M&R
DE-AI-03
79ET 33062
8.1

DOE/ET/33062--T1

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

715-53

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

PROGRESS REPORT NO. 35
FOR A PROGRAM OF
THERMOELECTRIC GENERATOR TESTING
AND
RTG DEGRADATION MECHANISMS EVALUATION

Submitted to

The US Department of Energy
Division of Advanced Nuclear Systems and Projects
Washington D.C.

Prepared by

A. Lockwood

V. Shields

Project Engineers

AI 03-79 ET 33062

Approved by

Jack F. Mondt

J. F. Mondt, Supervisor
Nuclear Thermal-to-Electric Power Group

by

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

May 1980

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

REPORT DISTRIBUTION LIST FOR JPL
INTERAGENCY AGREEMENT NO. E(04-3)-959

Carl Alexander (BMI) (1 copy)
D. Buden (LASL) (1 copy)
California Patent Group (DOE, SAN) (1 copy)
Norbert Elsner (GA) (1 copy)
E. F. Hampl, Jr. (3M Company) (3 copies)
W. Hudson (NASA-OAST) (1 copy)
C. E. Kelly, Jr. (GE) (1 copy)
H. Kling (Fairchild) (1 copy)
John McKiernan (Sandia) (1 copy)
J. Lombardo (DOE-NRA) (1 copy)
J. McNeff (USAF) (1 copy)
J. P. Mullin (NASA-OAST) (1 copy)
P. O'Riordan (DOE-NRA) (6 copies)
W. Osmeyer (Teledyne Isotopes) (4 copies)
Valvo Raag (Synca1) (1 copy)
Hilary Rauch (DOE, SAN) (1 copy)
R. Riebling (NASA-OAST) (1 copy)
A. C. Schaffhauser (Oak Ridge) (1 copy)
G. Silverman (GE) (1 copy)
W. Von Flue (DOE, SAN) (1 copy)
William W. Ward (Lincoln Lab) (1 copy)

INTERNAL DISTRIBUTION

F. Bell	277-102
G. Bodt	177-102
A. Bridgeforth	198-220
R. Campbell	277-102
J. Casani	169-427
A. Cherniack	198-112D
K. Dawson	198-102
R. Draper	233-307
R. Goldstein	122-123
R. Heacock	264-443
T. Hsieh	277-102
R. Ivanoff	277-102
H. Johnson	198-220
J. Klimberg	177-102
J. Leising	180-701
A. Lockwood	277-102
J. Longoria	180-530G
J. Mondt	277-102
L. Noon	277-102
L. Packard	198-220
L. Putnam	277-102
J. Savino	198-112D
J. Schwartz	233-307
V. Shields	277-102
R. Spehalski	169-427

INTERNAL DISTRIBUTION (Continued)

G. Stapfer	277-102
P. Wiener	198-220
A. Zoltan	277-102
D. Zoltan	277-102

FOREWORD

This report is submitted to the Department of Energy covering work conducted under Interagency Agreement No. E(04-3)-959 by the Jet Propulsion Laboratory and documents all activities covering the period of March - April 1980 performed under the technical direction of Mr. Patrick O'Riordan Power Systems Section, Space and Terrestrial Systems Branch of the DOE Division of Advanced Nuclear Systems and Projects.

CONTENTS

I.	SUMMARY -----	1
II.	SELENIDE TECHNOLOGY EVALUATION -----	2
	A. THERMAL CONDUCTIVITY TESTS -----	2
	B. INGRADIENT TESTING -----	2
	C. THERMOPHYSICAL PROPERTIES AND COMPATIBILITY TESTS -----	13
III.	SILICON GERMANIUM MATERIALS TECHNOLOGY -----	18
	A. PROPERTIES OF SiGe PRODUCED BY GE -----	18
	B. PROPERTIES OF SiGe ALLOYS WITH GaP ADDITIONS -----	18
IV.	THERMOELECTRIC GENERATOR TEST AND EVALUATION -----	24
	A. HIGH PERFORMANCE HPG S/N-2 -----	24
	B. MHW GENERATOR Q1-A -----	26
	C. 18 COUPLE MODULES S/N-1,2,3 -----	26
V.	MHW FLIGHT PERFORMANCE -----	40

