000	>0.0015	120	ND	610	60	ND	ND
2	>2000	>0.0030	160	ND	750	22	330	6
3	150	0.00023	330	ND	590	ND	ND	ND
4	225	---	250	ND	320	ND	ND	ND

*Specimen No. 1 - 33% RH, 75F

Specimen No. 2 - 90% RH, 90F

Specimen No. 3 - Evacuated at 1050F

Specimen No. 4 - Empty tube

TABLE 31.
FIRST WATER AND RESIDUAL GAS CONTENT AT 1400F

Specimen No.*	Water		Residual Gas, ppm						
	ppm	% by weight	<u>N₂</u>	<u>O₂</u>	<u>CO₂</u>	<u>CO</u>	<u>H₂</u>	<u>CH₄</u>	<u>C₂H₆</u>
1	>2000	>0.002	530	ND	1100	480	3600	33	7
2	>2000	>0.002	260	ND	1750	550	10,000	120	22
3	>2000	>0.002	400	6	500	820	10,000	140	7
4	<1	---	260	ND	ND	ND	560	ND	ND

*Specimen No. 1 - 33% RH, 75F

Specimen No. 2 - 90% RH, 90F

Specimen No. 3 - Evacuated at 1050F

Specimen No. 4 - Empty

TABLE 32.
SECOND WATER AND RESIDUAL GAS CONTENT AT 1400F

Specimen No.*	Water		Residual Gas, ppm					
	ppm	% by Weight	<u>N₂</u>	<u>O₂</u>	<u>CO₂</u>	<u>CO</u>	<u>H₂</u>	<u>CH₄</u>
1	>1000	>0.001	150	ND	120	75	1000	15
	<2000	<0.002						
2	270	0.0003	260	ND	ND	75	12,000	80
3	4	nil	450	ND	ND	ND	11,400	71
4	<1	---	450	ND	ND	ND	790	ND

*Specimen No. 1 - 33% RH, 75F

Specimen No. 2 - 90% RH, 90F

Specimen No. 3 - Evacuated at 1050F

Specimen No. 4 - Empty tube

TABLE 33.

WATER AND RESIDUAL GAS CONTENT AT 1400F AFTER PROLONGED EXPOSURE

Specimen No.*	Water		Residual Gas, ppm					
	ppm	% by Weight	N ₂	O ₂	CO ₂	CO	H ₂	CH ₄
After 500 hr at 1400F								
1	1,000	0.001	710	ND	135	265	2,300	43
2	6	nil	750	ND	ND	42	26,500	75
3	5	nil	16,500	3,500	10	ND <100**	20,700	56
4	<1	---	1,250	ND	ND	ND <50**	1,500	18
After 1000 hr at 1400F								
1	1,000	0.001	1,200	ND	330	500	3,200	43
2	5	nil	1,200	ND	ND	66	25,000	11
3	5	nil	7,500	1,100	ND	ND <100**	21,000	17
4	<1	---	1,800	ND	ND	ND <100**	1,900	15
After 1500 hr at 1400F								
1	>1,000	>0.001	1,300	ND	360	530	4,300	40
2	<1	nil	1,450	ND	ND	ND <100**	22,500	<4
3	1.5	nil	4,300	ND	ND	ND <100**	21,000	7
4	<1	---	2,300	ND	ND	ND <100**	2,500	14
After 2000 hr at 1400F								
1	>1,000	>0.001	2,100	ND	330	570	6,200	45
2	2	nil	2,100	ND	7	ND <100**	26,000	<4
3	2	nil	5,700	ND	ND	ND <100**	24,000	12
4	3	---	3,000	ND	ND	ND <100**	3,500	14

- *Specimen No. 1 - 33% RH, 75F
 Specimen No. 2 - 90% RH, 90F
 Specimen No. 3 - Evacuated at 1050F
 Specimen No. 4 - Empty tube

**Sensitivity of CO measurement decreases as N₂ content increases.

The only outgassing which could be attributed to the insulation with reasonable certainty was the moisture. As one would expect, the higher the temperature, the more water was given off. However, this did not appear to be a continuing phenomenon with time at constant temperature as shown by the constant water content over the 2000-hr period. Although the amounts of moisture given off are indefinite, since the quantity was at times beyond the sensitivity of the measuring device, it must also be remembered that this test was conducted isothermally, thus magnifying this effect. For comparison purposes, 1000 ppm represents 0.18 g of water by this test.

The fact that even specimen No. 3, which was preconditioned in vacuum at 1050F, gave off 2000 ppm of water when the temperature reached 1400F raises the question: Is the 1050F vacuum preconditioning which is currently part of certain generator assembly requirements adequate or necessary? This could be argued either way. Obviously, it does not remove all of the water, so consequently, the preconditioning temperature should be increased to the maximum anticipated in service. (It has been assumed that once the insulation is preconditioned, it is sealed to prevent moisture re-adsorption.)

