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POST-ENCAPSULATION PLUTONIA REDUCTION
FOR GALILEO AND ULYSSES GPHS MODULES:
THE MODULE REDUCTION AND MONITORING FACILITY (MRMF)

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ABSTRACT

In heat source systems of the type C/Ir/PuO₂, ingrowth of CO and CO₂ is evident. This is due to a cyclical reaction between the C and PuO₂ constituents. Gas tap results show that repeated exchanges using a pure inert gas backfill reduces the CO/CO₂ ingrowth rate. Also, the temperatures experienced during Radioisotope Thermoelectric Generator (RTG) processing reduces further the effect such that normal RTG storage temperatures do not result in this deleterious effect.

A 36-station vacuum/inert gas manifold has been developed at Mound Facility to serve as a Module Reduction and Monitoring Facility (MRMF) for up to 68 GPHS-type heat source modules. This method of storage effectively prevented atmospheric contamination of modules while reducing the CO/CO₂ ingrowth rate. This paper describes in detail the theoretical, practical, facility, and quality/reliability aspects of this processing facility that has supported the Galileo and Ulysses RTG programs.

INTRODUCTION

EG&G-Mound Applied Technologies is charged with processing encapsulated plutonia heat sources into RTGs to support deep space missions such as Galileo and Ulysses. One of the problems associated with the assembly and storage of these RTGs (Figure 1) is that there is a marked ingrowth of carbon monoxide and carbon dioxide in the gas phase due to the cyclical reaction established between the fuel (²³⁸PuO₂) and the carbon components of the module. This ingrowth proceeds according to the two equations:

$$\begin{aligned} & x(\text{CO}) + \langle \text{PuO}_2 \rangle = x(\text{CO}_2) + \langle \text{PuO}_{2-x} \rangle \quad (1) \\ \text{and} \quad & x(\text{CO}_2) + x \langle \text{C} \rangle = 2x(\text{CO}), \text{ etc.} \quad (2) \end{aligned}$$

Here, () signifies gas phase and < > solid phase components.

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FACILITY

The need for a reduced plutonia fuel form was identified in late 1979. It is apparent from the above discussion that one cannot reliably process the GPHS fuel pellet, encapsulate it into the iridium clad and still verify the retention of an O/Pu < 2.0. Therefore, a facility was conceived which would create a desirable substoichiometry and maintain it during the subsequent RTG assembly.

The MRMF is located a _____ x _____ m cell and consists of a manifold system with 34 usable stations to which cans containing two GPHS modules each (Figure 2) may be attached. The cans are sized to permit installation of carbon felt (insulation as well as stand-offs to protect the GPHS modules from the stainless steel inner surface of the can) which causes the fuel surface to reach a calculated 1410 K, the same temperature as the fuel attains in an argon-filled GPHS RTG. The schematic arrangement of the MRMF is given in Figure 3. The control panel is located in an access corridor that is separated from the manifold (and thus, the GPHS modules that are undergoing reduction) by about 760 mm (30 in.) of reinforced concrete. Even with all stations containing two GPHS modules each, the radiation levels to operators in the corridor is less than 20 μ Sr/hr. ?

All valves (except the mechanical can valves and the RGA metering valve, V-43) are remote solenoid operated. This individual valving scheme enables isolation of active stations when attaching new cans to the manifold, choosing batches of cans for gas exchange or analysis, and removing cans. The use of a certified calibration gas (used each time a gas exchange was made) ensured that CO and CO₂ levels were accurately measured. From the system pressure (measured on the Wallace and Tiernan gauge) and the CO and CO₂ pressures, it was possible to ascertain O/Pu ratios. The system was evacuable to 0.1 Pa and usually less than 1 Pa with the module cans open to the manifold.

Formal procedures were employed throughout the processing of the Galileo and Ulysses GPHS modules. As gas exchanges were performed at a frequency of at least biweekly, a large quantity of information regarding this process is available. The specification for acceptable GPHS fuel reduction was that the observed CO pressure must be less than 500 Pa for three consecutive gas exchange analyses. This implied an O/Pu of around 1.98 : sufficient to obviate the effects of CO on the RTG components and yet not too low such as to affect adversely the compatibility between the plutonia fuel pellet and iridium clad.

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This reaction stops after launch because the two solid-phase reactants are physically separated when the inside of the RTG is evacuated to space for performance reasons. When the RTG is stored under an atmosphere, however, the product gases become established and can cause degradation of the solid-state thermoelectric elements. Controlling the reduction of the plutonia to such an extent that Equation 1 becomes thermodynamically unfavorable minimizes the continued generation of CO and CO₂.

To minimize this effect, the GPHS modules, after assembly, are welded into stainless steel containers and attached to the manifold of the Module Reduction and Monitoring Facility (MRMF) which permits controlled analyses, gas exchanges, and evacuations of the cover gas. Two 250-W modules are placed in each MRMF container. The insulation properties of the carbon parts both used as physical barriers between the container and the module itself result in a fuel temperature calculated to be 1410 K.

