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Data Sheets for PPO Radioisotopic Fuel

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

MASTER

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DATA SHEETS FOR PPO RADIOISOTOPIC FUEL

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ABSTRACT

PPO is the acronym for Pure Plutonium Oxide. The thermal energy of this fuel results from the radioactive decay of ^{239}Pu and this energy is converted into usable electric power for space probe or other applications.

The basic fuel module associated with the current MHW heat source is a PPO sphere 1.485 ± 0.015 in. diam and containing 100 ± 2 thermal watts. The spheres are individually encapsulated and then assembled into geometric arrays to form the working heat source.

The following document lists certain properties of PuO_2 with emphasis on behavior at the proposed operational conditions. Since many of the desired properties are still being determined, this document is preliminary in nature and will be revised periodically.

LASL has the responsibility for fuel form development and characterization. Mound Laboratory, operated by the Monsanto Research Corporation (MRC) has the responsibility for production of spheres. Characterization studies will be carried out on material representative of that produced at MRC when deemed necessary. Insofar as possible, a distinction will be made in this document if the reported data values are (1) calculated or estimated, (2) literature values not necessarily representative of MRC Flight Quality material, or (3) actual determinations carried out on MRC specimens.

This report is the first revision of LA-5160-MS (issued 2/73) and incorporates additional and more specific data.

1. **Plutonium Content of Typical $^{238}\text{PuO}_2$ (80 at%) produced at the USAEC Savannah River Plant**

a. <u>Plutonium Isotope</u>	<u>wt%</u>	<u>Half Life (yr)</u>
^{238}Pu	~0.001	2.8
^{239}Pu	80 ⁽¹⁾	87.80 ± 0.02
^{240}Pu	16.5	2.4×10^4
^{241}Pu	2.5	6.6×10^3
^{242}Pu	0.8	13.0
	0.1	3.7×10^5

b. **Pure Plutonium Oxide (PuO_2)**

Pu	88.15
O	11.85

c. **Impurities**

The analyses reported in the following section represent averages of analytical studies carried out by LASL on typical MRC Flight Quality specimens.

1) **Actinide Impurities**

<u>Element</u>	<u>wt%</u>
Th	0.29
U	0.64*
Np	0.12
Am	0.05

2) **Common Impurities, Specified and Determined**

<u>Element</u>	<u>Specified Impurity Level, (ppm)⁽²⁾</u>	<u>Typical Analyses (ppm avg.)</u>
Al	150	50
Ca	300	200
Co	50	30
Cr	250	85
Cu	100	5
Fe	800	300
Mg	50	20
Na	250	40
Ni	150	15
Pb	100	5
Si	200	160
Sn	50	15
Ta	200	100
Zn	50	10
C	---	250

* ^{238}U grows in at the rate of ~525 ppm/mo as a result of the decay of ^{238}Pu . Therefore, the U content is a function of the age and initial isotopic composition of the particular specimen.

2. **Calculated Power Factors (Based on 0.453 w/g of total Pu)**

- 0.399 watts per gm
- 12.1 curies per gm
- 30.4 curies per watt
- Note: The above values are calculated based on pure 100% dense $^{238}\text{PuO}_2$ with 80 at% enrichment in the 238 isotope. From the specified diameter and thermal inventory of a typical sphere, one may then calculate an "effective" sphere power density as 3.71 ± 0.2 watts/cc.

3. **Radiation**

In describing radiation from 80 at% $^{238}\text{PuO}_2$, several factors must be considered: (1) whether the values are based on an unshielded or shielded source. For example, a significant L X-ray emission rate is associated with ^{238}Pu . However, the energy is low (0.015 MeV) and these X-rays are easily absorbed by ordinary thicknesses (~0.030 in.) of common encapsulating materials such as stainless steel or Ta, (2) actual percentages of both other Pu isotopes and actinides. For instance, the ^{238}Pu content is specified⁽¹⁾ as ≤ 2 ppm; typical Savannah River oxide averages 0.6 - 1.2 ppm. However, the exact value is a function of the processing history of the particular "batch" and may vary from lot to lot. The isotope ^{238}Pu has ^{234}Th in its decay chain; ^{234}Th has an energetic gamma (2.6 MeV) which grows in as the ^{238}Pu decays. The varying amounts of Th, U, Np, and Am also contribute to the gamma spectrum. Therefore, a variety of qualifications must be considered in a tabulation of radiation characteristics. To avoid these ambiguities, unless otherwise specifically stated, the data in sections 3. a through 3. c refer to ^{238}Pu only.

a. <u>Alpha</u>	<u>Energy (MeV)</u>	<u>Particles/watt-sec</u>
1.	5.491	7.95×10^{11}
2.	5.448	3.20×10^{11}
3.	5.352	1.5×10^9
4.	5.200	5.0×10^7
5.	5.000	7.0×10^4
6.	4.700	1.3×10^4

b. **Beta - None**

3. (cont'd)

TABLE I⁽³⁾

c.

