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PROGRESS REPORT NO. 23

MASTER

FOR A PROGRAM OF

THERMOELECTRIC GENERATOR TESTING

AND

RTG DEGRADATION MECHANISMS EVALUATION

Submitted to

The US Energy Research and Development Administration
Division of Nuclear Research and Application
Washington, D. C.

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FOREWORD

This report is submitted to the Energy Research and Development Administration covering work conducted under Interagency Agreement No. E(04-3)-959 by the Jet Propulsion Laboratory and documents all activities covering the period June, July and August 1977. This work is being performed under the technical direction of Mr. Patrick O'Riordan, Office of Technical Development and Special Projects of the ERDA Division of Nuclear Research and Application.

The portion of the report covering the selenide thermoelectric material evaluation is jointly sponsored by ERDA and NASA. The NASA portion is under the technical cognizance of Mr. Lee Holcomb.

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I. Selenide Technology Evaluation

A. Thermal Conductivity Tests

The long-term testing of p-type, singly partitioned thermoelectric legs is continuing. The thermal conductivity data of the experiments which are operated over a temperature gradient ($800^{\circ}\text{C}/400^{\circ}\text{C}$) are summarized in Figure 1. At the present, 6000 hours of thermal conductance data have been accumulated on this set of experiments. The thermal conductivity values shown on this figure all indicate similar trends, i.e., an apparent decrease in value which tends to level off after about 4000 hours of operation. The decreasing thermal conductivity during the early portion of the test may not be real however, since very small changes of thermal interface temperature drops would yield similar results.

The same type of data are presented in Figure 2 illustrating the behavior of the original five p-legs which are operating at a much smaller temperature difference. These samples are also maintained at a constant hot side temperature of 800°C and have accumulated a total of 14,000 hours of test time. A similar decrease of the thermal conductivity values is noticed on these samples. The same phenomenon may be responsible for this change (i.e., a changing interface temperature drop). None of the samples of either experiment is directly instrumented with thermocouples; this may become necessary to determine the real nature of the change and its feasibility is being investigated. All of the samples are continuing on test.

B. In-Gradient Tests

Five p-legs are operated at a constant hot side temperature of 800°C , a total current of 4.8 amps, in a hard vacuum environment. The singly partitioned p-legs are surrounded by fiberfrax insulation and the average cold side temperature is 120°C . At this time, 3300 hours of operating time has been accumulated. However, it was found that some of the data became unstable as

Figure 1. Thermal Conductivity of P-legs

Figure 2. P-leg Thermal Conductivity

the current started to fluctuate considerably. The problem appeared to be an "opening" of the thermoelectric leg. The experiment has been temporarily interrupted, and the system (unfortunately all samples operate on a common vacuum system) opened to air. An evaluation of the problem is in progress, and preliminary indications are that due to rather small spring travels some of the legs might have lost contact. A sample analysis and possible remedies are planned during the next reporting period.

C. Thermophysical Properties and Compatibility Tests

The material loss measurements of the p-type samples are continuing. The experiments may be classified into three different operating conditions: (1) operating environment, vacuum, inert atmosphere (argon), partial CO atmosphere; (2) effect of current gradient on samples and (3) the effect of baffling of various types of insulations versus free sublimation.

The p-type samples in a vacuum environment at a current gradient of 1.6 amp/cm and baffled versus unbaffled have accumulated up to 4800 hours of operation and the loss rate has reached equilibrium (See Figure3). The testing of these samples has been discontinued. As previously reported, the effect of baffling with Fiberfrax 970A paper under these conditions results in a reduction of sublimation by a factor of 7. The loss rate increase factor (LRI) due to the 1.6 current gradient versus zero current gradient is approximately 4-5, and was found to be identical for both baffled and unbaffled samples.

The p-type samples in a low pressure environment of carbon monoxide, 2×10^5 torr, have accumulated 3000 hours of operation and their loss rates also reached equilibrium. The pressure of the CO in the system is maintained at 2×10^{-5} torr (dynamically pumped, i.e., the vacuum pumps are operated normally and the CO gas is continuously leaked into the system). The weight loss rate of these samples is compared to the weight loss rate of samples in a hard vacuum environment, both sets operating under identical conditions; both sets of samples are baffled with Fiberfrax 970A paper insulation and operated without a current gradient

(See Figure 4). The data shows a slight accelerating effect on the weight loss rate due to the CO environment. To evaluate this apparent effect of the CO gas, the pressure has been increased to 2×10^{-4} torr, and a new set of experiments have been initiated at this condition. An initial data point is plotted in Figure 5 versus weight loss in a vacuum environment. Comparing Figures 4 and 5 there appears to be a slight increase in loss rate due to increasing the CO gas pressure from 2×10^{-5} to 2×10^{-4} . However, the increased loss may be partially due to the rather short operating time, 120 hours. The continuation of this, and additional experiments at different pressure levels should identify the potential material loss attributed to the CO mechanism and also complete characterization of the effect of CO on the sublimation rate.