On the other hand, the preconditioning was devised originally to remove the binder in MIN-K 1301. Therefore, since the new formulations contain no binder, would a generator outgassing procedure, with emphasis upon isothermal heating and evacuation up to the temperature limit of the cold end hardware, suffice to remove most of the water? The answers to these questions obviously involve a separate program using actual or simulated T/E modules.

J. COMPATIBILITY BETWEEN 2N, 2P, 3N, AND 3P LEAD-TELLURIDE ELEMENTS AND FORMULATIONS 1999 AND 2002

The compatibility test between Formulations 1999 and 2002, and the four lead-telluride thermoelectric elements, was designed to establish if any gross incompatibility existed. Consequently, a designed experiment calculated to provide sufficient data for statistical analyses of minor effects at each exposure level (500, 1000, 1500, and 2000 hr) was not included in the program. Following the collection of all data, however, certain trends, particularly after the 2000-hr exposure, indicated that a limited analysis might uncover statistically significant changes, even with the minimum of data. In no case did the results indicate gross incompatibility. The analysis indicated in certain instances, however, possible effects due to intimate contact with the insulations.

The measurement of the element properties before and after exposure, the detailed analysis of the results, and the conclusions derived from the analysis was conducted by Martin-Marietta Corporation, Nuclear Division, Baltimore, under the direction of W. J. Taylor. Due to the depth to which this study was carried, and the potential interest of the data to those concerned primarily with the electrical properties of the elements beyond the influence of the insulations, the Martin-Marietta report is included herein as Appendix A (Volume 2).

The conditions to which the elements were exposed were 1000F isothermal, and approximately 800 mm Hg argon. Since the effect of any outgassing constituents from the insulations, and the extent to which the test system was outgassed prior to "life testing" were not variables under investigation, major emphasis was placed upon eliminating their effect entirely. All insulation specimens were initially subjected to active vacuum (≤ 2 microns) for 24 hr at 1400F (isothermal). After cooling to 250F under active vacuum, the furnace chambers were backfilled with argon to slightly above 1 atmosphere pressure. Each insulation specimen was then removed individually, and the coded elements pressed into predrilled holes in the insulation. The insulations, together with appropriate "blanks" (elements contained in small ceramic crucibles, but not in contact with the insulation) were then returned to the furnace chamber.

Each chamber, or tube, of which there were four, was then subjected to a rigorous schedule of evacuation and argon backfill cycles at various temperature levels. At 400F, each chamber was actively evacuated to less than 2 microns for 24 hr, followed by an argon backfill to approximately 760 mm Hg. Two more short-term evacuation (≤ 5 microns) and backfill cycles completed the 400F preconditioning. The system was heated to 600F in argon, and the evacuation and backfill cycles repeated (one 24-hr evacuation, plus two short-term evacuations). At 1000F, three more cycles were conducted, for a total evacuation time of 15 min. The tubes were then pressurized to approximately 800 mm Hg argon during the last backfill and maintained at this pressure for the balance of the test.

Since each tube contained only those specimens assigned for exposure for a given period (500, 1000, 1500, or 2000 hr), none of the elements underwent thermal cycling. Cooling of the furnace tube and specimens was accomplished by removing the sealed tube from the common heat source, and allowing it to cool slowly (overnight) to room temperature. The tube was then opened and the specimens removed (in air). When not on test, all elements were sealed individually in an argon purged plastic bag, which was then placed into a small plastic bottle containing a desiccant.

As previously noted, the data and analyses presented in Appendix A showed no gross incompatibility between the elements and the insulations. It also was concluded in the Martin-Marietta report that the exposure and property measurement techniques employed in this program yielded accurate measures of thermoelectric behavior which can be correlated with the behavior of operational equipment.

K. CHEMICAL COMPATIBILITY OF FORMULATION 2020 AND SILICON-GERMANIUM ELEMENTS

As with several of the fibrous insulations, Formulation 2020 was subjected to a test to establish the extent of its gross incompatibility with silicon-germanium N and P elements. Holes were drilled into the blocks, and the elements (0.444 in. diameter, 0.271 in. long) were pressed fit into these holes to insure good physical contact between insulation and element. The isothermal test conditions of 1600F $\pm$ 20F in air and vacuum, the periodic removal of elements for analysis, and the technique for sampling the surface of the elements for analysis were identical to the procedures used with the fibrous insulations (see Section IV, paragraph E).

Tables 34 and 35 present the spectrographic analysis data. As before, three sets of elements were carried to the 2000-hr time level, whereas only one set was removed at the 500, 1000, and 1500-hr levels. These tables report the results as t/t, for example, meaning the quantity of impurity found in the N element/quantity of impurity found in the P element. Where a dash appears on either side of the slash, no impurity was found in that particular element.

As may have been anticipated, there was very little evidence of impurities on the extreme outer surface of the elements, following exposure to Formulation 2020.