Gamma	(keV)	Gamma-Ray	Avg. Std.	Specific Neutron Yields from Light Element	
	Energy	Intensity (gammas per alpha)		Dev. (%)	Impurities in ²³⁸ Pu
				Element	n/sec/g ²³⁸ Pu for 1 ppm
1.	15.0	0.13	-	Li	5.7
2.	43.5	2.51 x 10 ⁻⁴	1	Be	162
3.	99.6	7.66 x 10 ⁻⁵	1	B	51
4.	152.5	8.5 x 10 ⁻⁶	1	C	0.2
5.	201.2	4.3 x 10 ⁻⁸	2	O	0.1 (natural mixture)
6.	707.8	3.3 x 10 ⁻⁹	7	¹⁷ O	0.62
7.	742.4	5.25 x 10 ⁻⁸	1	¹⁸ O	6.25
8.	765.8	2.31 x 10 ⁻⁷	1	F	22
9.	785.8	3.3 x 10 ⁻⁸	2	Na	2.7
10.	807.6	8.5 x 10 ⁻⁹	5	Mg	2.6
11.	851.3	1.36 x 10 ⁻⁸	1	Al	1.2
12.	882.9	9.4 x 10 ⁻⁹	2	Si	0.2
13.	926.5	5.3 x 10 ⁻⁹	1	P	< 0.03
14.	941.8	5.3 x 10 ⁻⁹	4	S	< 0.03
15.	1001.1	9.5 x 10 ⁻⁹	1		
16.	1041.8	2.2 x 10 ⁻⁹	8		
17.	1085.1	7.0 x 10 ⁻¹⁰	9		

d. Bremsstrahlung - Negligible

e.

Neutrons ⁽³⁾	Source	(MeV)	Emission Rate, n/sec/g Pu (Total)
1.	Spontaneous Fission	0 - 10	2200
		(Avg. = 2.0)	
2.	α/n Reactions, light elements only. At Z=14, the coulomb barrier reaches 5.5 MeV		See Table I

f. Specified Emission Rate⁽²⁾ for Typical Sphere:

g. Typical Determined Emission Rate on MRC Flight Quality Spheres:

h. Dose Rate

A more meaningful value associated with radiation is a typical dose rate (β, γ) from a Flight Quality

Note that "normal" oxygen in ²³⁸PuO₂^{nat} could contribute significantly to the overall emission rate. However, the mass-16 oxygen isotope does not undergo the α, n reaction to any practical extent. Therefore, if ²³⁸PuO₂^{nat} is enriched in ¹⁶O, the contribution to the overall neutron emission rate may approach that of the spontaneous fission rate of the nucleus. The "efficiency" of this enrichment, or exchange, depends upon a variety of processing parameters. Typical ²³⁸PuO₂^{nat} has an emission rate of 12,500 n/sec/g Pu (Total); the spontaneous fission rate is 2200 n/sec/g Pu (Total. Section 3.g above indicates a nominal emission rate of ~5000 n/sec/g Pu (Total) for a Flight Quality Sphere.

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A more meaningful value associated with radiation is a typical dose rate (β, γ) from a Flight Quality MRC Sphere. This value now includes the contribution from various plutonium isotopes, other actinides and all daughters. Dose rates are usually measured at 10 cm from the encapsulated source. Using MRC MHFT-17, a dose rate of 0.2 mr/hr was measured at 10 cm through 0.020 in. of Ir.

4. Critical Mass

Transport calculations⁽⁴⁾ indicate the mass of a bare critical sphere of PuO_2 to be 25.5 kg. The presence of a thick (15 cm) iron reflector would reduce this value by one-half.

5. Compatibility

Two series of compatibility tests of plutonium oxide radioisotopic fuels with precious metal alloys have been conducted.

The test matrix of the initial series of tests (Series I) included plutonium oxide of two compositions ($\text{O}/\text{Pu} = 2.00$ - High PPO and $\text{O}/\text{Pu} = 1.85$ - Low PPO) in the form of pellets hot-pressed from plutonium oxide powder obtained from the AEC Savannah River Plant.