The loss rate of the p-type material in an inert argon environment has reached equilibrium. Although the thermoelectric converter in the GDS units will use xenon gas, experiments to date have been conducted in argon because of the high cost of xenon. In an attempt to equate the relative baffling effectiveness of both gases, calculations were made using the Gilliland equation to obtain the diffusivity of selenium vapor in both argon and xenon. The diffusivity values were then used to calculate the baffling factor. The Gilliland equation which defines the diffusivity of the volatile species in a cover gas is given below:

$$(1) \quad D = \frac{3.26 T^{3/2} [(M_1 + M_2) / M_1 M_2]^{1/2}}{P [V_{b1}^{1/3} + V_{b2}^{1/3}]^2}$$

D - Diffusion Coefficient - cm^2/sec .

T - Absolute Temperature - K

M - Molecular Weight

V_{b1}, V_{b2} - Liquid Molar Volumes at the normal boiling points of the species

P - Pressure - Torr

For the constants listed below:

	Xenon	Argon	Selenium
M	131.3	39.95	78.96
Boiling Point	165 ⁰ K	87.3 ⁰ K	958 ⁰ K
Vbo	42.8cm ³	28.6 cm ³	20*
	gram-mole	gram-mole	gram-mole

* Based on estimate of material density.

At 1000⁰C for selenium/xenon:

$$(2) D = \frac{546}{P}$$

At 1000⁰C for selenium/argon

$$(3) D = \frac{867}{P}$$

The baffling factor was calculated using equations (2) and (3) above in the following equation:

$$(4) B = \frac{t}{D} \sqrt{\frac{RT}{2\pi M}} + 1$$

B = Baffling Factor

t = Boundary layer thickness for the cover gas

D = Diffusion coefficient of "volatile" species in the cover gas.

R = Gas Constant

T = Absolute Temperature

M = Molecular weight "volatile" species

Now using t= 0.15cm as the effective film thickness*, and

$$\sqrt{\frac{RT}{2\pi M}} = 100 \sqrt{\frac{8314T}{2\pi M}}$$

* This thickness is somewhat arbitrary, however it is not our attempt to calculate the actual baffling factor, but rather the ratio of these factors to ascertain if xenon test may be omitted.

Where the factor of 100 is to get the units from m to cm, we get the following baffling factor @ 1000°C:

	Pressure			
	1 Torr	10 Torr	100 Torr	1000 Torr
selenium/xenon	5	41	401	4001
selenium/argon	3.5	26	254	2531

The relative baffling effectiveness of xenon/argon is approximately a ratio of 3/2 based on these calculations. This small ratio thus leads to the conclusion that the exorbitant cost for xenon tests are not justified, as the difference in measured weight losses, using xenon, would fall within the present experimental errors of the argon tests.

The two experiments which have been conducted in argon are: 1) 0.75 atmosphere of argon which has accumulated approximately 3600 hours and 2) 2.0 atmospheres of argon which has accumulated approximately 2000 hours of operation. Analysis of the data (Progress Report #22, June 1977) indicated an anomaly in the test conditions; the weight loss of the samples in the 2.0 atmospheres argon is higher than that of the samples in the 0.75 atmosphere argon at the lower temperature range, 600°C - 800°C, while at the higher temperatures, up to 1000°C, the weight loss rates of the two experiments were comparable and lower than the vacuum environment as expected. The very low weight losses at the low temperature limit the accuracy of the samples for both experiments. The atmosphere of both experiments is being analyzed by gas mass spectrometry to determine the amounts of residual oxygen.

An additional set of experiments has been initiated at lower pressures of argon gas. Two sets of samples are operated (fiberfrax baffled) at argon pressures of 100 mm and 10 mm respectively. The data from these experiments is expected to

determine the effective vapor suppression due to the cover gas as a function of its pressure. Only preliminary data has been recorded on these experiments and longer operating times are required before meaningful analysis of the results are possible. The data from these experiments will be evaluated along with the earlier data of the 0.75 and 2.0 atmosphere argon tests to more accurately determine the baffling factor versus argon pressure.

A new set of tests have been initiated to evaluate the insulation compatibility and baffling effectiveness of the following four insulation materials, including several combinations of these insulations:

1. Fiberfrax 970A paper (Carborundum Co.)
2. Fiberfrax Hi-Fi 660 paper (Carborundum Co.)
3. Astroquartz yarn (J.P. Stevens Co.)
4. Min-K TE 1800 (John Manville Co.)

The Fiberfrax Hi-Fi 660 paper is the insulation presently selected to surround the selenide thermopile for the GDS converter. All of the tests conducted at JPL have been performed with Fiberfrax 970A. One of the purposes of this test is to verify that there is no difference in compatibility and/or baffling effectiveness between these two insulations so that all of the previous data conducted with Fiberfrax 970A will be applicable. The only differences between these two grades of Fiberfrax insulation according to the manufacturer are physical: these are given below.

