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SPACE NUCLEAR SAFETY AND FUELS PROGRAM

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ABSTRACT

This technical monthly report covers studies related to the use of $^{238}\text{PuO}_2$ in radioisotope power systems carried out for the Office of Coordination and Special Projects of the US Department of Energy by Los Alamos National Laboratory.

Most of the studies discussed here are ongoing. Results and conclusions described may change as the work continues. Published reference of the results cited in this report should not be made without the explicit permission of the person in charge of the work.

I. GENERAL-PURPOSE HEAT SOURCE

A. Impact Results (F. W. Schonfeld)

The second General-Purpose Heat Source (GPHS) module in the design iteration test series, DIT-2, was recovered and examined. The iridium clads on SR-107

and SR-110 had small failures and all four iridium clads were cracked inside in the manner of the four clads in the DIT-1 impact. The pre-existing weld cracks in SR-105 and SR-106 appeared to play no part in the impact event.

The recovered module is shown in Fig. 1. The impact face [shown in Fig. 1(a)] and the side of the reentry shell

(a)

(b)

Fig. 1. The reentry shell used in the DIT-2 impact was split in several places. (a) The impact face of the module still in the radiation shields (0.6X). (b) The back face of the module (0.45X).

have split longitudinally. The wire visible on the right side of the module was used to hold the thermocouples in the correct positions. The back surface of the module is visible in Fig. 1(b). It was split but not as severely as the front surface. The reentry shell in DIT-2 did not appear to be damaged as much as that in DIT-1.

The graphite impact shells (GIS) remained in the reentry shell, and their caps remained with the bodies but were displaced longitudinally. The impact shells were

removed easily from the remains of the reentry shell. GIS-1, the prime GIS containing the fueled clads with no defect indications (SR-107 and SR-110), is shown in Fig. 2. The impact side is cracked and crushed along 75% of its length, and the whole GIS is bent in an arc in the plane of the impact line. The second GIS, containing the ultrasonically rejected fueled clads (SR-105 and SR-106), was more severely damaged, as shown in Fig. 3.

Fig. 2. The GIS containing fueled clads SR-107 and SR-110 was cracked and deformed in the DIT-2 impact. (a) Impact face; (b) side view with impact face to the left.

Fig. 3. The GIS containing the rejected fueled clads was damaged more than the prime GIS in the DIT-2 impact. (a) Impact side; (b) side view.

The fueled clads were easily extracted from the impact shells. Fueled clads SR-107 and SR-110, from GIS-1, had the same deformation asymmetry as all four clads in the DIT-1 impact, but the clads from the second GIS, SR-105 and SR-106, had nearly symmetrical deformations (Fig. 4). The impacted dimensions of the four fueled clads are compared to the initial dimensions in Table I.

The calculated strains for both DIT-1 and DIT-2 are shown on the schematic drawings of the modules in Fig. 5. Inspection of the strain distributions shows that the magnitudes of the gross strains cannot be related to specific secondary design features. The asymmetry of all four clads in DIT-1 and of two clads of DIT-2 indicates that the internal reentry shell window does affect the details of the strain.

Both clads in GIS-1 were cracked. The small cracks, which are barely visible in Fig. 4, were circumferential and occurred on the impact faces in the radius on the

TABLE I. The Dimensions of the Fueled Clads Used in the DIT-2 Impact

Capsule	Dimensions (mm)			
	Diameters			Length
	Vented	Weld	Unvented	
SR-105				
Original	29.79	29.97	29.82	30.12
Final, min	28.12	28.70	28.78	30.00
Final, max	31.50	31.62	31.50	31.17
SR-106				
Original	29.97	29.97	29.85	30.18
Final, min	28.37	28.37	28.32	30.48
Final, max	31.60	31.88	31.04	31.19
SR-107				
Original	29.87	29.97	29.87	30.12
Final, min	28.39	28.70	28.07	30.10
Final, max	31.24	32.18	31.29	31.75
SR-110				
Original	29.85	30.00	29.85	30.12
Final, min	27.94	28.24	27.66	30.73
Final, max	32.39	32.64	32.26	32.11

Fig. 4. The DIT-2 fueled clads after impact at 58 m/s and 930°C. The impact face is at the left of each row and the clad is rotated 90° clockwise in each of the three succeeding views. The non-vented and vented end views complete the rows. 0.7X.

