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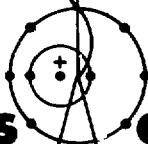
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AN INFORMAL REPORT

MASTER

Data Sheets for PMC Radioisotopic Fuel



los alamos
scientific laboratory

of the University of California

LOS ALAMOS, NEW MEXICO 87544



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by


T. K. Keenan
R. A. Kent
R. N. R. Mulford

*Supported by Isotopes Technology Branch, Space Nuclear Systems Division, AEC.

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DATA SHEETS FOR PMC RADIOISOTOPIC FUEL

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T. K. Keenan, R. A. Kent, and R. N. R. Mulford

ABSTRACT

PMC is the acronym for Plutonia Molybdenum Cermet. Plutonia, PuO_2 , forms the ceramic phase of the cermet and contains ~ 80 atom % ^{238}Pu . Molybdenum is the metallic phase of the cermet. The thermal energy resulting from the radioactive decay of the ^{238}Pu isotope is converted into usable electrical power for space probe or other applications. The basic cermet module is a disk 2.145 in. diam and 0.212 in. thick. The ceramic phase is nominally 83 wt % with the molybdenum contributing the balance of the weight. Stacks of disks are encapsulated in suitable containers to form the working heat source.

The following document lists the characteristics of this cermet with primary emphasis placed on proposed operational conditions and environments. LASL was responsible for the majority of the properties determinations and carried out some production support. Mound Laboratory, operated by the Monsanto Research Corp. (MRC) was responsible for the majority of disk production. Representative samples of cermet from both laboratories were used in many determinations.

1. Composition

a. <u>Plutonium</u>	<u>Isotope</u>	<u>wt/o</u>	<u>Half life (Yr)</u>
	²³⁶ Pu	~0.0001	2.8
	²³⁸ Pu	80 ⁽¹⁾	87.80 ± 0.02
	²³⁹ Pu	16.5	2.4 x 10 ⁴
	²⁴⁰ Pu	2.5	6.6 x 10 ³
	²⁴¹ Pu	0.8	13.0
	²⁴² Pu	0.1	3.7 x 10 ⁵

b. <u>Oxide</u>		<u>Min. wt/o</u>	<u>Max. wt/o</u>
	Pu	88.15	88.36
	O	11.64	11.85

O/Pu ratio 1.96 - 2.00

c. <u>Cermet</u>		<u>Min. wt/o</u>	<u>Max. wt/o</u>
	PuO ₂	81	84
	Mo	16	19

d. Impurities

The analysis reported in the following section represents averages of analytical studies carried out by both MRC and LASL.

1) Actinide Impurities

<u>Element</u>	<u>wt/o</u>
Th	0.14
U	0.74
Np	0.09
Am	0.06

2) Common Impurities

<u>Element</u>	<u>Specified Impurity Level⁽²⁾ (ppm)</u>	<u>Typical Analyses⁽³⁾ (ppm)</u>
Al	400	< 54
Ca	500	< 205
Co	250	< 53
Cr	350	< 52
Cu	300	< 50
Fe	500	< 346
Mg	50	< 40
Na	250	< 250
Ni	200	< 50
Si	300	< 53
F		< 100
Cl		< 100
Ta		< 200

2. Specific Power and Power Density of Typical Cermet⁽²⁾

- 0.31^{+0.4}_{-0.0} watts per gram
- 10.0^{+1.0}_{-1.0} curies per gram
- 3.2^{+0.4}_{-0.0} watts per cc
- 30⁺⁴₋₀ curies per watt