At the time the Series I tests were planned, it was thought that MHW fuel spheres might undergo reduction to PuO_{2-x} during fabrication and subsequent handling. Therefore, plutonia of two stoichiometries was tested in this series.

Pure plutonium oxide pellets were prepared from Savannah River process plutonium oxide of about 80% Pu-238 enrichment. The High PPO pellets were cold pressed and sintered at 1600°C and the Low PPO pellets prepared by treating cold pressed and sintered pellets in dry argon-6% hydrogen at 1300°C for 6 hours. The major impurities in the pellets were 0.44% uranium, 0.12% thorium, 200 ppm iron, and 80 ppm silicon.

Commercially pure iridium metal and two compositions of platinum-rhodium alloys were tested in environments of tantalum metal and graphite. The test configurations are shown schematically in Figure 1, and a summary of the descriptions and results of the series of tests are given in Tables II and III.

The results of this initial series of tests indicated that platinum-rhodium alloys were not compatible with sub-stoichiometric plutonium oxide at 1500°C and that molybdenum metal was not a suitable barrier material between plutonium oxide and iridium metal. Commercially pure iridium metal and plutonium oxide of reasonably high O/Pu ratio appeared to be compatible at the temperatures investigated and were selected for further testing.

Fig. 1. Compatibility Test Assemblies
(a) Tantalum Gettered Tests
(b) Graphite Gettered Tests

While these studies were in progress, other results showed that chemical reduction of a full fuel sphere would not take place. Therefore, the stoichiometry of a typical sphere would be PuO_2 .

The second series of compatibility tests (Series II) were designed to examine the compatibility of the three component system of plutonium oxide ($\text{O}/\text{Pu} = 2.00$) - iridium metal - graphite with solid interfacial contacts. The test configuration, shown in Fig. 2 allows for gas-phase communication between the plutonium oxide and the graphite through the vent ($0.0005''$) in the capsule partition. The entire test capsule assembly is exposed to a dynamic vacuum ($< 10^{-5}$ torr) through a vent in the capsule end-cap except in selected tests in which it is desired to maintain a helium atmosphere. The conditions and results of the tests examined thus far are given in Table IV.

The results of these tests confirm that iridium metal is compatible with stoichiometric plutonium oxide for relatively long periods of time at 1450°C and at temperatures up to 1900°C for short exposure times. The observation of vapor-deposited plutonium oxide on the capsule wall of the plutonium oxide compartment of the test capsule and the presence of non-metallic deposits in the partition vents indicate the importance of small temperature gradients in the vapor transport

TABLE II

SUMMARY OF Pt-Rh ALLOY-PLUTONIA COMPATIBILITY TESTS

Capsule	Configuration			No. of Tests	Temperatures °C	Time-hrs	Results
	Fuel	Barrier	Getter				
Pt-30 Rh	Lo PPO	---	Ta	2	1500°C	1000 1275	Extensive reaction, Pu-Pt-Rh liquid formation.
Pt-30 Rh	Lo PPO	---	C	1	1500°C	1275	Extensive reaction, Pu-Pt-Rh liquid formation.
Pt-30 Rh	Lo PPO	Ir	Ta	1	1500°C	1275	No detectable PuO ₂ -Ir reaction, Pu diffused into Pt-Rh surfaces.
Pt-26 Rh-8W	Lo PPO	---	Ta	1	1500°C	1275	Extensive reaction, Pu-Pt-Rh liquid formation.

TABLE III

SUMMARY OF Ir-PLUTONIA COMPATIBILITY TESTS
SU

Capsule	Configuration			No. of Tests	Temperatures °C	Time-hrs	Results
	Fuel	Barrier	Getter				
Ir	Lo PPO	---	Ta	5	1370 1500	1000 4000	No detectable PuO ₂ -Ir reaction.
Ir	Hi PPO	---	Ta	4	1370 1500	1000 4000	No detectable PuO ₂ -Ir reaction.
Ir	Lo PPO	Mo/NiO	Ta	2	1500	1000 4000	Mo-PuO ₂ reaction, Mo diffused into the Iridium surfaces.
Ir	Hi PPO	Mo/MgO	Ta	2	1500	1000	Mo-PuO ₂ reaction, Mo diffused into the Iridium surfaces.
Ir	Lo PPO	---	C	2	1370	1000 1800	PuO ₂ -Ir reaction in 1000 hr. test. No detectable reaction in 1800 hr. test.
Ir*	Hi PPO	---	C	1	1370	1000	PuO ₂ -Ir reaction.
Ir**	Hi PPO	---	C	2	1370	1000	No detectable PuO ₂ -Ir reaction.
Ir**	Hi PPO	---	C	2***	1370	1000	No detectable PuO ₂ -Ir reaction.