L. SEEBECK COEFFICIENT AND RESISTIVITY COMPATIBILITY WITH FORMULATION 2020

Section IV, paragraph F described the Seebeck coefficient and resistivity compatibility tests between Irish REFRASIL and silicon-germanium alloys in air and vacuum at 1600F (isothermal). The identical test series was conducted on Formulation 2020 also. Matching pairs of N and P alloy bars were embedded in Formulation 2020 and DYNAQUARTZ. The room temperature Seebeck coefficient and resistivity values obtained at zero, 1000, and 2000-hr isothermal exposure to 1600F in air and vacuum are given in Tables 36 and 37, respectively.

TABLE 34.

SiGe ANALYSIS AFTER ISOTHERMAL EXPOSURE TO
FORMULATION 2020 IN AIR AT 1600F

Impurity	Quantity of Impurity, N/P*					
	500 hr	1000 hr	1500 hr	2000 hr		
Aluminum	ND	ND	t/t	t/t,	t/t,	t/t
Barium	ND	ND	ND	ND,	ND,	ND
Calcium	ND	ND	t/t	ND,	ND,	ND
Chromium	t/t	t/t	ND	ND,	ND,	ND
Copper	s/vs	t/t	t/t	vs/t,	vs/t,	vs/t
Iron	ND	ND	t/t	t/t,	t/t,	t/t
Magnesium	ND	ND	t/t	t/t,	t/t,	t/t
Molybdenum	ND	ND	ND	-/t,	-/vs,	-/t
Nickel	ND	ND	ND	t/-,	t/-,	ND
Sodium	ND	ND	t/t	ND,	ND,	ND
Titanium	t/t	t/t	t/t	t/t,	t/t,	t/t

*ND = not detected

t = trace = <0.01 per cent

vs = very small = <0.1 per cent

s = small = <1.0 per cent

TABLE 35.

SiGe ANALYSIS AFTER ISOTHERMAL EXPOSURE TO FORMULATION 2020
IN VACUUM AT 1600F

Impurity	Quantity of Impurity, N/P*					
	500 hr	1000 hr	1500 hr	2000 hr		
Aluminum	ND	t/t	t/t	t/t,	t/t,	t/t
Barium	ND	-/t	ND	ND,	ND,	ND
Calcium	ND	t/vs	ND	ND,	ND,	ND
Chromium	t/t	vs/-	ND	ND,	ND,	ND
Copper	vs/t	s/t	s/vs	s/t,	vs/t,	vs/t
Iron	ND	vs/t	t/t	-/t,	ND,	ND
Magnesium	ND	t/vs	t/t	t/t,	t/t,	t/t
Molybdenum	ND	ND	ND	ND,	ND,	-/vs
Nickel	ND	ND	t/t	ND,	ND,	ND
Sodium	ND	t/s	ND	ND,	ND,	ND
Titanium	ND	t/t	t/t	t/t,	t/t,	t/t

* ND = not detected

t = trace = <0.01 per cent

vs = very small = <0.1 per cent

s = small = <1.0 per cent

TABLE 36.

SEEBECK COEFFICIENT AND RESISTIVITY COMPATIBILITY BETWEEN SiGe BARS
AND FORMULATION 2020 IN AIR AT 1600F

JOHNS-MANVILLE RESEARCH AND ENGINEERING CENTER	Element Type	Exposure Time hr	FORMULATION 2020				DYNAQUARTZ			
			Code No.	Manufacturer's I.D.	Seebeck Coefficient Microvolts/°C	Resistivity Milliohm Cent.	Code No.	Manufacturer's I.D.	Seebeck Coefficient Microvolts/°C	Resistivity Milliohm Cent.
N		0	N-5A	E483RN-5A	167	1.59	N-5B	E483RN-5B	152	1.50
		1000			159	1.64			159	1.64
		2000			166	1.66			170	1.71
		0	N-6A	E484RN-1A	163	1.43	N-6B	E484RN-1B	164	1.45
		1000			156	1.48			160	1.47
		2000			154	1.50			151	1.52
P		0	P-5A	E446RP-5A	99	0.84	P-5B	E446RP-5B	98	0.87
		1000			105	0.90			106	0.89
		2000			101	0.93			104	0.91
		0	P-6A	E448RP-1A	98	0.87	P-6B	E448RP-1B	98	0.88
		1000			103	0.87			104	0.85
		2000			93	0.90			97	0.89

TABLE 37.

SEEBECK COEFFICIENT AND RESISTIVITY COMPATIBILITY BETWEEN SiGe BARS
AND FORMULATION 2020 IN VACUUM AT 1600F

Element Type	Exposure Time hr	FORMULATION 2020				DYNAQUARTZ			
		Code No.	Manufacturer's I.D.	Seebeck Coefficient Microvolts/°C	Resistivity Milliohm Cent.	Code No.	Manufacturer's I.D.	Seebeck Coefficient Microvolts/°C	Resistivity Milliohm Cent.
N	0	N-9A	E484RN-4A	170	1.63	N-9B	E484RN-4B	169	1.52
	1000			137	1.60			138	1.43
	2000			151	1.51			155	1.51
	0	N-10A	E484RN-5A	169	1.52	N-10B	E484RN-5B	168	1.63
	1000			144	1.45			148	1.41
	2000			157	1.48			151	1.46
P	0	P-9A	E454RP-1A	100	0.95	P-9B	E454RP-1B	100	0.92
	1000			102	0.91			108	0.94
	2000			107	0.91			106	0.94
	0	P-10A	E454RP-2A	101	0.96	P-10B	E454RP-2B	100	0.92
	1000			109	0.93			108	0.91
	2000			107	0.96			103	0.93