	<u>Fiberfrax 970A</u>	<u>Fiberfrax HiFi 660</u>
Fiber Diameter	3 Microns	1.6 Microns
Fiber Length	4 Inches	1/2 Inch
Shot Content (Glass Beads)	Standard	Almost None

The Astroquartz insulation is a 99.95% SiO_2 (silica) fiber and of the type used to wrap the SiGe legs for the MHW converters. The Min-K TE-1800 (formerly Min-K 2020) is a molded insulation specifically developed for thermoelectric applications using SiGe alloys.

The insulation test matrix is shown in Table I and a sketch of the test samples is shown in Figure 6. All of these tests are in a common vacuum test station, but use individual furnaces (See Table II). The weight loss rates for the three fiberfrax samples at 900°C after 700 hours show reasonable agreement, with the original rate established for the Fiberfrax 970A, see Figure 7 (upper curve). The Astroquartz wrapped samples appear to show a slight improvement of the mechanical baffling compared to the Fiberfrax 970A. The Astroquartz yarn is wrapped around the sample as it is rotated on its axis, carefully maintaining sufficient tension on the yarn. At each down time when the samples are weighed, the Astroquartz yarn must be removed and new Astroquartz yarn placed on the samples prior to resuming tests. A "control" sample with Astroquartz yarn is being left on test at 900°C , for a longer period of time, to evaluate the effect, if any, of replacing the Astroquartz wrap at each down time.

The weight loss rates for Min-K TE-1800 samples versus the original Fiberfrax 970A data is shown in Figure 8. The baffling effectiveness of both Min-K TE-1800 only and Min-K TE-1800 and Astroquartz wrap versus Fiberfrax 970A after 650 hours at 900°C is improved by a factor of six. Since the baffling factor of Fiberfrax over bare surface sublimation was established to be a factor of seven, the effectiveness of which the Min-K System reduces weight loss is a factor of 42 (6×7).

TABLE I
INSULATION COMPABILITY TEST

Type Insulation	Temperature		
	800°C	900°C	1000°C
JM-MinK TE-1800	X	X	X
Astroquartz Yarn (300-2/8)+ JM-MinK-TE1800	X	X	X
Astroquartz Yarn (300-2/8)	X	X (+ control sample)	X
Fiberfrax 970A 970AH 660 HiFi		X X X	
Fiberfrax 970A + Astroquartz		X	

Figure 6. Insulation Compatibility Test

TABLE II
INSULATION COMPATIBILITY TEST

Type Insulation	Furnace No.					
	1	2	3	4	5	6
	900°C	900°C	800°C	800°C	900°C	1000°C
JM-MinK TE-1800				X	X	X
Astroquartz Yarn (300-28)+ JM-MinK - TE-1800				X	X	X
Astroquartz Yarn (300-28)		X		X		X
Fiberfrax 970A 970AH 660 HiFi	X X X					
Fiberfrax 970A + Astroquartz			X			

Figure 7. Loss Rate of P-Material for Different Insulation Material

Figure 8. Loss Rate of P-Material Comparing
Fiberfrax Insulation with Mink

Isothermal weight loss tests of n-type GdSe pellets, unbaffled and zero current, have been initiated at 1000°C, 1100°C, 1150°C, 1200°C, 1250°C and 1300°C. Prior to the start of these tests, experiments were conducted at 1300°C to determine if the n-type samples could be weighed in air without oxidation occurring. One sample was left on test for 246 hours and another sample was removed and weighed several times up to 169 hours. The sample removed periodically was oxidized and had less weight loss. To verify this occurrence, the samples were switched and again the sample removed periodically was oxidized. An examination of the test stations revealed that backstreaming of the diffusion pump -silicone oil which is a potential source of oxygen, had occurred in the test station in which the sample was periodically removed. The problem was found to be a defective high vacuum valve which occasionally did not operate properly, thus allowing a "burst" of diffusion pump oil into the test chamber during venting. This problem has since been corrected. A repeat of the test in the clean station showed no oxidation of the sample after repeated weightings in air. It was thus concluded that minute amounts of oxygen pick up during the weighing in an air environment would not significantly alter the weight loss rates. These initial weight loss rates vs. temperature after only 184 hours are plotted in Figure 9. The loss rate is compared in this Figure with the p-type material loss rate under identical conditions (i.e. - vacuum-unbaffled) and shows the n-type GdSe rate to be about three decades lower than the p-type material.

Figure 9. Loss Rate of N-Material in Vacuum (Unbaffled)

D. Accelerated Resistance Module Tests

One of the objectives of this experiment is to determine whether the electrical resistance of the fiberfrax insulation deteriorates as a result of either material sublimation deposits or copper whisker growth. The method of accelerating the operating time for the experiment was discussed in some detail in the previous report (Progress Report No. 22). Briefly, a p-type pellet is operated at an enhanced current gradient to simulate the equivalent material loss, which a doubly segmented p-leg of the current flight system design (SIG) would experience during a 5 year mission. The size of the p-pellet and the current gradient across it was selected to achieve this equivalency after 1300 hours of operation.