* Some substoichiometric PPO seen after test completed.

** Vent ~ 0.005" in top of capsule.

*** 1 Test included a small amount of carbon, 2 Tests with Ir/HfO₂ vent cover.

of low vapor pressure materials when exposed for long periods of time at elevated temperature.

6. Thermophysical Properties

a. Thermal Expansion:

The following equation for thermal expansion

is based on measurements of 80 ΔT % ²³⁸PuO₂ to 1400°C⁽⁵⁾:

$$\Delta L/L_0 = -1.22 \times 10^{-4} + 7.59 \times 10^{-6} t + 5.69 \times 10^{-9} t^2 - 5.98 \times 10^{-12} t^3 + 4.41 \times 10^{-15} t^4 - 1.29 \times 10^{-18} t^5$$

(L₀ refers to 25°C; t = °C)b. Specific heat and heat content⁽⁶⁾.

Values are given in Table V.

$$C_p \text{ (kcal/mole - } ^\circ\text{K)} = 18 + 3.9 \times 10^{-3} T - \frac{2.46 \times 10^5}{T^2}$$

$$\Delta H_{293} = -6.36 + 0.0180T + 1.95 \times 10^{-6} T^2 + 2.46 \times 10^{-2} T^{-1}$$

c. Latent heats of phase transformations

1. The heat of melting for the PuO₂ is

65 cal/g.

2. The heat of sublimation for PuO₂ is

490 ± 10 cal/g.

Fig. 2 -- Series II Computability Capsule

d. Vapor Pressures

1. Plutonia

Plutonia undergoes congruent vaporization to yield gaseous PuO , PuO_2 , O and O_2 above solid PuO_{2-x} , the value of x depending on the temperature. Values for the congruently vaporizing composition as a function of temperature are:

Temp. °C	Congruently Vaporizing Composition
1327	$\text{PuO}_{1.72}$
1527	$\text{PuO}_{1.83}$
1727	$\text{PuO}_{1.86}$
1927	$\text{PuO}_{1.85}$
2127	$\text{PuO}_{1.84}$

Mass spectrometric-Knudsen effusion studies performed at LASL yield the following vapor pressure equations for PuO and PuO_2 gases above plutonia:

$$\log_{10} P_{\text{PuO}} (\text{atm}) = 6.806 - 28257/T^\circ\text{K}$$

$$\log_{10} P_{\text{PuO}_2} (\text{atm}) = 7.687 - 29928/T^\circ\text{K}$$

Combining these equations:

$$\log_{10} P_E (\text{atm}) = 7.557 - 29096/T^\circ\text{K},$$

where $P_E = P_{\text{PuO}_2} + (M_{\text{PuO}_2}/M_{\text{PuO}})^{1/2} P_{\text{PuO}}$. The heat and entropy of vaporization for P_E are 493 ± 10 cal/g and 0.13 ± 0.02 cal/g - °C, respectively.

e. Thermal Diffusivity

Lagedrost, et. al.,⁽⁷⁾ measured the thermal diffusivity of $^{238}\text{PuO}_2$ to 1200°C. The following equation is an adequate representation of their data to 1000°C: $\alpha (\text{cm}^2/\text{sec}) = 11.5 \times 10^{-3} - 13.8/t + 11.4 \times 10^{-3}/t^3 - 2.2 \times 10^{-6}/t^3$ where t is °C.

f. Thermal Conductivity

From the above data⁽⁷⁾ and specific heat⁽⁶⁾ values, the following equations may be derived for thermal conductivity. $k (\text{cal/cm-sec-}^\circ\text{C}) = 8.14 \times 10^{-3} - 7.45/t + 6.41 \times 10^{-3}/t^2 - 1.11 \times 10^{-6}/t^3$ ($t = ^\circ\text{C}$ to 1000°C)

However, reproducible measurements involving temperature gradients in flight-quality spheres are difficult to explain using the above equation only. These results are described more fully in Section 8 below.

g. Viscosity (estimated)

The viscosity of the ceramic phase is estimated to be 32 centipoise ($\pm 25\%$) at the melting point.

h. Surface tension

The surface tension of the ceramic phase is 523 dyne/cm ($\pm 15\%$) at the melting point.⁽⁸⁾