As was the case with the Irish REFRASIL tests, the Seebeck coefficient and resistivity values for the N elements varied according to their thermal history, and in most cases, the variation was predictable. Elements N-9A and N-9B (Table 37), however, were the exceptions. It will be noted that the 1000-hr data did not satisfy the condition of predictability. However, since both the initial data, and the 2000-hr data did satisfy the condition, it was concluded that the 1000-hr data were in error. This conclusion was further supported by the fact that both samples of the pair behaved similarly, although each was enclosed in a different insulation.

The results of this investigation showed a complete lack of interaction between Formulation 2020 and the silicon-germanium alloys under the test conditions employed.

M. DYNAMIC RESPONSE OF FORMULATIONS 2002 AND 2020

GENERAL

A series of room temperature tests was conducted to determine the dynamic modulus of elasticity (E), the structural damping (G), and the first natural (resonant) frequency of Formulations 2002 and 2020. The 2.5-in. diameter by 2-in. thick specimens were statically preloaded, and dynamically excited by light tapping in the direction parallel to the cylindrical axis of the specimen. The output of an accelerometer, mounted directly above the specimen on a steel fixture comprising part of the static preload, was recorded on an oscillograph. The test was conducted at various levels of preload, and the insulation was afforded no lateral restraint. The test setup and procedure, and the equations used to calculate the dynamic properties were presented in the Fourth Quarterly Report No. AL0-3633-4, dated April 3, 1967.

FORMULATION 2002

Six specimens were subjected to ten static preloads each, ranging from approximately 13 psi to approximately 114 psi, in order of increasing preload. One specimen was also subjected to the same evaluation under decreasing preload conditions.

The effect of static preload on the frequency of first resonance is plotted in Figure 26. Figure 27 represents the change in calculated dynamic modulus of elasticity with static preload. The method of least squares for fitting a curve of the form $y = a + bx$ was used to arrive at the equation:

$$E = 1431 + (9.79)(\text{preload, psi})$$

FIGURE 26.
EFFECT OF STATIC PRELOAD ON FREQUENCY OF FIRST RESPONSE
OF FORMULATION 2002

FIGURE 27.

CHANGE IN DYNAMIC MODULUS OF ELASTICITY
WITH STATIC PRELOAD FOR FORMULATION 2002

The first three preload conditions were not used in the calculation of the above equation since this region appeared to be non-linear. A similarity appears to exist between this region and the one encountered in the static stress-strain data below 35 psi. This non-linearity may be caused by the expansion of the product normal to the laminar plane immediately after molding. It is believed that this expansion is concentrated near the top and bottom surfaces of the product, resulting in a low apparent compression resistance at these low stress levels. It should be noted that the average dynamic modulus of 2100 psi differed only slightly from the static modulus of 2000 psi. No explanation could be found, however, for the increase in dynamic modulus of elasticity with increasing static preload as depicted in Figure 28.

The structural damping averaged approximately 0.5 per cent. The values ranged from 0.41 per cent to 0.52 per cent, and tended to decrease with increasing static preload. The slope of this relationship, however, was considered too small to have any engineering or design significance.

All of the specimens completed the test series without failure.

FORMULATION 2020

The identical test was conducted on six specimens of Formulation 2020. The number of static preloads, however, was limited to four at approximately 12, 46, 79, and 112 psi. The effect of static preload on the frequency is plotted in Figure 28. Although the relationship parallels that for Formulation 2002, the frequency averages about 12 to 13 per cent higher at a given static preload. Figure 29 represents the change in the calculated dynamic modulus of elasticity with static preload. Note that the modulus of 2259 psi, corresponding to the static preload of 12 psi was not plotted, nor considered when fitting the regression to the remaining three data points. The grand average of the dynamic modulus of elasticity values was 2640 psi, which was higher than both its static modulus (1950 psi), and the dynamic modulus of Formulation 2002 (2100 psi). As with Formulation 2002, no explanation can be given for the change in dynamic modulus with static preload.

The damping factor for Formulation 2020 averaged 0.5 per cent. It also varied slightly with static preload (decreasing with increasing load), but this small change was not considered significant.

The load-bearing capability of Formulation 2020 was not as good as Formulation 2002 despite the apparent higher dynamic modulus. Delamination cracks (parallel to the top and bottom surfaces of the specimens) and spalling in the area of the cracks was noted on four of the six specimens

FIGURE 28.

EFFECT OF STATIC PRELOAD ON FREQUENCY OF
FIRST RESPONSE OF FORMULATION 2020

FIGURE 29 .