The module thus was operated in a vacuum environment with a current gradient of 10 amp/cm at a hot side temperature of 850°C. The original test plan assumed that after 1300 hours of operation under these conditions, the amount of material loss would equal that of a flight p-leg in five years of operation. This original calculation will only be valid, if the dimension of the leg does not change, since any change (decrease in length) will reduce the current gradient. After 1320 hours of operation, the experiment was stopped. By this time it was found that the current path of the sample had opened. The disassembly of the module showed that the pellet had reduced in length as a result of both the weight loss and deformation. Figure 10 shows a sketch of the p-pellet after disassembly. The original

Figure 10. Sketch of P-Pellets after Accelerated Testing

size and geometry of the pellet is superimposed on the sketch for comparison. A total reduction in length of 0.26 cm (25%) had occurred. This shortening was responsible for the "opening" of the current path, since the compression of the springs which were used to provide an original 150 psi of pressure, no longer provided positive contact between the pellet interfaces.

The shortening of the pellet combined with the somewhat increased diameter at the hot side, changed the ℓ/A ratio considerably. For example, the loss rate of the very top most (hottest) portion of the pellet with the original geometry, loses weight at a rate of 1.73×10^{-3} g/cm-hr, while the same segment, at the end of the test with its final geometry, only loses 3.2×10^{-4} g/cm-hr. The total loss of the sample was therefore considerably reduced from the originally calculated weight loss. The actual weight loss of the sample during the 1300 hr. test has been calculated and measured by several methods i.e. measured weight loss, weight loss calculated by accounting for a changing ℓ/A etc. Based on these calculations, the weight loss was determined to be about 0.17 grams. This corresponds to an equivalent flight system operating time of roughly 22,000 hrs. *

The measured shunt resistance between the pellet and all three resistance probes remained essentially unchanged throughout the length of the experiment at an average value of 2×10^8 ohms. The rather stable and high value of resistance is a preliminary indication that a shunt resistance degradation might not take place in the actual SIG generator. However, the equivalent operating time of approximately 20,000 hours is too short to conclusively eliminate this mechanism. A new module is presently being assembled, using softer, and thus larger springs, which will allow the experiment to operate for a longer time period.

* Based on the weight loss data vs. operating time given in the May '77 Selenide Design Review (Page 47)

E. Liaison

A working group meeting on Selenide Insulation compatibility which was held at ORNL on July 27, 1977 reviewed the status of current effort and outlined future tasks to be conducted by the various participants. Highlights of the meeting and an agenda are given below.

GDS Design Studies (Teledyne)

The fabrication of the GDS-I unit is scheduled to start this Fall and be completed the first month of CY 1978. The insulation for the thermoelectric module will be Fiberfrax HiFi 660H paper. There is a sufficient quantity at TES and 3M for the GDS units. 3M anticipates changing to JM Co.'s TE 1800 Min-K insulation for the flight system. The replacement of the load bearing insulation "Cotronics" 360 has not been resolved. The prime candidate currently is ORNL's Carbon Bonded Carbon Fibrous Insulation (CBCF). The getter alloy and design has been selected and preliminary tests are now being planned. 3M has used the same getter alloy in some of their module tests. Getter alloy selected is Zr + 12.5 a/o Ti.

Compatibility and Outgassing Studies (3M)

A detailed procedure as evolved by 3M for the "preliminary" (as received insulation) and secondary (after ass'y into unit) bake out and out-gassing procedures for the fibrous insulation was described in detail.

The proposed limit of 0.3 mg oxygen level in the TE module section was reviewed by 3M and reiterated that this was a "safe" level (worst case). Their calculations indicated the following relationship of oxygen level vs TE efficiency.

Insulation Development - Carbon Bonded Carbon Fibrous Insulation (CBCF) ORNL/BMI

The CBCF insulation is fabricated at the Y-12 plant, and tests to date have shown high compressive strength as fabricated. Outgassing studies at BMI (Report BMI-X-682, July 12, 1977) recommends a 1500°C outgassing schedule. Tests at ORNL show that some graphitization occurs at 1300°C. This high temperature processing may affect thermal conductivity, residual impurities, and compressive strength. The "as fabricated" density, outgassing techniques, application requirements, low 'K' and 150 psi compressive strength, have to be resolved.

Graphite-Carbon Outgassing (BMI)

Outgassing studies including chemical analysis will be continued on:

- (1) Heater Block - Purified ATJ Carbon, Grafoil, CBCF, pyrolytic-graphite, etc.
- (2) All fibrous insulations
- (3) Compatibility of Carbon/Graphites with fibrous insulation.