1. Total hemispherical emittance. The following equation is based on measurements to 1000°C: $\epsilon = 0.593 + 1.65 \times 10^{-4} t$ ($t = ^\circ\text{C}$)

j. Crystallography

PuO_2 has a FCC structure with a lattice parameter of 5.3950 ± 0.005 Å, when corrected for self-heating effects.⁽⁹⁾

TABLE IV
SUMMARY OF PLUTONIA-IRIDIUM-GRAPHITE COMPATIBILITY TESTS

Test No.	Description *	Avg. Iridium Microhardness Partition/Vent Cover	Results
II-1	MRC fuel/RI Graphite 1450 °C 2333 hours Vacuum	309/378 VHN	- No detectable Plutonia-Iridium reaction. - Vapor deposited plutonia on the capsule wall of the fuel compartment.
II-2	MRC Fuel/RI Graphite 1450 °C 2333 hours Vacuum	289/339 VHN	- No detectable Plutonia-Iridium reaction. - Vapor deposited plutonia on the capsule wall of the fuel compartment.
II-3	MRC fuel/RI Graphite 1450 °C 2333 hours Vacuum	324/334 VHN	- No detectable Plutonia-Iridium reaction. - Vapor deposited plutonia on the capsule wall of the fuel compartment.
II-28	SRP fuel/RI Graphite 1450 °C 1662 hours Vacuum	322/389 VHN	- No detectable Plutonia-Iridium reaction. - Vapor deposited plutonia on the capsule wall of the fuel compartment.
II-10	MRC fuel/RI Graphite 1450 °C 5885 hours Vacuum	269/293 VHN	- No detectable Plutonia-Iridium reaction. - Vapor deposited plutonia on the capsule wall of the fuel compartment. - Nonmetallic deposits in the vent containing Ca, Al, Si, Pu, and O.
II-14	MRC fuel/RI Graphite 1450 °C 5937 hours Vacuum	269/307 VHN	- No detectable Plutonia-Iridium reaction. - No vapor deposited plutonia on the capsule wall of the fuel compartment. - Nonmetallic deposits in the vent containing Ca, W, and O.
II-29	SRP fuel/RI Graphite 1450 °C 1662 hours Vacuum	272/302 VHN	- No detectable Plutonia-Iridium reaction. - Vapor deposited plutonia on the capsule wall of the fuel compartment. - Nonmetallic deposits in the vent containing Pu, Si, Ca, Al, and O.
II-23	MRC fuel/CVD Graphite 1450 °C 5885 hours Vacuum	269/307 VHN	- No detectable Plutonia-Iridium reaction. - Vapor deposited plutonia on the capsule wall of the fuel compartment. - Nonmetallic deposits in the vent containing Ca, O, Pu, Al, and Mg.
II-24	MRC fuel/CVD Graphite 1450 °C 5885 hours Vacuum	274/319 VHN	- No detectable Plutonia-Iridium reaction. - Vapor deposited plutonia on the capsule wall of the fuel compartment.
II-46	MRC fuel/RI Graphite 1950 °C 5 minutes, Vacuum	275/311 VHN	- No detectable Plutonia-Iridium reaction. - No indication of solid effusate from the fuel compartment through the vent.

*MRC fuel = Monsanto Research Corporation Production Grade Plutonium Oxide.

SRP fuel = Savannah River Plant Plutonium Oxide.

RI Graphite = Resin Impregnated Thornel-50 graphite.

CVD Graphite = Chemical Vapor Deposited carbon infiltrated Thornel-50 graphite.

TABLE V (6)

THERMODYNAMIC VALUES FOR PPO

Temp., °K	C _p , kcal/mole-°K	H ^o _T -H ^o _{25°C} kcal/mole
298	16.4	0
500	19.0	3.62
1000	21.6	13.8
1500	23.8	25.2
2000	25.8	37.6
2400	27.3	48.2

1. Melting Point

Observed m.p. of typical PuC₂ is 2365 ± 30°C.

m. Helium Migration

Helium migration has been measured in various specimens from flight quality spheres. These measurements were carried out in part to demonstrate the equivalence of spheres made from (1) MRC hydroxide precipitation process, and (2) SRP oxalate precipitation process. The mechanism of the determination involved a thermal hold at the stated temperature and time followed by a ramp to 1900°C to completely outgas the specimen. From these measurements and appropriate calculations of generation rates, one may determine the amount of residual He retained after the thermal equilibrium. The data are shown in Table VI.

The obvious trend in the data indicates more complete release with increasing temperature and the equivalence of the MRC/LASL sphere-derived specimens.