3. Radiation

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

b. Beta - None

c. <u>Gamma</u>	<u>Energy (MeV)</u>	<u>Photons/watt-sec</u>
1.	0.015 (L X-ray)	1.5 x 10 ¹¹
2.	0.043	4.4 x 10 ⁸
3.	0.099	1.0 x 10 ⁸
4.	0.150	1.2 x 10 ⁷
5.	0.203	4.4 x 10 ⁴
6.	0.760	5.8 x 10 ⁵

d. Bremsstrahlung - Negligible

e. <u>Neutrons</u>	<u>Source</u>	<u>Energy (MeV)</u>	<u>Particles/watt-sec</u>
1.	Spontaneous Fission	0-10, Av. = 2.0	4.7 x 10 ³
2.	(a/n) Reactions, Light elements only. At Z = 14, the coulomb barrier reaches 5.5 MeV.		See Table I
3.	Oxygen - 18 content shall be such that the neutron emission rate shall be no greater than 1 x 10 ⁴ neutrons per second per gram of Pu		
4.	Total neutron emission rate specified ⁽²⁾ as ≤ 3 x 10 ⁴ n/sec/g Pu.		

TABLE I

Specific Neutron Yields from Light Element
Impurities in ²³⁸Pu⁽⁴⁾

<u>Element</u>	<u>Neutrons per Second for 1 ppm</u>
Li	4.6
Be	133
B	41
C	0.2
N	0.0 (α, n threshold too high)
O	0.1 (natural mixture)
F	18
Na	2.2
Mg	2.1
Al	1.0
Si	0.2
P	0.03
S	0.03

4. Critical Mass

Transport calculations⁽⁵⁾ indicate the mass of a bare critical sphere of PMC to be 47.5 kg. Such a sphere would contain 35 kg of plutonium, of which 28 kg would be ²³⁸Pu. The presence of a thick (16 cm) iron reflector would reduce these values by one-half. Calculated partial densities of the cermet components are:

²³⁸ Pu	: 6.413 g/cc
²³⁹ Pu	: 1.61 g/cc
Mo	: 1.854 g/cc
Oxygen	: 1.024 g/cc

5. Compatibility

One set of compatibility tests with PMC was designed to examine the interaction of the fuel with Ta-10 W and T-111 (90 Ta-8 W-2 Hf) alloys. It is believed that the major mechanism of interaction between plutonium oxide and the tantalum alloys is the transfer of oxygen from the fuel to the solid solution and/or precipitation of the oxygen in the alloy with possible concomitant changes in the properties of the alloy. The compatibility test capsules were designed to simulate the Transit/Pioneer type of capsule, the ratio of fuel mass to tantalum mass being

about 0.9 in the tests. Each test capsule consisted of a T-111 disk completely enclosed (welded) within a 0.020 in. wall Ta-10 W can. The can was held in contact with a PMC fuel pellet and the assembly was sealed within a Mo container. Oxygen transport from the fuel to the T-111 thus had to take place through the Ta-10 W, as is the case in the Transit/Pioneer heat source. After being held at temperature for various lengths of time, the oxygen contents of the tantalum alloy parts was determined by chemical analysis. Microhardness measurements were also made. Test results are below:

PMC vs Tantalum Alloy Compatibility Results^a

<u>Test No.</u>	<u>Temperature (°C)</u>	<u>Time (hr)</u>	<u>Alloy</u>	<u>Hardness Change (DPHN avg)</u>	<u>Oxygen Content Change (wt ppm)</u>
TPMT-9 uncoated fuel	1050	500	Ta-10 W T-111	186 to 236 197 to 252	45 to 540 75 to 2500
TPMT-10 coated fuel	1050	1000	Ta-10 W T-111	189 to 189 200 to 212	20 to 40 75 to 90
TPMT-11 uncoated fuel	810	3523	Ta-10 W T-111	205 to 260 216 to 238	65 to 430 25 to 110
TPMT-12 uncoated fuel	900	2585	Ta-10 W T-111	210 to 225 210 to 218	65 to 150 60 to 60
TPMT-13 uncoated fuel	1050	3034	Ta-10 W T-111	192 to 282 204 to 243	-- to 320 -- to 1600
TPMT-14 Mo coated fuel	1050	7488	Ta-10 W T-111	277 to 285 273 to 286	30 to 110 45 to 20

^(a) The tabulated values represent the difference observed after test between a control capsule containing no fuel and the test capsule with fuel.