Fig. 5. The gross strains in the clads used in the DIT impacts were not affected by secondary design features of the reentry shells. (a) DIT-1. (b) DIT-2.

vent end of each clad. Short longitudinal cracks were found on the inner surfaces of the reverse-bend regions of all four fueled clads in DIT-2.

B. Temperature Response (C. Frantz and R. Zocher)

As we reported last month,¹ the clad temperatures of SR-107 in GIS-1 and SR-106 in GIS-2 varied throughout the heating period, with SR-106 consistently hotter (967° vs 925°C when the gun was triggered). In two

prior tests, variations from the DIT-2 behavior were also noted. In the thermal test conducted prior to DIT-1, only one fueled GIS was used along with a simulant-fueled GIS. Neither GIS had the pyrolytic graphite corner coating, but the module was otherwise complete. In DIT-1, a completely fueled module was used, but the temperature of only one fueled clad was measured. The temperature histories of the four instrumented clads in the three tests are plotted in Fig. 6. The exact starting time of the DIT-1 temperature recording is not known, but it was between 18 and 22 min.

Fig. 6. The temperature histories of the instrumented clads in the Thermal Test, DIT-1, and DIT-2 were significantly different.

The history of DIT-1 differs from the others in two important respects: its initial heating rate was significantly lower than any of the others and the time required for it to reach the impact temperature was twice as long as that needed for the DIT-2 clads. (The thermal-test clad could not reach the DIT impact temperature because it contained only 125 W of fuel, whereas the other modules contained 248 W.) The early linear heating rates are listed in Table II.

The early temperature rise of the GPHS clad in the evacuated gun is controlled by thermal conduction; the conduction paths are fuel to clad to GIS to reentry shell to the bullet assembly or fuel to clad to GIS to insulation to reentry shell to bullet assembly. Obviously, in DIT-1, one or both paths conducted more heat from the clad than they did in the other tests. The axial clearances between the impact shells and the reentry shells were established identically in all cases. The corners of the thermal-test impact shells were not coated, but those in DIT-1 and DIT-2 were. The CBCF insulation components used in the thermal test and in DIT-2 had similar densities, but the sleeves used in DIT-1 were less dense (Table III), a condition that should have led to a lower thermal conductivity.

The three test assemblies were the same, except that thermocouples were used on the two clads in DIT-2. The impact temperatures of DIT-1 and DIT-2 evidently were similar because of the many similarities in the fueled clads after impact; therefore, the variations in heating rate must have been real. It is obvious that a series of self-heating tests should be conducted on a range of production components. The earliest these will be available will be March 1982, when the safety tests begin.

II. LIGHT-WEIGHT RADIOISOTOPE HEATER UNIT (R. E. Tate)

The weights of production components of the Light-Weight Radioisotope Heater Units (LWRHUs) were determined and are listed in Table IV.

The remaining three LWRHUs, which had been subjected to a reentry-heating simulation, were impacted at 49 m/s and ambient temperature. None of the LWRHUs failed. Radiographic examinations revealed no apparent damage to the fuel capsules.

TABLE II. Linear Self-Heating Rates of GPHS Fueled Clads in the Los Alamos 7-in. Gun (Evacuated)

Test	Fueled GIS	Instrumented Clads	Linear Rate (°C/min)
Thermal	1	1	28
DIT-1	2	1	10
DIT-2	2	2	24, 29