Insulation Compatibility (ORNL)

Results of outgassing experiments or reducing the impurities levels in Zircar, Min-K 1400 and 1800 and Fiberfrax HiFi 660 H were presented. The high outgassing temperatures used, although effective, resulted in significant densification and additional shrinkage at service temperatures: Lower temperature outgassing procedures are being evaluated.

Pt 3008 - Insulation Compatibility Studies (ORNL)

Pt 3008 in contact and/or close proximity with 'outgassed' Fiberfrax, Min-K TE 1800, and Cotronics 360 in ampoule tests at 1000°C in vacuum showed no loss in physical strength or reactions. However, in close proximity to Cu₂Se at 950°C, a reaction occurred with severe degradation in physical strength.

Samples of TPM217 p-type were exposed to Pt3008 by 3M at 850°C for 1000 hours in Xenon atmosphere, and showed no reaction or loss of strength. This was attributed to the baffling effectiveness of Xenon.

Temperature gradient tests, which simulate the SIG condition show at low partial pressures of Se- (3×10^{-3} - 5×10^{-2}) no embrittlement of Pt 3008 occurred. Another gradient test with Cu_2Se at 850°C ; Pt 3008 at 1025°C and a "cold finger" at 200°C ; the Se plated out at the cold end, and no significant reaction occurred with the Pt 3008. These gradients were designed to simulate the GDS operating conditions.

Outgassing Studies - (GA)

Knudson cell experiments and mass spectrometry analysis will be conducted on insulations before and after primary and secondary outgassing. Weight change and dimensional shrinkage will also be monitored. The thermodynamics of the various systems will also be analyzed for possible reactions.

Insulation Compatibility - TPM217 (JPL)

The results of the tests conducted to date on the compatibility and baffling effectiveness of the various types of insulation were presented and are described in an earlier section of this report.

Summary

- (1) The load bearing insulation replacement for Cotronics 360 has to be resolved.
- (2) The primary and secondary outgassing procedures for all of the insulations in the GDS systems have to be specified. As part of establishing these procedures, TES will furnish samples for chemical analysis to GA, ORNL, BMI, and 3M in an attempt to correlate results.
- (3) The flight system will use Min-K TE 1800 in the thermoelectric module.
- (4) Getter Design and Material Testing to be conducted.
- (5) Elimination of Min-K TE 1400 as load bearing requires use of Zircar and design change.
- (6) Compatibility of all the insulation will require extensive testing once all the outgassing procedures are specified.

Insulation Compatibility Working Group Meeting ORNL - July 27, 1977

AGENDA

Start 9:00 a.m.

Status presentations on work in
"Progress" and "Planned"

W. Barnett/TES

GDS - Design Status and Program
Tasks

J. Hinderman/3M Co.

R. Ericson

A. Schaffauser/ORNL

ORNL Effort - Insulation Program
Status

J. Keiser/ORNL

Pt-3008 Compatibility Studies

G. Wei/ORNL

Insulation Characterization and
Development of Fibrous Insulation

E. Skrabek/TES

Insulation Studies

L. Garvey/JPL

Insulation/TPM217 Studies

II. Silicon Germanium Technology

A. Thermoelectric Property Characteristics of SiGe

The characterization of the time and temperature dependence of the thermoelectric properties of n- and p-type 78 a/o Si - 22 a/o Ge and 80 a/o Si - 20 a/o Ge alloys was continued during the present reporting period. The characterization is being performed in terms of two different types of isothermal annealing tests. The first type of annealing test involves the isothermal annealing of parallel-epipedal samples, with continuous monitoring of electrical resistivity. The annealing is being conducted in two separate test facilities, with each facility being devoted to silicon-germanium alloy test samples of one of the two compositions. The second type of annealing test involves the isothermal annealing of cylindrical test samples which are periodically evaluated in a comparative thermal conductivity apparatus for changes in that property. Because of the curtailed nature of the present program, no measurements have been performed during the present fiscal year on the thermal conductivity test specimens; it is anticipated that some measurements will be performed prior to the end of the program. All of the isothermally annealed test samples in both types of annealing tests are being annealed at temperatures in the range of 300 to 1000°C. The annealing is being conducted in a vacuum environment.