PMC - Ir Compatibility Results

Another series of tests of PMC fuel against iridium was done. The configuration consisted of a PMC pellet enclosed in a welded Ir container. In the tests listed as "vented" a slot in the Ir allowed gaseous communication between the container interior and exterior. The Ir container was sealed within an external tantalum container. At the relatively high temperatures of these tests, it was found that an iridium-molybdenum intermetallic compound was formed on all Ir inner surfaces. It is inferred that the mechanism of interaction between PMC and Ir consists of gaseous Mo transport via volatile Mo oxide gaseous species, the oxygen being supplied by the plutonium oxide constituent of the PMC. The tests are listed below:

PMC - Ir Tests

<u>Test No.</u>	<u>Temp.</u>	<u>Time</u>	<u>Configuration</u>	<u>Result</u>
MHW-13	1370	995	vented	Mo-Ir reaction
MHW-15	1370	995	unvented	Mo-Ir reaction
MHW-16	1500	1012	vented	Mo-Ir reaction

6. Thermophysical Properties

- Density equation - Not available
- Coefficients for thermal expansion (estimated)

The following estimated equation for thermal expansion is assumed valid in view of the very good agreement between estimated and measured values for SSC. ⁽⁵⁾

$$\Delta L/L = -2.225 \times 10^{-3} + 11.45 \times 10^{-6} T(^{\circ}C), (200 - 2000^{\circ}C).$$

- Specific heat and entropy (estimated for cermet, 83 wt/o PuO₂, 17 wt/o Mo). Values are given in Table II.

$$C_p (\text{cal/g} - ^{\circ}C) = 0.069 + 15.0 \times 10^{-6} T$$

$$- 5.24 / T^2$$

$$H_T^{\circ} - H_{25^{\circ}C}^{\circ} = \int_{25^{\circ}C}^T C_p dT$$

TABLE II

Thermodynamic Values for PMC

<u>Temp., ^oC</u>	<u>cal/g - deg C</u>	<u>H_T^o - H_{25^oC}}</u> <u>cal/g</u>
25	0.061	0
500	0.076	34
1000	0.084	75
1500	0.091	118
2000	0.099	166

- Temperatures of phase transformations ⁽⁶⁾
 - The ceramic phase melts at 2365 ± 30^oC (solidus) vs 2400 ± 20^oC for pure PuO₂.
 - The Mo metal phase melts at 2615 ± 20^oC.
- Latent heats of phase transformations ^(6,7)
 - The heat of melting for the ceramic phase is 65 cal/g.

- The heat of melting for the Mo metal phase is 69 cal/g.
- The heat of sublimation for the ceramic phase is 490 ± 10 cal/g.
- The heat of sublimation for the Mo metal phase is 1640 ± 10 cal/g.

f. Vapor Pressures

- Plutonia

Plutonia undergoes congruent vaporization to yield gaseous PuO, PuO₂, O and O₂ 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:

<u>Temp. ^oC</u>	<u>Congruently Vaporizing Composition</u>
1327	PuO _{1.82}
1527	PuO _{1.89}
1727	PuO _{1.86}
1927	PuO _{1.85}
2127	PuO _{1.84}

Mass spectrometric - Knudsen effusion studies

performed at LASL yield for PuO and PuO₂ gases above plutonia, the vapor pressure equations

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

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

These equations yield

$$\log_{10} P_E (\text{atm}) = 7.537 - 29096/T^{\circ}K,$$

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 - ^oC, respectively

2. PMC

The vaporization behavior of a number of PMC samples has been studied by means of mass spectrometric-Knudsen effusion techniques. The results for a typical PMC sample in the range of 500-2100^oC are listed in the following table. Except for the gaseous PuO and PuO₂ produced at high temperatures, all of the vapor pressures are nonequilibrium and transitory and decrease with time. The data listed in the table for these transitory species are the initial values for the temperature stated.