7. Mechanical Properties

a. Hardness

At 25°C the hardness for PuO₂ ceramic phase is approximately 850 DPH.⁽⁹⁾

b. Mechanical Strength

A second facet of the equivalency demonstration of hydroxide/oxalate derived feed involved a mechanical properties determination. Instrument sample requirements would not permit use of a specimen from a

TABLE VI

HE MIGRATION RATES

specimen no.	origin	temp., °C	soak time yrs.	He inventory after soak STP cc/gm	% released during soak
SPO-33	MRC	1150	0.39	0.027	93.9
SPO-33	MRC	1250	0.42	0.017	96.2
SPO-33	MRC	1370	0.22	0.021	94.0
SPO-33	MRC	1450	0.38	0.006	98.6
SPP-52	LASL	1150	0.44	0.016	94.3
SPP-54	LASL	1150	0.21	0.015	92.9
SPP-53	LASL	1250	0.44	0.014	95.0
SPP-50	LASL	1370	0.23	0.011	93.1

flight quality sphere; however, pellets were fabricated from flight quality feed (of both sources) and the pellet microstructures were identical with those from spherical specimens.

Three separate types of mechanical strength tests were carried out at room temperature. A diametrical strength determination was completed by loading Al foil wrapped pellets to failure across a diameter. A "three-high" stack of pellets was loaded to failure uniaxially. A deflectometer was employed to obtain an estimate for Young's Modulus on selected pellets prior to the uniaxial test. The data are condensed in Table VII.

TABLE VII

ROOM TEMPERATURE SELECTED MECHANICAL PROPERTIES FOR PPO

specimen no. and origin	Avg. Ultimate Strength		Avg. Young's Modulus x 10 ⁶
	Ksi, Diametrical	Ksi, Uniaxial	
323 (LASL)	5.0	47.6	16
346 (MRC)	3.1	37.2	8.4

c. Impact

The results of engineering impact tests on full FSA's are given below. (Table VIII).

TABLE VIII

MHFT IMPACTS

No.	V ft/sec.	Temp. °C	Post-impact Dimens.		Response
			Height	Diameter	
2	274	1374	1.22	1.69/1.72	No breaks
3	276	1365	1.07	1.78/1.85	failure - loop strain
4	279	1375	1.14	1.71/1.75	Failure
12	286	reentry ~1480°C	1.19	1.74	failure - loop strain - P contamin. introduced at LASL - fuel plastic
32	285	1370	1.18	1.70/1.74	No break - fuel plastic
33	282	1370	1.14	1.69/1.72	No break - fuel plastic
26	247	reentry ~1550°C*	1.12	1.83/1.85	No break - graphite rotation ~110°
27	249	reentry ~1550°C*	1.46	1.66/1.68	failure - impact face
34	284	1375	1.17	1.66/1.72	No break

*Intended temperature, actual impact temperature not yet reduced from data readout.

8. Temperature Gradients Within a Sphere

A reasonable extrapolation of the conductivity data in Section 6.1 above would lead to predictions of an increasing ΔT from core to surface in a typical sphere as the surface temperature is increased from ambient (~400°C) to operational (~1350°C).

Certain experiments carried out at LASL showed more subtle and complicated energy balances were in effect. A spherical specimen was fabricated with a 0.061 in. thermocouple well extending from the surface to the core. A Pt-Pt/Rh thermocouple was positioned at the sphere surface. This system was placed in a furnace with the thermocouple leads attached to a DVM coupled to a 2-pen recorder. As the furnace temperature is increased, the ΔT across

the radius of the sphere was measured. The results are shown in Fig. 4. Note that the ΔT decreases with increasing surface temperature. The temperature was increased step-wise and allowed sufficient time for the specimen to attain thermal equilibrium before the indicated readings were made. The difference between the "Heat-Up" and "Cool-Down" curves is due to some residual sinterability in the sphere after fabrication. Subsequent heating and cooling cycles indicated that this sinterability had been removed by the first series of equilibrations and the "Cool-Down" curve was followed.

Fig. 4 Observed ΔT , Surface-to-core, in MHFT Sphere

The reasons for this behavior are complex and are not completely understood at the time of this report. However, this behavior is reproducible as corroborative determinations have such. Such studies have included duplicate specimens to SPP-59, a specially fabricated 50-watt sphere, a 100-watt sphere with the thermocouple positions at various points between

surface and core, and determinations of ΔT under a variety of cover gasses and vacuum.