THEORY

The first observed PuO₂/Ir/C system generation was reported by Mound Laboratory in 1974 (Mound 1974) on the first flight Multi-Hundred Watt heat source. Peterson (1976) postulated several mechanisms to explain this phenomenon. Based upon the large quantity of CO generated and the ¹⁸O/¹⁶O ratio that was in line with of ¹⁶O-exchanged PuO₂, "some mechanism that involves the fuel must be found" was the conclusion. Although the plutonia fuel is separated from the carbon components by a vent, the vent flow rate is high enough to allow diffusion into and out of the interior of the iridium clad (Johnson 1990).

One can calculate the partial molar free energy ($\Delta\bar{G}$) for O₂ over the plutonia by realizing that

$$(O_2)_{\text{ref}} = [O_2]_{\text{PuO}_x} \quad (3)$$

$$\Delta\bar{G} (O_2) = 2.3RT \log P (O_2)$$

and the oxygen pressure can be calculated from

$$(CO) + 1/2(O_2) = (CO_2)$$

$$\Delta G^\circ = 20.75T - 67500.$$

At 1410 K (the calculated fuel temperature of a stored GPHS RTG), $\log P (O_2) = -2[5.93 - \log P (CO_2) + \log P (CO)]$. From the CO and CO₂ data, ΔG values at 1410 K were calculated and compared favorably with other measurements as shown in Table 1 (Johnson 1982).

RESULTS

All GPHS modules used to support the Galileo and Ulysses missions were successfully processed through the MRMF. The summary quantities of modules are:

1. Fueled Test Modules	
2. Qual RTG	18
3. Galileo RTGs (2)	36
4. Ulysses RTG	18
5. Back-up RTG	18
6. Flight Back-up Modules.....	_____

Total

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The efficacy of this processing on GPHS modules when compared to similar unprocessed MHW heat source performance is demonstrated by:

1. No iridium transport has been noted in any tested GPHS modules whereas several instances were seen in test MHW Fuel Sphere Assemblies (FSAs).
2. Vent plugging noted often in tested MHW FSAs was not noticed in tested GPHS modules, in part due to the lowered vapor pressure (chemical activity) as a result of substoichiometry.
3. Processing time of RTGs (and subsequent risk to people and hardware) was reduced from up to 385 hours [MHW F-4 per Peterson (1976)] to 24 hours, the minimum specified dome-off GPHS RTG vacuum processing time in order to get $P(\text{CO}) \leq 1 \times 10^{-11}$ Pa.
4. Gas taps of stored GPHS RTGs gave no evidence of continued CO/CO₂ generation from fuel/carbon reaction.

SUMMARY

The Use of the MRMF has provided a mechanism to attain the desirable plutonia substoichiometry to enhance safety and performances of GPHS RTGs. Overall, the MRMF:

1. permitted controlled gas exchanges;
2. analyzed gas-phase constituents;
3. provided controlled storage temperatures;
4. verified "leak-tightness" of storage environment;
5. reduced exposure of operating people during RTG assembly; and
6. reduced CO/CO₂ present in converter interior during RTG assembly.

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Table 1: Calculated $\Delta\bar{G}(O_2)$ Values from MRMF Data

One-Can Data

<u>Tap No.</u>	<u>0/Pu</u>	<u>-Log P(CO) atm*</u>	<u>-Log P(CO₂) atm*</u>	<u>-Log P(O₂) atm*</u>	<u>- $\Delta\bar{G}(O_2)^+$ kcal/mol*</u>
1	1.99973	1.49	1.51	11.90	76.8
2	1.99953	1.40	1.80	12.66	81.7
3	1.99945	1.70	2.43	13.32	85.9
4	1.99942	2.12	3.05	13.72	88.5
5	1.99941	2.80	4.00	14.26	92.0

Four-Can Data

1	1.99776	0.71	1.56	13.56	87.5
2	1.99603	1.10	(2.17)*	13.99	90.3
3	1.99430	1.47	(2.78)*	14.46	93.3
4	1.99393	1.59	(3.38)*	15.44	99.6
5	1.99348	1.73	3.10	14.60	94.2

*Calculated. +Woodly (1994) gives a range of $-\bar{G}(O_2)$ of approximately 60 to 100 k cal/mol over a 0/Pu range of 200 to 1.993.

+Thermodynamic values used rather than SI; To convert -log atm to -log Pa, subtract 3.84 and k cal/mole to kJ/mol, multiply by 4.18.

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Figure 2: The MRMF can is of stainless steel and is approximately 150 mm in diameter. Each can can hold two GPHS modules ($\sim 500\text{W}$).

Figure 1: The GPHS RTG schematic, showing the heat source location.

Figure 3: Piping Schematic for the MRMF. Circles on V-1 and V-4 through V-36 represent stations to which MRMF Cans (Figure 2) may be affixed.