The isothermal annealing tests which provide data on the time and temperature behavior of the electrical resistivity of the test samples were continued throughout the present reporting period. The first of these tests includes 34 n- and p-type 80 a/o Si - 20 a/o Ge alloy test samples that had undergone continuous annealing of 46,978 hours as of the end of the present reporting period. The second isothermal annealing test involves 90 n- and p-type 78 a/o Si - 22 a/o Ge alloy test samples that had undergone 26,352 hours of continuous annealing as of the end of the present reporting period. A number of the higher temperature test specimens in each test had lost one or more of their instrumentation lead wires and/or thermocouples as of the end of the present reporting period. Nevertheless,

the tests are being continued because it is anticipated that electrical resistivity data will be obtained on each test sample at room temperature upon the termination of the tests at the end of the program. The room temperature data thus obtained can be extrapolated to appropriate test temperatures with reasonable accuracy. In this manner, electrical resistivity data will be obtained for all of the test samples, even though the data for the highest temperature samples are intermittent. Before the end of the program, it is anticipated that the test data will be subjected to detailed analysis that will culminate in a final projection of electrical property data as a function of time and temperature for the silicon-germanium alloys being tested; the electrical resistivity data will come directly from the test results, while the corresponding Seebeck coefficient data will be derived from a previously established relationship between electrical resistivity and Seebeck coefficient.

The isothermal annealing of the thermal conductivity test specimens includes 48 n- and p-type samples of 78 a/o Si - 22 a/o Ge and 80 a/o Si - 20 a/o Ge alloys, with 15 samples possessing the latter composition and 33 samples possessing the former composition. As of the end of the present reporting period, the thermal conductivity test specimens had undergone isothermal annealing in the range of times of 14,000 to 21,000 hours, with different test samples having been annealed for different times within this time range. As already stated, these test samples are being annealed without interruption and without the thermal conductivity data being obtained on them. Prior to the end of the program, it is planned to perform thermal conductivity measurements on some of these test samples. At that time, thermal conductivity projections on the two types of alloy will be made as a function of time and temperature. In combination with similar projections on the electrical properties, the thermoelectric properties of the silicon-germanium alloys with the two different compositions will be completely characterized. In view of the mathematical models being used in data analyses, the thermoelectric property projections will extend far beyond the actual test times of the test samples in both types of annealing tests.

A power failure was experienced by all of the isothermal annealing tests during the present reporting period. The power failure lasted for several hours and during this time, all of the test samples cooled to essentially room temperature. Upon the resumption of power, the test samples were heated to their original temperatures and temperatures were closely monitored in order to assure the obtainment of proper test temperatures. Inasmuch as both the cooling and the heating of the test samples occurred very rapidly, no change in the properties due to this occurrence is anticipated. In fact, the electrical resistivity of the parallel-epipedal test samples was compared prior to and after the power failure and no noticeable change was apparent. It is thus concluded that also the higher temperature test samples that no longer possess instrumentation wires and also the thermal conductivity test specimens without instrumentation did not experience any property change during the interruption of test.

B. MHW-TBC-1 Generator

After 37,100 hours of operation, the generator developed a massive short and power output decreased to zero. The unit was removed from the test station and a detailed analysis of the generator test conditions and postmortem examination of the generators has been initiated. The forward end pressure dome has been taken off and the heater removed. Initial resistance measurement of the modules appear reasonable, but the modules are shorted to the shell (ground).

Photographs will be taken as disassembly proceeds and an analysis of the foil material, SiGe unicouples, etc., will be conducted to evaluate the cause for the generator failure. As part of this analysis, it is planned to relate the findings, where applicable, to the current Voyager flight generators.

C. Power Prediction for LES 8 and LES 9

Output Power Predictions for the LES Flight RTGs

The four thermoelectric generators which provide the power for the Lincoln Laboratory Experimental Spacecrafts LES-8 and LES-9 are of the same type and similar in design as are used for the Voyager spaceflight mission. The computer code DEGRA, which was developed and is used for the performance prediction of the Voyager RTGs, was modified to predict the available output power of the LES type generator. These four generators have accrued about 8,000 hours of actual flight operation in an earth orbit flight path. The modified DEGRA code predicts the available output power from these generators for extended time periods (up to 90,000 hours). At the same time, the accuracy of the code is compared with the actual telemetry data obtained from the flight generator. The result indicates excellent agreement between the real data compared with DEGRA and predicts a 12-13% total power loss for the LES power system after five years of mission time.

DEGRA Output Power Predictions

The DEGRA computer code was developed for the Voyager type RTGs and had to be slightly modified to simulate the LES converters. The code was then programmed to produce an initial (1500 hours) generator output power of 152 watts. This particular output power level was selected as being representative of the LES generators which produced an average initial power of this magnitude. This average output power represents the mean of the maximum and minimum power produced as a result of a cyclic cold junction temperature. The temperature variation is due to the particular orbit of the spacecraft around the earth which causes a change in the incident solar flux intercepted by the generators.