Figures

1.	Thermal Conductivity Test N-Type -----	3
2.	Thermal Conductivity Test N-Type, Normalized -----	4
3.	Ingradient Test, O/C Voltage, N-Type -----	5
4.	Ingradient Test Seebeck Voltage, N-Type -----	6
5.	Ingradient Test Resistivity, N-Type -----	7
6.	Ingradient Test Load Power, N-Type -----	8
7.	Ingradient Test O/C Voltage Versus Time, P Type -----	9
8.	Ingradient Test Seebeck Voltage, P Type -----	10
9.	Ingradient Test Resistance Versus Time, P Type -----	11
10.	Ingradient Test, Load Power, P Type -----	12
11.	Ingradient Test, Load Voltage Traces, Legs #3 and #4 -----	14
12.	Ingradient Test, Load Voltage Traces, Legs #1 and #2 -----	15
13.	Ingradient Test, Load Voltage Traces, Legs #1 and #4 -----	16
14.	Isothermal Weight Loss N-Type O ₂ Environment, 10 ⁻⁴ Torr -----	17
15.	Free Sublimation N-Type SiGe 78% Si -----	19
16.	Free Sublimation P-Type SiGe 78% Si -----	20
17.	Free Sublimation N-Type SiGe 63% Si -----	21
18.	Free Sublimation P-Type SiGe 63% Si -----	22
19.	Sublimation Rates vs Reciprocal Temperature Comparisons -----	23
20.	HPG S/N-2 History -----	25
21.	Parametric Test of HPG S/N-2 -----	27
22.	Q1-A History -----	28
23.	Q1-A History -----	29
24.	Q1-A Power Out Versus Time -----	30
25.	Parametric Test of ETG Q1A -----	31
26.	18 Couple Module S/N-1 Resistance, Foil to Module -----	33

27.	18 Couple Module S/N-1 Test History -----	34
28.	18 Couple Module S/N-1 Parametric Test -----	35
29.	18 Couple Module S/N-3 Resistance, Foil to Module -----	37
30.	18 Couple Module S/N-3 Test History -----	38
31.	18 Couple Module S/N-3 Parametric Test -----	39

SECTION I

SUMMARY

The n-type selenide legs after 14,000 hours continue to show reasonable agreement with the 3M Co. published data.

In the ingradient testing after 14,700 hours the n-legs show serious degradation in power to load.

Weight loss measurements on the first samples of material produced by G.E. match the results previously obtained on R.C.A. material from the MHW program.

The remaining MHW generator on test Q1-A has accumulated 22,519 hours and performance remains stable. The 18 couple modules S/N-1 and -3 previously tested at RCA show no significant change in operation during the current JPL testing.

No changes in the trends of degradation of LES 8 and 9 and the Voyager RTGs have been observed.

SECTION II

SELENIDE TECHNOLOGY EVALUATION

A. THERMAL CONDUCTIVITY TESTS

The long-term testing of the n-type legs has been continued, using calorimeters similar to those used for the p-type legs (see reports No. 26, 5/78 and No. 27, 8/78 for experimental details). The legs operate over a temperature gradient of $T_H = 800^{\circ}\text{C}$ and a maximum $T_C = 250^{\circ}\text{C}$ and have accrued approximately 14,000 hours of operation. The thermal conductivity values for the four legs are shown in Figure 1 and normalized to the original value ($K_0 = 20$ hours) in Figure 2, as a function of operating time. The thermal conductivity values for three of the four legs has remained relatively stable; the sharp upward shift in thermal conductivity of No. 4 evident at 10,000 hours has apparently stabilized at the higher level.

B. INGRADIENT TESTING

Testing of both n and p type selenide thermocouple legs is continuing. Experimental details of the test setup may be found in Progress Report No. 27, pp 9, 14, and in Progress Report No. 25.