TABLE III. GPHS Module Tests. CBCF-3C Part Identities and Densities

	Test Weight (g)	Est. Density (g/cm ³)
Thermal Test (Two Fueled Clads)		
Discs (ORNL)		
P-3-1 #2	0.4014	0.25
P-3-1 #4	0.3998	0.25
P-8-1 #2	0.3978	0.25
P-8-1 #5	0.3804	0.23
Sleeves		
C-27-8	4.1147	0.24
C-27-9	4.1398	0.24
DIT-1 Impact (Four Fueled Clads)		
Discs		
P-3-1 #10	0.3902	0.24
P-3-1 #11	0.3992	0.25
P-8-1 #1	0.3852	0.24
P-8-1 #15	0.3783	0.23
Sleeves		
C-15-4	3.6630	0.21
C-15-2	3.6546	0.21
DIT-2 Impact (Four Fueled Clads)		
Discs		
P-3-1 #12	0.3922	0.24
P-3-1 #13	0.3969	0.24
P-3-1 #14	0.4110	0.25
P-3-1 #15	0.3865	0.24
Sleeves		
C-27-6	4.0602	0.24
C-27-7	4.0942	0.24

TABLE IV. Weights of LWRHU Production Components

Component	Weight (g)	Subtotals
Aeroshell, S/N $\phi \phi 2$	21.070	
Aeroshell plug	2.543	
Aeroshell components		23.613
Cement	not determined	
Insulator top cap	1.269	
Insulator bottom cap	1.263	
Insulator outer tube	3.166	
Insulator middle tube	1.486	
Insulator inner tube	0.624	
Insulator components		7.808
Fueled capsule, S/N 133	8.366	
Fuel pellet	2.664	2.664
Capsule, as welded and vented (by difference)	5.702	5.702
Totals:		39.787

III. SYSTEMS SUPPORT (D. Pavone)

Multi-hundred Watt (MHW) test assembly MHFT-71 was aged for 12.8 months in vacuum at a GIS temperature of 1210°C, subjected to a simulated orbital-decay reentry temperature pulse to 1500°C, and impacted on a polished granite target at a velocity of 81.6 m/s and at an iridium clad temperature of 1430°C.

Initial results of the post-mortem examination were reported last month.¹ No fractures were observed. Abnormal observations included the emittance of white smoke from the tantalum impact can, the presence of a medium-gray surface coating containing tantalum and aluminum on the exterior of the iridium clad, and the presence of a coating on the inside of the GIS.

To preserve this last coating for analysis, a portion of the GIS debris including the interior surface of the cap was withheld when the remainder of the debris was submitted for plutonium analysis. The GIS debris submitted contained 602 μg of plutonium. In view of the absence of fractures of the iridium clad, this is a large amount, and analysis of the withheld portion of the GIS is warranted to obtain a reliable result for the total plutonium. This analysis has not yet been received.

Electron microprobe (EMP) analysis of a spot on the exterior surface of the tantalum can that had been discolored by the white smoke indicated the presence of

carbon, oxygen, chlorine, and titanium. It is difficult to account for the presence of carbon in this location except to postulate that carbon monoxide gas was released from the interior along with the white smoke. The presence of titanium and chlorine suggests that the white smoke was a gaseous titanium-chlorine compound that hydrolyzed on exposure to the air atmosphere of the glovebox, although the possibility of a tantalum-chlorine species cannot be excluded. While a chlorine-containing compound normally is not seen in the MHW system, data obtained from analysis of material deposited in the interstices of the vent filter indicate that the plutonia sphere was the source of the chlorine and titanium.

Metallographic examination of cross sections through the vent assemblies revealed both features that are observed in all MHW test assemblies and a few that are unique to MHFT-71. Both assemblies had a porous nonmetallic deposit located near the entrance of the vent hole, as illustrated in Fig. 7. Analysis by EMP indicated the principal constituent of this material was plutonium with minor concentrations of iron, chromium, and tungsten. Figure 7 also illustrates a relatively heavy metallic deposit on the walls of the vent hole and the exterior surface of the clad surrounding the vent hole. This material has been observed frequently and consists of iridium and tungsten, with a tungsten concentration greater than that of the base material.

Iridium-silicon and iridium-plutonium intermetallic phases were observed on the exterior surface of the iridium clad, near the vent exit, as shown in Fig. 8. In Fig. 8(a), an iridium-silicon intermetallic phase penetrating along a grain boundary is illustrated, and in Fig. 8(b), a two-phase constituent containing plutonium and

Fig. 7. Metallographic cross section through the vent hole of a vent assembly of MHFT-71. The porous nonmetallic deposit contained primarily plutonium with iron, chromium, and tungsten. 77X.