CHANGE IN DYNAMIC MODULUS OF ELASTICITY WITH
STATIC PRELOAD FOR FORMULATION 2020

when the static preload approached 100 psi (see Figure 30). This may have been due to the reduction in reinforcing value provided by the prefired MICRO-QUARTZ as noted in the modulus of rupture tests. The fact that the stress-strain tests did not uncover the cracking and spalling phenomenon could have been a result of the difference in width to thickness ratios of the test specimens. The stress-strain tests utilized 4-1/2 x 4-1/2 x 1-in. specimens, whereas the dynamic tests utilized 2-1/2-in. diameter x 2-in. thick specimens.

These results, together with the load-relaxation results at 1800F hot face, indicated that Formulation 2020 should not be required to sustain significant static loads.

N. DYNAMIC VERIFICATION OF FORMULATION 2002

As a result of the static and dynamic data generated for Formulation 2002, it was decided to continue the evaluation further with the determination of the dynamic load limits of the material. It also appeared pertinent to determine if the structural properties of Formulation 2002 were sufficiently predictable to permit their use in design calculations. This effort is presented in greater detail since it has not been reported previously.

TEST CONFIGURATION

A dynamic test configuration was devised whereby a steel mass 3 in. in diameter and 6 in. tall weighing 11.9 lb was suspended between two discs of Formulation 2002, each 6 in. in diameter and 1 in. thick. This configuration was then confined within a 6-in. ID x 8-in. high aluminum cylinder, the bottom of which was mounted on an electrodynamic shaker, while a solid plate was bolted to the top end of the cylinder. Specimen access, and insertion of 6-in. diameter shims (to permit variation of the specimen preload) was done through the top. Visual inspection of the specimens and steel mass during the test was provided by cutouts in the wall of the containing cylinder (see Figure 31 for a photograph of the test fixture, minus the top cover).

Accelerometers were attached to the side of the steel mass to measure the motion of the mass in the axial and lateral directions. The response of these accelerometers was used to determine the resonant frequency of the assembly. The total response of the accelerometers (amplitude and frequency) provided indication of any slippage of the mass.

FIGURE 30.

FORMULATION 2020 DYNAMIC RESPONSE SPECIMEN SHOWING SPALLING

FIGURE 3J.
DYNAMIC VERIFICATION TEST FIXTURE

The input acceleration at the test fixture was recorded in "g" units. A transmissibility plotter, which electronically divided the output of the axial mass-mounted accelerometer by the magnitude of the input accelerometer, was used to record response of the system during resonant searches. The resulting ratio was plotted versus frequency. Data from the lateral accelerometer was of secondary importance.

TEST DESCRIPTION

The original intent of this test was to investigate the dynamic characteristics of Formulation 2002 to a maximum vibration input of 20 g. However, after the first several test runs, it was found that the specimens were unable to constrain the steel mass while vibrating near resonance with an input of 10 g. At this point, the intent of the program was altered so that the dynamic characteristics could be investigated as a function of compression preload.

Table 38 summarizes the following description of the six tests. In the first test, the resonant frequency of the specimen/steel mass assembly was determined. A 0.5 g sweep, from 100 to 500 cps, was conducted and the resonant frequency was found to be approximately 180 cps. Investigation of the Formulation 2002 discs did not reveal any indication of slipping.

The second test, conducted with a static preload of 80.4 psi (based on a 3-in. diameter loading area) investigated low level sustained vibration. After sweeping at 0.5 g to determine resonance (185 cps at 0.5 g), the test assembly was subjected to a 2 g dwell for 10 min at the resonant frequency (172 cps at 2 g). Visual examination indicated no slippage of the mass, although some permanent set of the contact surface was apparent. Figure 32 is a photograph of one of the specimens following this test. They were used again in test No. 5, which will be described later.

Test No. 3, conducted with a static preload of 85.0 psi was conducted to determine if the discs could constrain the steel mass for an input of 10 g at the resonant frequency. A sweep was started at 100 cps while a constant 10 g input was maintained. At approximately 160 cps (approaching resonance), slippage of the mass was indicated by data on the transmissibility plotter as well as by visual reference. The approximate acceleration of the mass, at the time of slippage, was 63 g. Figure 33 is a photograph of a specimen following the test.

The remaining specimens were used to evaluate the effect of preload compression on the maximum dynamic load that could be maintained by

TABLE 38.
SUMMARY OF THE DYNAMIC VERIFICATION TESTS ON FORMULATION 2002

<u>Test No.</u>	<u>Sample No.</u>	<u>Static Preload, psi</u>	<u>f_n cps @ 0.5 g input</u>	<u>Remarks</u>
1	-47 & -48	---	180	0.5 g sweep only.
2	-49 & -50	80.4	185	2 g dwell, 10 min, no slippage.
3	-51 & -52	85.0	180	Constant input of 10 g slippage before reaching resonance.
4	-49 & -50	180.6	230	Vibration at resonance, increasing input acceleration, slippage at 6.0 g.
5	-53 & -54	116.5	205	Vibration at resonance, increasing input acceleration, slippage at 5.5 g.
6	-55 & -56	43.0	186	Vibration at resonance, increasing input acceleration, slippage at 2.5 g.