In all cases, the surface-to-core ΔT decreased with increasing surface temperature, the magnitude of the decrease depending on the thermal inventory of the specimen and the point of surface-to-core temperature measurement. All of these results suggest that all possible care be taken to avoid thermal shock in the regimes of greatest ΔT , that is, at the lowest ambient surface temperatures. In addition, a post-fabrication equilibrium at $\sim 1400^\circ\text{C}$ will remove any remaining sinterability and lead to lower ΔT values during other manipulations.

9. Chemical Properties

a. The heat and entropy of formation for the ceramic phase at 25°C are -935 ± 10 cal/g and 0.16 cal/g- $^\circ\text{C}$, respectively.

b. Chemical Reactions -- based on thermodynamic calculations. The thermodynamic values are taken from a number of sources. (10-13) A more complete tabulation of thermodynamic calculations involving interactions of Pu, O, C, and Ir is available. (14)

1. Water

Water vapor does not react with PuO_{2-x} below 2000°C . At lower temperatures, water vapor can oxidize PuO_{2-x} ; see the table under hydrogen. Solubility, as distinct from chemical reaction, is not considered in these statements.

2. Hydrogen

Hydrogen may reduce $\text{PuO}_{2.00}$ to PuO_{2-x} , with water vapor as the by-product. Values for PuO_{2-x} produced at various temperatures are listed in the accompanying table. Below the listed temperatures, the reaction is reversed and water vapor can oxidize PuO_{2-x} .

Reaction	Temperature of Calculated Equilibrium
$\text{PuO}_{2.00} + 0.02 \text{ H}_2 = \text{PuO}_{1.98} + 0.02 \text{ H}_2\text{O}$	$1290 \pm 10^\circ\text{C}$
$\text{PuO}_{2.00} + 0.05 \text{ H}_2 = \text{PuO}_{1.95} + 0.05 \text{ H}_2\text{O}$	$1420 \pm 20^\circ\text{C}$
$\text{PuO}_{2.00} + 0.08 \text{ H}_2 = \text{PuO}_{1.92} + 0.08 \text{ H}_2\text{O}$	$1520 \pm 20^\circ\text{C}$
$\text{PuO}_{2.00} + 0.10 \text{ H}_2 = \text{PuO}_{1.90} + 0.10 \text{ H}_2\text{O}$	$1590 \pm 20^\circ\text{C}$
$\text{PuO}_{2.00} + 0.15 \text{ H}_2 = \text{PuO}_{1.85} + 0.15 \text{ H}_2\text{O}$	$1760 \pm 20^\circ\text{C}$
$\text{PuO}_{2.00} + 0.20 \text{ H}_2 = \text{PuO}_{1.80} + 0.20 \text{ H}_2\text{O}$	$1920 \pm 20^\circ\text{C}$

3. Oxygen

There is a dissociative equilibrium between solid PuO_2 and gaseous PuO , PuO_2 , O and O_2 . However, the dissociation pressures do not become appreciable below about 1900°C . At lower temperatures, the reaction of oxygen with PuO_{2-x} to form PuO_2 is favored.

4. Carbon

Carbon may react with PuO_2 to give PuO_{2-x} . The reduced Pu oxides formed at various temperatures are listed in the accompanying table.

Reaction	Temperature of Calculated Equilibrium
$\text{PuO}_{2.00} + 0.02 \text{ C} = \text{PuO}_{1.98} + 0.02 \text{ CO}$	$1050 \pm 20^\circ\text{C}$
$\text{PuO}_{2.00} + 0.05 \text{ C} = \text{PuO}_{1.95} + 0.05 \text{ CO}$	$1050 \pm 20^\circ\text{C}$
$\text{PuO}_{2.00} + 0.10 \text{ C} = \text{PuO}_{1.90} + 0.10 \text{ CO}$	$1120 \pm 20^\circ\text{C}$
$\text{PuO}_{2.00} + 0.15 \text{ C} = \text{PuO}_{1.85} + 0.15 \text{ CO}$	$1160 \pm 20^\circ\text{C}$
$\text{PuO}_{2.00} + 0.20 \text{ C} = \text{PuO}_{1.80} + 0.20 \text{ CO}$	$1200 \pm 20^\circ\text{C}$
$\text{PuO}_{2.00} + 0.39 \text{ C} = \text{PuO}_{1.61} + 0.39 \text{ CO}$	$1360 \pm 20^\circ\text{C}$

5. Nitrogen

Nitrogen gas does not react with PuO_2 below 2000°C .

6. Tantalum

Tantalum metal may react with PuO_2 to form $\text{PuO}_{1.61}$ and Ta_2O_5 at $680 \pm 20^\circ\text{C}$.