The rates of most degradation mechanisms, other than isotope fuel decay,

are temperature sensitive. As a result of the varying cold side temperatures, the hot side temperatures of the generator and consequently the "effective degradation" temperature also change. Different output power profiles can conceivably result by varying the degradation temperature. Two sets of DEGRA runs were therefore made; (1) the cold side temperature was assumed to be 290°C (the average of the daily variations) and (2) the cold side temperature was increased to 300°C which corresponds to the upper value of the daily temperature cycles. For each of these temperatures, the generator output power was projected for two basic conditions: (1) our present model for nominal degradation which assumes that the silicon nitride (Si_3N_4) coating remains intact throughout the life of the generator and (2) our "most likely worst case" model, in which case the Si_3N_4 coating is postulated to have ceased any useful function after 10,000 hours of operation. The "most likely worst case" model further assumes that the shunt power losses (the losses which are caused by a decreasing shunt resistance between the thermopile and the metallic thermal insulation) are increasing at a high rate of change. (For a more detailed description of the various degradation mechanisms and their rates, see Reference 1.)*

The output power profile as a function of operating time, assuming a cold side temperature of 290°C , is illustrated in Figure 11. The upper curve shows the output power for the nominal degradation model. The lower curve corresponds to the "most likely worst case" degradation mode. Similar data is depicted in Figure 12 for the case where the cold side temperature was raised to 300°C .

The nominal performance predictions for either degradation temperature (i.e., $T_{\text{cold}} = 290^{\circ}\text{C}$ or 300°C) shows the output power of the generators to decrease by 20% at the end of 90,000 hours. More significantly, it appears that even

* Reference 1. "Degradation Model for an RTG with a Silicon Germanium Thermopile", G. Stapfer, JPL report 900-755, September 1976.

POWER PROFILE

Figure 11. Output Power Prediction at 290°C Cold Junction Temperature

POWER PROFILE

Figure 12. Output Power Prediction at 300°C Cold Junction Temperature

with the higher degradation temperature, the same amount of power loss will occur.

Performance Comparison

The comparison between the DEGRA predicted output power and the flight generator data has to be normalized to the initial output power since the output power from the flight generators continuously varies between a minimum and maximum value, following the radiator temperature profile. The ratio of output power to the original output power at launch (P/P_0) is illustrated in Figure 13 for the four flight generators. Three of the four generators (LES 9-1, LES 9-2 and LES 8-1) degrade at almost identical rates, while the fourth generator (LES 8-2) exhibits a somewhat faster initial degradation rate. The normalization of the DEGRA data as shown in this figure is based on an initial Beginning of Mission (BOM) "age" of 1500 hours. That is, all four generators were assumed to have the same BOM age. The determination of the age at launch is critical, since the early degradation rate of any generator which uses the SiGe alloy strongly depends upon the dopant precipitation which proceeds rapidly during the initial operating time. An additional uncertainty as to this age lies in the fact that some of the output power which is lost due to the dopant precipitation mechanism will be regained (if the generator was stored at a lower temperature, i.e., in short circuit condition, prior to launch) at the resumption of normal operating temperatures. All of these variables are reflected in the early degradation rate, however a comparison with DEGRA is still possible by selecting different BOM ages. Figure 14 compares the LES 8-2 generator with the DEGRA predictions based on a 500 hour BOM age. The good agreement which thus results with this lower BOM age suggests that this generator had a different time-temperature history prior to launch. A check of the total storage and operating time of this generator is in progress.

Also shown in Figure 13 are the rates of decrease in output power as predicted

by DEGRA. The upper curve again represents our best estimate for nominal behavior while the lower curve shows the rapid change which would result from a premature (10,000 hours) loss of the Si₃N₄ coating. The correlation between the predicted rate and the actual observed rate is excellent as is evident from the graph. If the flight generators continue to follow the DEGRA predictions, the available output power after five years of operation will have decreased by 12-13% from the original BOL power.

III. Thermoelectric Generator Test and Evaluation

Thermoelectric generators, representing recent and advanced technology, assembled with lead telluride, TAG-85 and silicon-germanium materials are being tested at JPL. These generators are: the HPG, the Transit, the Ring Converter and the 25 W(e) Reference Generator. Also generators E-5 and F-1-E representative of the MHW type generators, are on test.

A. High Performance Generator, HPG SN-2

This generator has operated for a total time of 27,456 hours. During the 2,206 hours of operation the generator output power has decreased by 2 watts, to its present value of 139 watts. In this same period of time the generator open circuit voltage has slightly decreased to 26.09 volts, but the internal resistance of the generator remained essentially the same (1.19 ohms). The generator hot and cold junction temperatures have decreased by 10°F to the present values: $\text{avg } T_h = 994^{\circ}\text{F} \pm 5^{\circ}\text{F}$ and $\text{avg } T_c = 350^{\circ}\text{F} \pm 3^{\circ}\text{F}$. These changes in the generator hot and cold junction temperatures occurred at 25,906 hours, at which time the generator environmental chamber was evacuated and backfilled with helium to improve the thermal conductance of the system.

The generator degradation rate during the past 5000 hours has been 0.15%/1000 hours. The generator history is illustrated in Figure 15.

B. Transit Generator, QM-III

This generator has operated for a total accrued time of 30,532 hours. During the last 1104 hours of operation the generator power output has decreased by 0.59 watts to its present value of 14.27 watts.