FIGURE 32.
FORMULATION 2002 SPECIMEN FOLLOWING 2 g,
10 MIN VIBRATION DWELL

FIGURE 33.

TYPICAL FORMULATION 2002 SPECIMEN AFTER
MASS SLIPPAGE DURING VIBRATIONAL TESTING

Formulation 2002. Test condition 4, utilizing the samples from test condition 2 (2 g dwell), was conducted with a preload of 180.6 psi while vibrating at the resonant frequency (230 cps at 0.5 g). The input acceleration was increased in 0.5 g increments and maintained for 30 sec at each increment. Upon reaching an input acceleration of 6.0 g, the change in acceleration pattern indicated that the mass was no longer constrained. Visual examination also revealed that the mass had slipped.

Test condition 5 was conducted with a preload of 116.5 psi. While vibrating at resonance (205 cps at 0.5 g), the input acceleration was increased in 0.5 g increments and maintained for 30 sec at each increment. Mass slippage occurred at an input acceleration of 5.5 g.

Test condition 6 was conducted for a preload of 43.0 psi. While vibrating at the resonant frequency (186 cps at 0.5 g), slippage was observed at an input of 2.5 g.

CORRELATION OF RESONANT FREQUENCIES

The equivalent effective loaded area is of primary importance in calculating the theoretical resonance of a suspended mass system such as the one in this test program. In this case, the assumed area could range from a minimum value equivalent to the 3-in. diameter of the steel mass, to a maximum value equivalent to the 6-in. diameter of the Formulation 2002 disc. Due to the limited information pertaining to the structural load path which may be assumed through a thickness of Formulation 2002, an arbitrary 45 degree conical distribution was assumed in calculating the equivalent effective area. This was defined as the area bounded by the 45 degree conical load path, and the insulation surface opposite the mass-insulation interface.

From the dynamic response tests (see Section VII, paragraph M), it was found that the average dynamic modulus of elasticity, E, for this material was 2100 psi. The effective spring constant of the two specimens is:

$$K = \frac{2AE}{L}$$

where: A is the effective area, and L is total thickness of the material.

The equivalent effective area previously defined is determined from a diameter of:

$$(\text{mass diameter}) + 2 \tan 45^\circ (\text{thickness})$$

or

$$3 + 2 \tan 45^\circ = 5 \text{ in.}$$

and

$$A = 25 \pi/4 = 19.63 \text{ sq in.}$$

The single-degree-of-freedom resonant frequency is:

$$f = 1/2 \pi \sqrt{\frac{2AEg}{LW}}$$

where: W is the weight of the suspended mass, 11.9 lb, and g is the acceleration of gravity, 386 in./sec². Then:

$$f = 1/6.28 \sqrt{\frac{2(19.63)2100(386)}{2(11.9)}}$$

$$= 184 \text{ cps}$$

This correlated well with most of the experimental resonances listed in Table 38. Results from test No. 4 did not correlate well, however, and some deviation was noticeable in the results from test No. 5. Therefore, there was presumed to be some dependency on preload when the pressures approach 120 to 180 psi.

The close agreement of theoretical and experimental results for preload pressures from 43 psi to 116 psi confirmed the validity of the dynamic modulus of elasticity data obtained in earlier tests at lower preload pressures.

DYNAMIC LOAD LIMITS

The vibration response level of the suspended mass was measured in tests 3 and 4 (static preloads of 85 psi and 181 psi), and found to be 63 g and 108 g, respectively. The total load exerted on the Formulation 2002 interface by the dynamic response at resonance may be calculated by multiplying the weight of the steel and the response in g's. Thus, the total loads exerted at the time of slippage, or separation, in tests 3 and 4 were:

$$\text{Test No. 3: } (11.9 \text{ lb})(63 \text{ g}) = 750 \text{ lb}$$

$$\text{Test No. 4: } (11.9 \text{ lb})(108 \text{ g}) = 1290 \text{ lb}$$

These values may be compared to the total force exerted by the preload on the steel mass, by multiplying the area of the steel mass by the preload in psi. Thus:

$$\text{Test No. 3: } (7.07 \text{ in.}^2)(85 \text{ psi}) = 600 \text{ lb}$$

$$\text{Test No. 4: } (7.07 \text{ in.}^2)(181 \text{ psi}) = 1270 \text{ lb}$$

From this comparison, it was obvious that slippage of the mass occurred when the resonant response forces of the system overcame the preload forces. This was to be expected if the Formulation 2002 was acting as an elastic body and no structural failure had occurred. The agreement between the calculated preload and experimental separation force in test No. 4 was surprisingly close. The 20 per cent discrepancy in test No. 3 was easily attributable to uncertainties in the method of adjusting preload pressures, and in recognizing the precise time at which slippage actually occurred.