VAPOR SPECIES FROM PMC

T = 500°C		T = 675°C	
Species	Initial Pressure (atm)	Species	Initial Pressure (atm)
He	2.0×10^{-3}	He	7.8×10^{-4}
H ₂	6.0×10^{-3}	H ₂	7.8×10^{-4}
H ₂ O	4.5×10^{-4}	H ₂ O	1.0×10^{-4}
HF	2.0×10^{-3}	HF	6.2×10^{-4}
HCl	8.0×10^{-3}	HCl	1.6×10^{-4}
Ar	3.4×10^{-7}	Cl ₂	2.3×10^{-3}
		Ar	3.0×10^{-7}
		MoF ₆	1.2×10^{-7}
		MoCl ₅	1.6×10^{-3}

T = 775°C		T = 825°C	
Species	Initial Pressure (atm)	Species	Initial Pressure (atm)
He	1.8×10^{-3}	He	1.7×10^{-3}
H ₂	3.2×10^{-3}	H ₂	1.4×10^{-3}
H ₂ O	1.5×10^{-3}	H ₂ O	6.3×10^{-7}
HF	1.1×10^{-3}	HF	1.3×10^{-3}
HCl	8.0×10^{-3}	HCl	1.4×10^{-3}
Ar	4.3×10^{-7}	Cl ₂	1.0×10^{-3}
MoF ₆	1.1×10^{-7}	Ar	5.8×10^{-7}
MoCl ₅	1.3×10^{-4}	MoF ₆	1.5×10^{-7}
		MoCl ₅	6.5×10^{-4}

T = 875°C		T = 1000°C	
Species	Initial Pressure (atm)	Species	Initial Pressure (atm)
He	3.1×10^{-3}	He	1.2×10^{-3}
H ₂	1.2×10^{-3}	H ₂	1.2×10^{-3}
H ₂ O	5.0×10^{-7}	H ₂ O	4.4×10^{-7}
HF	9.3×10^{-3}	HF	7.2×10^{-3}
HCl	1.2×10^{-3}	HCl	1.2×10^{-3}
Cl ₂	9.3×10^{-3}	Cl ₂	8.4×10^{-3}
Ar	2.6×10^{-7}	Ar	6.2×10^{-7}
MoF ₆	9.3×10^{-7}	MoF ₆	1.3×10^{-7}
MoCl ₅	2.6×10^{-2}	MoCl ₅	2.4×10^{-2}

T = 1164°C		T = 1280°C	
Species	Initial Pressure (atm)	Species	Initial Pressure (atm)
He	3.1×10^{-3}	He	6.1×10^{-3}
H ₂	2.1×10^{-3}	H ₂	1.2×10^{-7}
H ₂ O	1.4×10^{-3}	H ₂ O	4.0×10^{-3}
HF	1.7×10^{-3}	HF	5.6×10^{-3}
HCl	2.1×10^{-3}	HCl	6.1×10^{-3}
Cl ₂	1.5×10^{-3}	Cl ₂	3.7×10^{-3}
Ar	2.6×10^{-7}	Ar	3.2×10^{-7}
MoF ₆	1.7×10^{-7}	MoF ₆	3.0×10^{-7}
MoCl ₅	1.5×10^{-3}	MoCl ₅	1.8×10^{-3}
PuF ₃ *	2.1×10^{-3}		

* Initial PuF₃ pressure above PMC is about 2×10^{-4} times the equilibrium pressure above pure PuF₃ at the same temperature.

T = 1000°C		T = 1461°C	
Species	Initial Pressure (atm)	Species	Initial Pressure (atm)
He	8.6×10^{-3}	He	6.7×10^{-3}
H ₂	1.7×10^{-7}	H ₂	6.7×10^{-3}
H ₂ O	6.5×10^{-3}	H ₂ O	4.0×10^{-3}
HF	8.6×10^{-3}	HF	6.7×10^{-3}
HCl	8.6×10^{-3}	HCl	6.7×10^{-3}
Cl ₂	6.0×10^{-3}	Cl ₂	3.4×10^{-3}
Ar	2.6×10^{-7}	Ar	2.9×10^{-7}
MoF ₆	5.2×10^{-7}	MoF ₆	3.0×10^{-7}
MoCl ₅	2.6×10^{-2}	MoCl ₅	2.0×10^{-2}
PuF ₃	5.2×10^{-3}	PuF ₃	3.4×10^{-2}