Results for the three remaining GdSe legs (Nos. 1, 3, 4): The performance data is updated in Figures 2 through 5. 14,700 hours of testing had accrued 5/1/80. This set of legs continues to suffer serious degradation of power output (Figure 6).

Figures 7 through 10 show the results for four unsegmented p-type Cu_2Se legs of more recent design using Astroquartz silica fiber and Min-k slurry wrapping. The obvious dichotomy in results for the two pairs of samples 1 and 2

Figure 1. Thermal Conductivity Test N-Type

Figure 2. Thermal Conductivity Test N-Type, Normalized

OPEN CIRCUIT VOLTAGE VS. TIME
 N TYPE, GD-SE, TH=800C, TC=150C, I=3.7A, VAC. BAFFLED 78-1.

Figure 3. Ingradient Test, O/C Voltage, N-Type

Figure 4. Ingradient Test Seebeck Voltage, N-Type

RESISTIVITY VS. TIME
 N TYPE, GD-SE, TH=800C, TC=150C, I=3.7A, VAC. BAFFLED 78-1.

Figure 5. Ingradient Test Resistivity, N-Type

LOAD POWER VS TIME
 N TYPE, GD-SE, TH=800C, TC=150C, I=3.7A, VAC. BAFFLED 78-1.

Figure 6. Ingradient Test Load Power, N-Type

OPEN CIRCUIT VOLTAGE VS. TIME
P TYPE, TPM-217(WRAPPED), TH=800C, TC=150C, I=3.6A, VAC. BAFFLED 79-2.

Figure 7. Ingradient Test O/C Voltage Versus Time, P Type

SEEBECK VOLTAGE VS. TIME

P TYPE, TPM-217(WRAPPED), TH=800C, TC=150C, I=3.6A, VAC. BAFFLED 79-2.

Figure 8. Ingradient Test Seebeck Voltage, P Type

RESISTIVITY VS. TIME

P TYPE, TPM-217(WRAPPED), TH=800C, TC=150C, I=3.6A, VAC. BAFFLED 79-2.

Figure 9. Ingradient Test Resistance Versus Time, P Type

LOAD POWER VS TIME

P TYPE, TPM-217(WRAPPED), TH=800C, TC=150C, I=3.6A, VAC. BAFFLED '79-2.

Figure 10. Ingradient Test, Load Power, P Type

compared to 3 and 4 may be explained by different contact pressures. 1 and 2 have 600 psi spring force on the contacts while 3 and 4 have 150 psi.

The load voltages for these p type legs have been monitored with Brush recorders to detect possible "ratcheting" during testing. The results have been somewhat obscured by 60 cycle A.C. components picked up from the current controller and from radiation through the wiring harness. Abrupt changes in voltage at constant current have been observed in two of the samples — #2 at 600 psi and #4 at 150 psi contact pressure; both show ragged resistance change patterns with variations at several percent. The other two legs have shown steady load voltages with iL/A value about 7. Figure 11 shows a trace of the load voltage vs time for 3 and 4 (150 psi). Figure 12 shows the same thing for 1 and 3 (600 psi). Figure 13 shows legs 1 and 4 when 4 was particularly unsteady.

C. THERMOPHYSICAL PROPERTIES AND COMPATIBILITY TESTS

Compatibility testing with the measurement of the isothermal weight loss for n legs in oxygen is continuing. Weight loss results over a temperature range of 800°C to 1050°C are presented in Figure 14. Further testing at 10^{-4} Torr O_2 is showing a falling off in the weight loss rate. Perhaps formation of Gd_2O_3 coating is providing some baffling at this pressure as the test goes on.