7. Tungsten

Tungsten may react with PuO_2 to form PuO_{2-x} and WO_3 and/or WO_2 . The equilibrium reduced oxides formed are $\text{PuO}_{1.90}$ at $1300 \pm 20^\circ\text{C}$, $\text{PuO}_{1.85}$ at $1480 \pm 20^\circ\text{C}$, and $\text{PuO}_{1.80}$ at $1700 \pm 20^\circ\text{C}$.

8. Molybdenum

Molybdenum may react with PuO_2 to form PuO_{2-x} and MoO_3 and/or MoO_2 . The equilibrium reduced oxides formed are $\text{PuO}_{1.90}$ at $1300 \pm 20^\circ\text{C}$, and $\text{PuO}_{1.85}$ at $1630 \pm 20^\circ\text{C}$.

9. Iridium

Iridium does not react with PuO_2 . However, there is some evidence that PuO_{2-x} ($x \geq 0.1$), reacts with Ir to form PuIr_2 .⁽⁹⁾

10. Titanium

Titanium metal does not react with PuO_2 below 2000°C . TiO_2 does not react with PuO_2 , but will react with PuO_{2-x} to form PuO_2 and Ti_2O_3 .

11. Hafnium, Thorium and Zirconium

Hafnium, thorium, and zirconium metals will reduce PuO_2 to Pu metal. HfO_2 , ThO_2 , and ZrO_2 do not react chemically with PuO_2 but may form solid solutions.

12. Biological Tolerances

The radiobiological tolerances for ^{238}Pu are shown in the following table. (13)

Radionuclide and Type of Exposure	Organ of Reference	Maximum Permissible Dose in Total Body (rads)	Maximum Permissible Concentration (MPC)			
			For 60-yr man (MPC) ₆₀	For 30-yr man (MPC) ₃₀	For 15-yr man (MPC) ₁₅	For 10-yr man (MPC) ₁₀
^{238}Pu (in. 11)	Stom	0.04	10^{-11}	3×10^{-11}	5×10^{-11}	7×10^{-11}
	Liver	0.1	5×10^{-11}	5×10^{-11}	5×10^{-11}	5×10^{-11}
	Spleen	0.3	5×10^{-11}	10^{-11}	5×10^{-11}	5×10^{-11}
	GI (L27)	--	5×10^{-11}	5×10^{-11}	5×10^{-11}	5×10^{-11}
	Total Body	0.5	10^{-11}	10^{-11}	5×10^{-11}	5×10^{-11}
(in. 11)	Lung	--	--	5×10^{-11}	--	10^{-11}
	GI (L28)	--	5×10^{-11}	10^{-11}	5×10^{-11}	5×10^{-11}

* The abbreviations GI and LL refer to gastrointestinal tract and lower large intestine, respectively.

** MPC: Maximum permissible concentration in water [(MPC)_w] or air [(MPC)_a].

13. Shielding Data

As discussed above in Section 3, the total radiation associated with a "lot" of $^{238}\text{PuO}_2$ may vary as a function of age and processing history. Therefore, the following tables list attenuation data for different materials over energy ranges which might be encountered in processing ^{238}Pu . Appropriate calculations for required shielding thickness may be made as required.

a. Gamma Radiation

TABLE IX (17)

MASS ABSORPTION COEFFICIENTS (cm^2/g) FOR VARIOUS MATERIALS AS A FUNCTION OF GAMMA ENERGY

Energy (MeV)	Fe	Pb	U	Air	H ₂ O	Concrete
0.1	0.344	5.29	1.06	0.151	0.167	0.169
0.5	0.093	0.114	0.176	0.087	0.097	0.0870
1.0	0.059	0.068	0.0757	0.065	0.071	0.0635
2.0	0.0424	0.046	0.0484	0.044	0.049	0.0445
4.0	0.033	0.042	0.0440	0.031	0.034	0.0317

b. Neutron Radiation

TABLE X (8)

ATTENUATION FACTORS FOR NEUTRON SHIELDING MATERIALS

Thickness (cm) required to reduce intensity of neutrons of indicated energies to one-half of incident value.

Material	1 MeV	2 MeV	4 MeV
Polystyrene	2.7	3.9	5.0
Paraffin	3.2	4.6	6.0
Water	3.2	4.6	6.0
Lucite	4.2	6.0	7.8
Chemtree-13	4.9	6.6	8.2
Concrete	5.8	8.3	10.8
Masonite	6.7	9.7	12.6
LiH	3.6	5.2	6.8
Benelex-70	2.7	3.9	5.0

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