T = 1602°C		T = 1690°C	
Species	Initial Pressure (atm)	Species	Initial Pressure (atm)
He	8.5×10^{-3}	He	2.2×10^{-2}
H ₂	1.9×10^{-7}	H ₂	2.2×10^{-7}
H ₂ O	8.0×10^{-3}	H ₂ O	1.0×10^{-3}
HF	8.5×10^{-3}	HF	6.8×10^{-3}
HCl	7.6×10^{-3}	HCl	6.6×10^{-3}
Cl ₂	5.7×10^{-3}	Cl ₂	4.4×10^{-3}
Ar	6.9×10^{-7}	Ar	6.6×10^{-7}
MoF ₆	3.5×10^{-7}	MoF ₆	2.2×10^{-7}
MoCl ₅	3.8×10^{-2}	MoCl ₅	4.4×10^{-2}

Above 1600°C, the degassing of the PMC sample is near completion and the only vapor species observed in significant amounts other than He, are the equilibrium species PuO and PuO₂. Values for P_E for PMC are compared with those calculated for plutonia below.

T°C	PE (atm) - PMC	PE (atm) - Pure Plutonia
1602	1.16×10^{-8}	1.09×10^{-8}
1680	4.56×10^{-8}	4.56×10^{-8}
1759	1.72×10^{-7}	1.73×10^{-7}
1675	4.28×10^{-8}	4.18×10^{-8}
1778	2.21×10^{-8}	2.35×10^{-7}
1834	5.51×10^{-8}	5.59×10^{-7}

- g. Thermal Conductivity (estimated)
 k (cal/cm - sec - °C) = $0.027 - 7.0 \times 10^6 T$ (°C), (25 - 2000°C).
- h. Thermal diffusivity (estimated)
 α (cm²/sec) = $0.036 - 11.0 \times 10^{-6} T$ (°C), (25 - 2000°C).
- i. Viscosity (estimated)
 The viscosity of the ceramic phase is estimated to be 32 centipoise (\pm 25%) at the melting point.
- j. Surface tension
 - 1. The surface tension of the ceramic phase is 523 dyne/cm (\pm 15%) at the melting point. (8)
 - 2. The surface tension of the Mo metal phase is 2080 dyne/cm at the melting point. (9)
- k. Total hemispherical emittance - Not available.
 - 1. Spectral emissivity
 The spectral emissivity for Mo is 0.38 at 1700°C (wavelength = 0.467μ). (9) Preliminary data yield 0.7 for the emittance of PMC. (6).
 - m. Crystallography
 The ceramic phase has FCC structure with a lattice parameter of $5.9350 \pm 0.0005 \text{ \AA}$, when corrected for self-heating effects. (6)
 The Mo metal phase has BCC structure with a lattice parameter of $3.1468 \pm 0.0005 \text{ \AA}$. (10)

n. Solubility in sea water

The accompanying table shows the amount of plutonium, in μg per mm^2 of PMC surface area, dissolved from a 1/2-in. dia PMC specimen during the stated times of exposure in 75 liters of synthetic seawater. (11)

Time (days)	Total Pu in Seawater ($\mu\text{g}/\text{mm}^2$)
0.1	2.1×10^{-2}
1	4.0
5	4.13
10	4.17
20	4.64
35	5.38
50	6.00
70	6.57

o. Helium Migration

1. Release Rates

Helium release rate data are available from four PMC disks. The data have been fitted by a mathematical model developed from classical diffusion theory. The model describes the helium content of the fuel by the following equation:

$$\frac{Q}{Q_0} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 \pi^2 D^1 t) - \frac{B}{D^1 C_0} \frac{6}{\pi^4} \sum_{n=1}^{\infty} \frac{1}{n^4} \exp(-n^2 \pi^2 D^1 t) + \frac{B}{15 D^1 C_0}$$

$$\frac{1}{n^4} \exp(-n^2 \pi^2 D^1 t) + \frac{B}{15 D^1 C_0}$$

- where
- Q is the quantity of helium in the sample [cc(STP) g^{-1}] at time t (sec),
 - Q_0 is the quantity of helium in the sample at t = 0,
 - D^1 is the effective diffusion coefficient (sec^{-1}),
 - B is the (constant) helium generation rate [cc(STP) g^{-1}], and
 - C_0 is the uniform concentration at t = 0 [cc(STP) g^{-1}].