Figure 11. Ingradient Test, Load Voltage Traces, Legs #3 and #4

LEG #3 150 psi contact pressure

LEG #4 150 psi contact pressure

Figure 12. Ingradient Test, Load Voltage Traces, Legs #1 and #2

LEG #1 600 psi contact pressure

LEG #4 150 psi contact pressure

Figure 13. Ingradient Test, Load Voltage Traces, Legs #1 and #4

Figure 14. Isothermal Weight Loss N-Type O_2 Environment, 10^{-4} Torr

SECTION III

SILICON GERMANIUM MATERIALS TECHNOLOGY

A. PROPERTIES OF SiGe PRODUCED BY GE

Samples from the early production from the reactivated SiGe thermoelectric program at GE have been tested at JPL for comparison to RCA materials. During this reporting period improvements in temperature instrumentation are under way. The first results for isothermal weight loss are presented. Figures 15 and 16 summarize the results for 78% silicon material and Figures 17 and 18 show results for 63% silicon material. The loss rates match prior data¹ for RCA materials very closely; Figure 19 compares the present data with RCA material data. As we would expect, the 63% silicon material loss rate is considerable above the rate observed for the 78% silicon alloy.

B. PROPERTIES OF SiGe ALLOYS WITH GaP ADDITIONS

Test on research samples from Synkal Corporation are continuing for thermoelectric properties. The objective of the Synkal project is the improvement of the figure of merit, Z , for SiGe alloys so that the conversion efficiency of RTGs may be improved with little or no sacrifice in other properties--such as fabricability of bonded uncouples with high strength. Preliminary results in the previous report are being rechecked before long term testing is started. The results of duplicate runs for thermal conductivity produced divergent results. The instrumentation is being examined and further confirmatory runs are under way. These results will be reported later.

¹Synkal Corporation Thermoelectric Properties of Silicon Germanium Alloys.
Report to Jet Propulsion Laboratories 12 July 74.

Figure 15. Free Sublimation N-Type Sige 78% Si

Figure 16. Free Sublimation P-Type Sige 78% Si

Figure 17. Free Sublimation N-Type Sige 63% Si

Figure 18. Free Sublimation P-Type SiGe 63% Si

Figure 19. Sublimation Rates vs Reciprocal Temperature Comparisons

SECTION IV

THERMOELECTRIC GENERATOR TEST AND EVALUATION

Thermoelectric generators, representing recent and advanced technology, assembled with lead telluride, TAGS-85, and silicon-germanium materials are being tested at JPL. These generators are: The HPG (PbTe) and the generator Q1-A (SiGe), representative of the MHW type generators. Three 18 couple modules (S/N-1, S/N-2, S/N-3) that were extensively tested at RCA were received for JPL evaluation in support of the Galileo Program. Both the S/N-1 and the S/N-3 generators were on test during this reporting period. A post-mortem examination is presently being performed on the S/N-2 generator to determine its present condition. The results of this examination will be presented in a separate report. One important question to be dealt with is the evaluation of storage effects on the thermoelectric modules.

A. HIGH PERFORMANCE HPG S/N-2

This generator has operated for a total time of 50,974 hours. During the last 1610 hours of operation, the generator power out has decreased by 2.6 watts. Presently the generator power out is 120.6 watts. The generator open circuit voltage has decreased from its last reported value of 24.63 volts to its present value of 24.46 volts; the internal resistance has remained virtually the same at 1.17 ohms. The generator hot and cold junction temperatures have decreased from $\text{AVG } \bar{T}_H = 1019^{\circ}\text{F}$ and $\text{AVG } \bar{T}_C = 369^{\circ}\text{F}$ to $\text{AVG } \bar{T}_H = 1011^{\circ}\text{F}$ and $\text{AVG } \bar{T}_C = 366^{\circ}\text{F}$. ΔT has decreased by 5°F .

The generator life history is illustrated in Figure 20. The generator degradation rate for the last 5,000 hours of operation was 0.86 percent per 1,000 hours. This average degradation rate is not significantly different from

Figure 20. HPG S/N-2 History

what it was initially and has remained substantially the same throughout the test. Parametric test results are shown in Figure 21.

B. MHW GENERATOR Q1-A

This generator has operated for a total time of 22,519 hours. During the last 1344 hours of operation the generator power out has remained virtually unchanged. Presently the generator power out is 132.0 watts. Both the generator open circuit voltage and the internal resistance have increased slightly from $E_{oc} = 57.00$ volts and $R_{int} = 6.12$ ohms to $E_{oc} = 57.08$ volts and $R_{int} = 6.15$ ohms. The generator heat source temperature has decreased from $AVG \bar{T}_H = 1030^{\circ}C$ to $AVG \bar{T}_H = 1023^{\circ}C$ while the case temperature has increased from $AVG \bar{T}_C = 262^{\circ}C$ to $AVG \bar{T}_C = 263^{\circ}C$.