Fig. 8. Metallographic cross sections illustrating the presence of iridium intermetallic compounds in MHFT-71. (a) Iridium-silicon compound penetrating along a grain boundary, 190X. (b) Iridium-plutonium compound (dark gray) and iridium-silicon compound (light gray), 190X.

iridium is shown, along with the light-gray iridium-silicon compound. The occurrence of these compounds indicates that nonmetallic species containing at least plutonium and silicon were transported through the vent, probably during the aging treatment. The aging furnace operating records indicate that the furnace pressure was very unstable, particularly during the final months of the aging treatment. At the time this characteristic was being observed, it was believed to be the result of helium release by "burping" of the vent assemblies. (Three MHW test assemblies were being aged simultaneously.) Now, in light of the observations indicating transport of fuel components through the vents of MHFT-71 and the

stability of the furnace pressure after its removal, it appears that the unstable furnace pressures were caused by reaction of vapor-transported species with graphite to produce carbon monoxide.

A photomicrograph of the entrance to one of the vent assemblies is shown in Fig. 9. In addition to plutonia (medium gray), a somewhat darker gray multi-phase constituent is present in the pores of the iridium filter. This material contained silicon, plutonium, titanium, iron, magnesium, aluminum, chlorine, and a trace of tungsten. The distributions of plutonium, silicon, titanium, and chlorine in the area indicated by the arrow in Fig. 9(a) are shown in Fig. 9(b). The composition of

Fig. 9. (a) Metallographic cross section at the vent entrance of MHFT-71. Nonmetallic deposits contain plutonium, silicon, titanium, iron, magnesium, aluminum, and chlorine. 190X. (b) Distributions of plutonium, silicon, titanium, and chlorine in the area indicated by the arrow in (a).

this material differs from that observed as vent deposits in other test assemblies in that calcium is not present, plutonium and titanium are present as major constituents, and chlorine is present in a substantial concentration. The existence of this material in the vent assembly indicates that its vapor pressure was slightly greater than that of PuO_2 . It is surprising to find material of this composition in an assembly operating at high temperature; however, a titanium-oxygen-chlorine compound with a melting point of 982°C has been reported.² Thus, it seems quite possible that a complex chlorine-containing compound could exist at the aging and impact test temperatures.

A summary of analytical information obtained in an effort to explain the abnormal observations is listed below.

- Tantalum, iridium, and aluminum are present in the gray coating of the iridium clad.
- Tantalum, iridium, and silicon are present in the nonmetallic deposit on the exterior of the iridium clad.
- Tantalum is present in the nonmetallic deposit on the interior of the GIS.
- Plutonium, tantalum, oxygen, aluminum, titanium, silicon, calcium, and chromium are present in the deposits on the exterior surface of the plutonia sphere and the interior of the iridium clad.
- Titanium, zirconium, and calcium are present in higher than normal concentrations in the plutonia sphere.
- Plutonium, silicon, titanium, and chlorine are present in the vent deposit material.
- Titanium, oxygen, carbon, and chlorine were detected on the surface of the tantalum impact can.

The observation of titanium and chlorine on the exterior of the tantalum and the white smoke suggests the existence of gaseous TiCl_x in the post-impact assembly, although a TaCl_x compound is also possible. The appearance of vent deposits containing titanium and chlorine indicates that the plutonia sphere was the source of these elements.

There are two possible sources of the tantalum found in the coating of the iridium clad: the plutonia sphere or the tantalum impact can. Evidence pointing to the plutonia sphere as the source includes (1) the appearance of nonmetallic material containing tantalum, iridium, and silicon on the exterior of the iridium clad, (2) the yellowish deposits on the exterior surface of the plutonia sphere and the interior of the iridium clad that contained plutonium, tantalum, and other elements in minor con-

centrations, and (3) the fact that the coating contained aluminum in addition to the tantalum. If, however, the fuel were the source of the tantalum, one might logically expect to find it concentrated near the vent as was the silicon (Fig. 8), instead of as a uniform coating on the outside of the clad and on the inside of the GIS.