The effective diffusion coefficients, D^1 , were determined for each of the disks by the best fit of the data to the model. The values obtained are listed in the following table.

Effective Diffusion Coefficients for PMC Disks

Disk No.	Temp. ($^{\circ}\text{C}$)	D^1 (sec^{-1})	Time in test (days)
PMC-101	800	$1.5 \times 10^{-10} - 1 \times 10^{-11}$	402
PMB-74	800	1×10^{-9}	192
PM-89T	850	1.2×10^{-9}	283
PFT-88	850	3×10^{-7}	67

* Through 300 days the helium content predicted by a D^1 of $1.5 \times 10^{-10} \text{ sec}^{-1}$ was in reasonably good agreement with the experimental value for this disk. The helium release rate then changed very rapidly so that a D^1 of $1 \times 10^{-6} \text{ sec}^{-1}$ throughout the duration of the experiment was necessary to obtain the helium content of the fuel at 402 days.

2. Microstructural Effects

Helium movement and observable helium release begin at temperatures above 500°C . It is thus assumed that fuel storage at temperatures below 500°C results in the interstitial accumulation of helium in the solid. When the temperature is raised, not only is gaseous helium released but bubbles form in the ceramic grain boundaries of the fuel. At temperatures in the approximate range 700 to 1100°C , the general effect appears to be a separation of grain boundaries which could affect the mechanical properties of the fuel. At higher temperatures the bubbles migrate along grain boundaries and coalesce.

The formation of bubbles in the fuel is accompanied by some swelling. The maximum linear increase attributable to bubble formation observed in PMC fuel has been about 1%.

The fuel from Pioneer capsule PF-1 which had operated for 219 days at $800-850^{\circ}\text{C}$ exhibited no helium bubble formation but had swelled about 0.6%, linear.

7. Mechanical Properties

a. Hardness

At 25°C the hardness for the Mo metal phase is approximately 150 DPH, that for the PuO_2 ceramic phase is approximately 850 DPH. (6)

b. Impact

The results of impact tests on PMC samples after various treatments are given below. The samples consisted of discs 0.5" in diameter by approximately 0.21" thick.

Impact Tests on PMC

Impact velocity 325 fps, Impact temperature 454°C

<u>Sample No.</u>	<u>Condition</u>	<u>Fraction < 10 μ</u>	<u>Fraction < 4 μ</u>
111-A	as fabricated	0.012	n. d. *
111-B	as fabricated	0.008	0.0019
111-C	82 days at 815°C	0.022	0.0024
117-1	as fabricated	0.010	n. d. *
117-2	75 days at 1370°C	0.027	0.0043
PMT-67-A	42 days at 815°C plus reentry pulse to 1400°C	0.013	0.0027
PMT-67-B	42 days at 815°C plus reentry pulse to 1400°C	0.021	n. d. *
PMT-67-E	as fabricated	0.009	0.00085
PMT-67-F	as fabricated	0.015	0.0012

* n. d. = not determined

8. 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-°C, respectively.

b. Chemical Reactions -- based on thermodynamic calculations. The thermodynamic values are taken from a number of sources. (12 - 15)

1. Water

Water vapor does not react with PuO_2 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 will reduce PuO_2 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} .