The generator operation was interrupted for approximately 1100 hours, due to a number of leaks in the vacuum system. The generator was cooled down to ambient room temperature and the vacuum system is being repaired.

1) Subgenerator G_1 . This generator performance remained constant in that period of time. ($P_o = 6.11$ watts, $E_{oc} = 2.35$ volts ± 0.05 volts, $R_{int} = 217$ milliohms,

Figure 15. HISTORY OF HPG S/N-2 QIN 2430 W E. 151

± 5 milliohms, avg $T_h = 408^{\circ}\text{C} \pm 5^{\circ}\text{C}$ and avg $T_c = 150^{\circ}\text{C} \pm 3^{\circ}\text{C}$.) During the last 5000 hours of operation, the subgenerator output power has practically remained the same. The history of generator #1 is illustrated in Figure 16.

2) Subgenerator G_2 . During the last 1104 hours of operation, this generator output has decreased to 2.92 watts (decrease of 0.13 watts). In the same time, the generator open circuit voltage remained practically the same at 2.30 volts ± 0.05 volts, and the internal resistance has slightly increased to 430 milliohms. The generator hot and cold junction temperatures remained the same ($T_h = 413^{\circ}\text{C} \pm 5^{\circ}\text{C}$, $T_c = 143^{\circ}\text{C} \pm 3^{\circ}\text{C}$). The generator degradation rate for the last 5000 hours of operation was 2.3%/1000 hours. The history of generator #2 is illustrated in Figure 17.

3) Subgenerator G_3 . This generator output power performance has decreased 0.36 watts in the last 1,104 hours of operation, to its present value of 5.24 watts. During the same time, the open circuit voltage remained the same at 3.84 volts ± 0.05 volts, but the internal resistance has increased to 699 milliohms (increase of 34 milliohms). The generator average hot and cold junction temperature remained constant at $411^{\circ}\text{C} \pm 5^{\circ}\text{C}$ and $146^{\circ}\text{C} \pm 3^{\circ}\text{C}$. The generator degradation rate for the last 5000 hours is 3.1%/1000 hours. The generator test is illustrated in Figure 18.

C. Ring Converter

This generator has operated for a total accumulated time of 28,012 hours. During the last 1299 hours of operation, the generator output performance remained constant ($P_o = 13$ watts, $E_{oc} = 4.067$ volts ± 0.05 volts, $R_{int} = 305$ milliohms ± 5 milliohms, $T_h = 448^{\circ}\text{C} \pm 5^{\circ}\text{C}$ and $T_c = 175^{\circ}\text{C} \pm 3^{\circ}\text{C}$). During the past 5000 hours of operation, there occurred no noticeable change in the generator performance characteristic.

The converter operation has been interrupted temporarily, as the vacuum system required a major overhaul. The converter history is illustrated in Figure 19.

D. RCA Reference Generator

This generator has operated for a total accrued time of 55,721 hours. During

Figure 16.

HISTORY OF TRANSIT GENERATOR NO. 1
ORIGINAL Q_{IN} 774 WATTS EL 1.4 VOLTS

Figure 17. HISTORY OF TRANSIT GENERATOR No. 2
ORIGINAL Q_{IN} 774 WATTS E_L 1.4 VOLTS

Figure 18. HISTORY OF TRANSIT GENERATOR No. 3
ORIGINAL Q_{in} 774 WATTS E_c 2.6 VOLTS

Figure 19. HISTORY OF RING CONVERTER
 P_{in} 388 WATTS E_L 2.9 VOLTS

the last 1474 hours of operation, the generator output power has decreased by 0.22 watts to its present value of 22.08 watts. During the same period of operation the generator open circuit voltage and internal resistance slightly increased ($E_{oc} = 12.63$ volts, $R_{int} = 1.80$ ohms).

Since the last report, the generator operation was interrupted for approximately 700 hours to replace one of the burned-out heater carbon rods and to repair the vacuum system. After these repairs, the generator resumed life tests.

The generator degradation rate over the last 5000 hours of operation was 0.96%/1000 hours. The history of the generator is illustrated in Figure 20.

E. MHW Generator Tests

The initiation of the life tests of the MHW generators was delayed by the transfer and installation of the test equipment in a new test location. During this operation, an accidental shutdown of the roughing pump contaminated the test system to be used for the test of F-1-E generator with oil. The generator itself was not affected, since it was kept in the shipping container during the relocation. The contamination required a disassembly and thorough degreasing of the vacuum system which has been since reassembled and is undergoing final checkout. The E-5 generator is at present starting again the life testing in the new system which utilizes an ion-pump.

The effect of the power input on the power output, based on experimental data, is shown for E-5 in Figure 21 and for F-1-E in Figure 22. In both cases, the voltage output was maintained at the nominal operating voltage of 30 volts.

Figure 20.

R.C.A. REFERENCE T/E GENERATOR

 E_L 6.00 VOLTS, Q_{IN} 425 WATTS