There was insufficient data concerning response of the suspended mass in tests 5 and 6 to substantiate further that the dynamic load limits are a function of the maximum restraint available from initial compression, rather than structural failure of the material. In neither case, however, was there any evidence of significant damage to the specimens. In test 6 the observation of slippage at 2.5 g input (uncertain response) did not appear consistent with results from tests 3, 4, and 5, even if adjusted numerically for the reduced preload in this test (see Table 38). However, this was not thought to invalidate the conclusion, but was considered to be a result of the uncertain surface contact between the MIN-K 2002 and the steel mass at this relatively low pressure.

It was particularly significant that no structural rupture of the insulation material took place in any of the vibration tests. Although the suspension of the steel mass became unstable, and the mass slipped when the resonant response overcame the preload, there was no effect more serious than minor gouging of the sample surface and some permanent set. With proper restraint, the material would, therefore, be suitable for practical applications in vibration environments as high as those applied in this test program.

O. GENERAL APPEARANCE

Formulations 1999, 2002, and 2020 all have an off-white color. As it is fired in air, it takes on a slight yellow shade. In vacuum, or in a reducing atmosphere such as that encountered during the outgassing tests when excessive amounts of hydrogen were present, the insulations turn a dark gray. In both cases, the extent of the shading is a function of the exposure time and temperature.

This phenomena is due to minor changes in the oxidation level and/or the crystalline form of the titania opacifier. The color changes appear to be a very sensitive indication of even the slightest change in the opacifier, particularly under reducing conditions. There is no indication to date, nor any reason to suspect that these changes will alter the radiation blocking efficiency of the titania. This will be evaluated further, however, during the thermal conductivity program which is still in progress.

P. CHEMICAL IMPURITY CONTENT OF FORMULATIONS 1999, 2002, AND 2020

Table 39 presents the typical impurity content of Formulations 1999, 2002, and 2020. The quantities, determined by spectrographic analysis, were reported in terms of the per cent by weight of the metallic ion, although it is probable that most of them occur in the insulation as oxides. The balance of the analysis would be silica.

The analysis for Formulations 2002 and 2020 are identical since the ingredients, and the relative amounts of each, are identical. Greater thermal stability was achieved in Formulation 2020, however, by prefiring the MICRO-QUARTZ to 1800F prior to blending it with the remaining ingredients.

The major improvements of these insulations over MIN-K 1301 were in the iron, sodium, and sulphur content, which were approximately 1.3, 0.5, and 0.4 per cent, respectively, in the standard product. These reductions in impurity levels were a result of the substitution of CAB-O-SIL M5 and silica fiber for SANTOCEL A and asbestos fiber, respectively. The values shown in Table 39 represent average impurity levels, and should not be used as specification maximums, although the variability of the insulation ingredients has been found to be relatively small.

Q. CONCLUSIONS

1. Formulations 1999, 2002, and 2020 at a density of 20 pcf, and containing no binder, had handling strengths adequate for installation into radioisotope thermoelectric generators.
2. The hot face temperature limit of Formulations 1999, 2002, and 2020 was 1200F, 1600F, and 1800F, respectively.
3. Formulations 1999 and 2020 should not be used under static loads while operating at their respective hot face temperatures. Formulation

TABLE 39.
IMPURITY CONTENT OF FORMULATIONS 1999, 2002, AND 2020

<u>Impurity</u>	<u>Weight, per cent</u>	
	<u>Formulation 1999</u>	<u>Formulations 2002, 2020</u>
Aluminum	0.02	0.02
Antimony	0.03	0.03
Barium	< 0.01	< 0.01
Boron	< 0.01	< 0.01
Calcium	0.02	0.01
Iron	< 0.01	< 0.01
Lead	< 0.01	< 0.01
Magnesium	0.02	0.01
Sodium*	< 0.05	< 0.05
Zirconium	< 0.01	< 0.01

* 0.05 per cent minimum estimate by this analysis.

2002 sustained initial static loads of up to 150 psi while at 1400F hot face, although the relaxation of the insulation resulted in a 50 per cent reduction of the static preload after 2000 hr.

4. All formulations rapidly adsorbed moisture from the air. Desorption was also rapid under 230F still-air drying conditions.
5. The thermal conductivity of these formulations in air was as good as or slightly better than the standard MIN-K products. The advantage gained in argon or vacuum was not as great at the higher mean temperatures as originally anticipated, however.
6. Formulations 1999, 2002, and 2020 had excellent machining characteristics. This was a major improvement over the standard MIN-K products.
7. Formulation 2002 was found to outgas only water during heatup to 1400F. This outgassing ceased, however, during the 2000-hr exposure at 1400F.
8. There was no gross incompatibility between Formulations 1999 and 2002 and 2N, 2P, 3N, and 3P lead-telluride thermoelectric elements after 2000 hr at 1000F (isothermal) in argon. A statistical analysis of the few data points indicated, however, that:
 - a. The 10 per cent increase in resistivity of the 2N and 3N elements was not due to the insulations.
 - b. The 10 per cent increase in resistivity of the 2P elements was probably due to contact with the insulations.
 - c. Approximately 10 per cent of the 35 per cent decrease in resistivity of the 3P elements was probably due to contact with the insulations.
9. Formulation 2020 was compatible with N and P silicon-germanium alloys.
10. Dynamic response tests on Formulation 2020 indicated that this material should not be subjected to excessive static preload due to a tendency to spall.
11. Between static preload pressures of 50 psi and 120 psi, the dynamic load limit of Formulation 2002 was reached when the resonant response forces of the system equaled the static preload forces.