<u>Reaction</u>	<u>Minimum Temperature For Reaction To Take Place</u>
$\text{PuO}_2 + 0.02 \text{ H}_2 = \text{PuO}_{1.98} + 0.02 \text{ H}_2\text{O}$	$1290 \pm 10^\circ\text{C}$
$\text{PuO}_2 + 0.05 \text{ H}_2 = \text{PuO}_{1.95} + 0.05 \text{ H}_2\text{O}$	$1420 \pm 20^\circ\text{C}$
$\text{PuO}_2 + 0.08 \text{ H}_2 = \text{PuO}_{1.92} + 0.08 \text{ H}_2\text{O}$	$1520 \pm 20^\circ\text{C}$
$\text{PuO}_2 + 0.10 \text{ H}_2 = \text{PuO}_{1.90} + 0.10 \text{ H}_2\text{O}$	$1590 \pm 20^\circ\text{C}$
$\text{PuO}_2 + 0.15 \text{ H}_2 = \text{PuO}_{1.85} + 0.15 \text{ H}_2\text{O}$	$1760 \pm 20^\circ\text{C}$
$\text{PuO}_2 + 0.20 \text{ H}_2 = \text{PuO}_{1.80} + 0.20 \text{ H}_2\text{O}$	$1920 \pm 20^\circ\text{C}$

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 will reduce PuO_2 to PuO_{2-x} . The reduced Pu oxides formed at various temperatures are listed in the accompanying table.

<u>Reaction</u>	<u>Minimum Temperature For Reaction To Take Place</u>
$\text{PuO}_2 + 0.02 \text{ C} = \text{PuO}_{1.98} + 0.02 \text{ CO}$	$1050 \pm 20^\circ\text{C}$
$\text{PuO}_2 + 0.05 \text{ C} = \text{PuO}_{1.95} + 0.05 \text{ CO}$	$1080 \pm 20^\circ\text{C}$
$\text{PuO}_2 + 0.10 \text{ C} = \text{PuO}_{1.90} + 0.10 \text{ CO}$	$1120 \pm 20^\circ\text{C}$
$\text{PuO}_2 + 0.15 \text{ C} = \text{PuO}_{1.85} + 0.15 \text{ CO}$	$1160 \pm 20^\circ\text{C}$
$\text{PuO}_2 + 0.20 \text{ C} = \text{PuO}_{1.80} + 0.20 \text{ CO}$	$1200 \pm 20^\circ\text{C}$
$\text{PuO}_2 + 0.39 \text{ C} = \text{PuO}_{1.61} + 0.39 \text{ CO}$	$1360 \pm 20^\circ\text{C}$

At temperatures above 1900°C, carbon reacts with PuO_2 to form PuC_2 and CO.

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 reacts with PuO_2 to form PuO_{2-x} and WO_2 and/or WO_3 . The reduced oxides formed are $\text{PuO}_{1.98}$ at $1300 \pm 20^\circ\text{C}$, $\text{PuO}_{1.95}$ at $1480 \pm 20^\circ\text{C}$, and $\text{PuO}_{1.90}$ at $1700 \pm 20^\circ\text{C}$.

8. Molybdenum

Molybdenum reacts with PuO_2 to form PuO_{2-x} and MoO_2 and/or MoO_3 . The reduced oxides formed are $\text{PuO}_{1.98}$ at $1300 \pm 20^\circ\text{C}$, and $\text{PuO}_{1.95}$ 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 .

10. Titanium

Titanium metal does not react with PuO₂ below 2000°C. TiO₂ does not react with PuO₂, but will react with PuO_{2-x} to form PuO₂ and Ti₂O₃.

11. Hafnium, Thorium and Zirconium

Hafnium, thorium, and zirconium metals will reduce PuO₂ to Pu metal. HfO₂, ThO₂, and ZrO₂ do not react chemically with PuO₂ but may form solid solutions.