If the tantalum can is to be posited as the tantalum source, a gaseous species must be identified as the transporting agent. Obviously, this species must be unique to MHFT-71, because the tantalum coatings were not seen in the other test assemblies. As indicated above, the unusual presence of chlorine suggests that a tantalum-chlorine compound, gaseous at the temperature of the reentry simulation, might satisfy the requirement for a transporting agent. During the simulated reentry pulse heating, the temperature of the tantalum safety can exceeds that of the iridium clad, so the temperature gradient is in the direction that would favor transport by a TaCl_x gas. Transport of tantalum by this mechanism requires the diffusion of the TaCl_x species along the threads and through the pores of the GIS. The assembly is exposed to the reentry thermal conditions for a relatively short time, making it questionable whether or not sufficient time at temperature could have been available to transport the tantalum. It appears, therefore, that no definite conclusion as to the source of the tantalum in the coating of the iridium clad can be reached.

While neither the formation of the coating on the iridium clad nor the silicon contamination altered the properties of the iridium to the extent that a catastrophic failure occurred, the presence of chlorine in the fuel apparently resulted in an increase in the amount of plutonium transported through the vents.

IV. HELIUM RELEASE

Three additional samples were removed from GPHS pellet GP-19 and exposed to a 450 to $1510^\circ\text{C}/140\text{-s}$ thermal pulse, during which the release was monitored. This exposure was followed by an isothermal heat treatment at 1600°C until the helium signal decreased to background. These data and some data from Mueller's studies³ of $^{238}\text{PuO}_2$ powders subjected to slow thermal pulses (500 to $1600^\circ\text{C}/1\text{ h}$) were analyzed using a simple diffusion model and compared to data from the reentry test of LWRHU RHU-027⁴ and to the 280-s data from previous GP-19 samples.¹

450° to 1510°C/ 140-s Pulse		Prior Experiments at Different Pulses	
Run No.	Symbol	Sample	Symbol
16	x	280-s pulse	☆
37	○	average	
39	△	RHU-027	□
		Powder	●

Fig. 10. Temperature dependence of effective diffusion constant D' calculated for helium release from $^{238}\text{PuO}_2$ exposed to 450° to 1510°C/140-s pulses and to 450° to 1487°C/280-s pulses (see Ref. 1).

TABLE V. Activation Energies (E_a) and Effective Diffusion Constants (D_0') for GP-19 Samples Exposed to 450° to 1510°/140-s Thermal Ramps

Run No.	Mass (g)	Age (yr)	Total Helium Released (%)	Low Temperature		High Temperature	
				E_a (kcal)	$\text{Log } D_0'$ (s^{-1})	E_a (kcal)	$\text{Log } D_0'$ (s^{-1})
16	0.103	0.578	83.0	29.3 ± 3.2	-3.312 ± 0.704	84.6 ± 4.9	6.676 ± 0.689
37	0.115	0.652	91.8	---	---	69.8 ± 2.1	6.005 ± 0.291
39	0.198	0.668	90.2	33.8 ± 3.2	-4.428 ± 0.708	69.6 ± 6.6	3.680 ± 0.902

In all cases, the temperature dependence of D' is different for higher and lower temperature regimes (Fig. 10), with the break coming around $10000/T = 8$, except in the case of RHU-027, where the break is nearer $10000/T = 7$. The calculated values of activation energy (E_a) and diffusion constants for the three 140-s samples are given in Table V.

Samples from the central and outer regions of pellet GP-19 were exposed to the 140-s pulse but not to the 1600°C isothermal treatment, prepared ceramographically, and examined microscopically. Photomicrographs of the two samples are shown in Fig. 11. The large variation in grain sizes is evident as is the difference in the distributions of porosity. These two structures might be expected to release stored helium differently.

(a)

(b)

Fig. 11. Microstructures of GPHS fuel pellet GP-19 following 450° to 1510°C/140-s pulse. (a) Center. (b) Outer edge. 380X, etched.

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