VIII. CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

MIN-K Formulations 1999, 2002, and 2020 at a density of 20 pcf, and containing no organic binder, were found suitable for use in radioisotope thermoelectric generators. Each has its specific area of application, although some degree of interchangeability does exist. The areas of application are defined as:

1. Intricate insulation surrounding the PbTe thermoelectric elements.
2. Bulk insulation surrounding the PbTe heat source.
3. Intricate or bulk insulation in an SiGe generator.

Formulation 1999 was specifically designed to allow molding of relatively intricate shapes. It has a hot face temperature limit of 1200F, and therefore is limited to lead-telluride (or lower temperature) service, in direct contact with the thermoelectric elements. Because of its molding capability, its physical strength is slightly below that of the other formulations. It does have excellent machining characteristics, as do all of the formulations. However, it is not recommended that small intricate parts be machined from Formulation 1999.

Although Formulation 2002 cannot be molded into relatively intricate shapes, it is stronger, and hence, is considered to be a better choice for machining operations (over and above incidental sanding or shaving). Formulation 2002 also has a design temperature limit of 1400F for bulk insulation service in PbTe generators. However, tests have shown it to be suitable for service up to 1600F hot face, thus extending its potential to non-load-bearing service in the SiGe generators. At hot face temperatures of 1400F, however, static loads (such as an assembly preload imparted to the heat source) can be sustained.

Formulation 2020 had an 1800F hot face temperature limit for service in an SiGe system. At this temperature, however, it cannot support any static preload without resulting in excessive load-relaxation. It cannot be molded into intricate shapes, but it can be machined easily, thus permitting its use adjacent to silicon-germanium elements.

None of the formulations showed any gross incompatibility with their respective thermoelectric elements. There were indications, however, that the PbTe 2P and 3P elements were affected slightly after prolonged exposure

to Formulations 1999 and 2002. The existence of any effect would have to be verified by more extensive testing due to the limited number of data points, and the isothermal nature of the exposure conditions. Based on the chemistry of these materials, however, there is considerably less likelihood of element contamination with either Formulation 1999 or 2002 than with MIN-K 1301. Although Formulation 2002 was not evaluated for compatibility with SiGe elements, its basic constituents and the relative quantity of those constituents is identical with Formulation 2020 which was found to be compatible.

Of the refractory fiber insulations evaluated, ASTROQUARTZ, DYNAQUARTZ, Irish REFRASIL, and MICRO-QUARTZ are satisfactory for 1800F hot face service adjacent to silicon-germanium elements. These insulations (with the exception of DYNAQUARTZ) were evaluated primarily as packing insulations between and around the N and P legs where module assembly requirements preclude the use of a rigid, premolded material. MICRO-QUARTZ, although superior to the others from a thermal efficiency standpoint, is slightly less stable dimensionally under 1800F isothermal heating. This apparently has not been a problem, however, on SiGe modules which have undergone thousands of hours of simulated service.

GLASROCK No. 25, a rigid foamed silica product, has the best load-bearing capability at 1800F hot face. This characteristic, coupled with its relatively low thermal conductivity (compared to other high density materials of comparable compressive strengths) combine to make this material the best candidate for load-bearing service in silicon-germanium systems.

B. RECOMMENDATIONS

Following the completion of Phase I, other areas of additional product development and improvement became evident. The hot face temperature limit of Formulation 2020 (1800F) has no safety factor for a short-term temperature override, nor is it suitable for service with some future SiGe heat source designed to operate in the 2000F to 2200F range. This stepup in temperature capability requires not just a formula modification, but a complete study of sintering phenomena and new, more stable submicron particles.

Formulation 2002 can support a preload of up to 150 psi at 1400F hot face, although this preload will fade with time due to relaxation of the insulation. A higher density form of this product, modified to minimize the thermal conductivity increase which would normally accompany the density rise, should be investigated, not only to permit greater static loads to be applied, but also to reduce the rate of relaxation under load.

Finally, although GLASROCK No. 25 is the best load-bearing insulation for 1800F hot face service, some reduction in its thermal conductivity is anticipated with the addition of an opacifier to the product.

These recommendations have been favorably received, and work in these areas is in progress under Phase II of this Contract.

It is further recommended that a program be considered to evaluate the effect of assembly conditions and generator outgassing procedures on the performance of lead-telluride thermoelectric elements. Certain procedures currently in effect are stringent primarily because of the outgassing characteristics of MIN-K 1301. It is possible that these procedures can be relaxed as a result of these new insulations, with a resultant decrease in assembly time and cost.