12. Biological Tolerances

The radiobiological tolerances for ²³⁸Pu are shown in the following table. (16)

Radionuclide and Type of Decay	Organ of Reference	Maximum Permissible Burden in Total Body Q(μCi)	Maximum Permissible Concentrations			
			For 40-Hr week		For 168-Hr week	
			(MPC) _w μCi/cc	(MPC) _a μCi/cc	(MPC) _w μCi/cc	(MPC) _a μCi/cc
²³⁸ Pu ^{α, γ}	Bone	0.04	10 ⁻⁴	2 × 10 ⁻¹³	5 × 10 ⁻¹³	7 × 10 ⁻¹³
	Liver	0.2	6 × 10 ⁻⁴	8 × 10 ⁻¹³	2 × 10 ⁻¹³	3 × 10 ⁻¹³
	Kidney	0.2	6 × 10 ⁻⁴	10 ⁻¹¹	3 × 10 ⁻¹³	4 × 10 ⁻¹³
	GI (LLI)*	--	8 × 10 ⁻⁴	2 × 10 ⁻⁷	3 × 10 ⁻¹³	8 × 10 ⁻¹³
	Total Body	0.3	10 ⁻³	10 ⁻¹¹	4 × 10 ⁻¹³	8 × 10 ⁻¹³
(Inhal.)	Lung	--	--	3 × 10 ⁻¹¹	--	10 ⁻¹¹
	GI (LLI)	--	8 × 10 ⁻⁴	10 ⁻⁷	3 × 10 ⁻¹³	8 × 10 ⁻¹³

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

13. Shielding Data

Shielding data are presented in the following table. (8, 17)

a. Attenuation Factors for Gamma Shielding Materials

Material	Density (g/cc)	Thickness Required to Reduce Intensity of 800 keV Gamma Rays to 1% of Incident Value (cm)	Attenuating Layer (g/cm ²)
Concrete	2.35	24.4	57.34
Iron	7.87	8.8	69.26
Hastelloy C	8.94	7.8	69.73
Haynes Alloy 25	9.13	7.7	70.30
Lead	11.36	4.7	53.39
Tantalum	16.6	3.6	59.76
Uranium	19.07	2.5	47.68
Tungsten	19.3	3.0	57.90

b. Attenuation Factors for Neutron Shielding Materials

Material	Density (g/cc)	Thickness Required to Reduce Intensity of 1-10 Mev Neutrons to 0.1% of Incident Value (cm)	Attenuating Layer (g/cm ²)
Polyethylene	0.938	50	47
Plexiglas	1.185	78	92
Paraffin	0.89	60	53
Benelex 70	1.40	50	70

For Pu²³⁹ Be neutron source with average neutron energy of ~ 4 Mev

References

1. Letter M. Klein AEC/SNS, to F. P. Baranowski, Nov. 18, 1968, "Savannah River Plutonium-238 Dioxide Feed Specification".
2. MRC Document 1-14531, Rev. 2, Nov. 6, 1970, "Plutonium-238 Dioxide Molybdenum Cermet Disc Specification".
3. MRC Reports MLM-1827 and MLM-1887.
4. G. M. Matlack and C. F. Metz, "Radiation Characteristics of Plutonium-238", LASL Document LA-3696, 1967.
5. LASL Document CMB-11-9740, April 15, 1971.
6. Experimental values measured at LASL.
7. Calculated at LASL.
8. MRC Report MLM-1691, 1969
9. C. J. Smithells, Metals Reference Book, Plenum Press, London, 1967.
10. W. B. Pearson, Handbook of Lattice Spacings and Structures of Metals, Pergamon Press Ltd., London, 1967.
11. LASL Document CMB-5-C-101, May 12, 1971.
12. R. J. Ackermann, R. L. Faircloth and M. H. Rand, J. Phys. Chem. 70, 3698 (1966).
13. T. L. Mackin and M. H. Rand, Proceedings of the Symposium on Thermodynamics with Emphasis on Nuclear Materials and Atomic Transport in Solids, IAEA, Vienna, 1965, p 145.
14. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Michigan, 1965 and Supplement.
15. High Temperature Oxides, Part II., edited by A. M. Alper, Academic Press, N. Y. 1970.
16. "Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and Water for Occupational Exposure", National Bureau of Standards Handbook 69, p. 87.
17. MRC Report, MLM-1564, 1968.