The resistance between the thermocouples and the thermal insulating foil has decreased to a value of approximately 50 ohms. This means that deposits have built up within the thermal insulation and the couples and potentially some of the output power could be shunted through this path.

The generator life history is illustrated in Figures 22 and 23. The generator degradation rate for the last 5,000 hours of operation was 0.24 percent/1,000 hours. This average degradation rate is observed to have not significantly varied over the period of the life test. Figure 24 shows power out versus $\sqrt{\text{time}}$. Parametric test results are shown in Figure 25.

C. 18 COUPLE MODULES SN-1,2,3.

Module S/N-1, has operated for a total time of 23,828 hours. The last 4412 hours of operation have been at JPL. During the last 1348 hours of operation the module power out has decreased by 0.04 watts. Presently the module output power is 9.70 watts. There has been no significant change in the

Figure 21. Parametric Test of HPG S/N-2

Figure 22. Q1-A History

Figure 23. Q1-A History

Figure 24. Q1-A Power Out Versus Time

Figure 25. Parametric Test of ETG Q1A

value of either the open circuit voltage or the internal resistance ($E_{oc} = 7.53$ volts and $R_{int} = 1.46$ ohms).

The hot junction temperature is not measured since the hot shoe thermocouples were not functional at the start of the present test. The module cold junction temperature has remained the same at $AVG \bar{T}_C = 306^{\circ}C$.

The resistance between the couples and the thermal insulating foil for both the 3-couple and 15-couple sides is shown in Figure 26. These values are presently 2,500 ohms and 2,560 ohms respectively, which is a decrease from the previous values of 2,710 ohms and 2,720 ohms.

The module life history is illustrated in Figure 27. The present performance is stable and the degradation rate for the last 4412 hours of operation was not significant. Parametric test results are shown in Figure 28. The only noticeable difference from the previous test is a slight change in the maximum output power versus load point which has shifted from 10.0 watts at 4.30 volts to 9.8 watts at 4.14 volts.

Module S/N-3 has operated for a total time of 21,121 hours. The last 2604 hours of operation have been at JPL. During the last 1345 hours of operation the power output has decreased by 0.03 watts to its present value of 8.34 watts. The open circuit voltage and the internal resistance have shown no significant change. Their present values are $E_{oc} = 6.85$ volts and $R_{int} = 1.40$ ohms. The hot and cold junction temperatures were stable during this period and have the values $AVG \bar{T}_H = 1021^{\circ}C$ and $AVG \bar{T}_C = 286^{\circ}C$.

The resistance between the module and the thermal insulating foil for both the 3-couple and 15-couple sides is shown in Figure 29. These values are presently 47,800 ohms and 55,900 ohms respectively, which is an increase from our initial values of 33,000 ohms and 37,500 ohms.

Figure 26. 18 Couple Module S/N-1 Resistance, Foil to Module

Figure 27. 18 Couple Module S/N-1 Test History

Figure 28. 18 Couple Module S/N-1 Parametric Test

The module life history is illustrated in Figure 30. The present performance appears to be a continuation of the trend previously recorded by RCA. The generator degradation rate for the last 2604 hours of operation was not significant. Parametric test results are shown in Figure 31. There is no apparent difference in the values of the parameters presented from those previously measured.

Figure 29. 18 Couple Module S/N-3 Resistance, Foil to Module

Figure 30. 18 Couple Module S/N-3 Test History

Figure 31. 18 Couple Module S/N-3 Parametric Test

SECTION V

MHW FLIGHT PERFORMANCE

The Power performance of LES 8 and 9 and the Voyager generators continues without change in the long term trends established. Further work with the data continues, but detailed reports will generally be made only twice per year except for unexpected events.