LA-DC-10,046

CMB-11-9455

CONF-681022--1

MASTER

RECEIVED BY DTIC NOV 5 1968

THE LASL PLUTONIUM-238 FUEL DEVELOPMENT PROGRAM
(SEPO/SNS/AEC)

prepared for presentation at
Plutonium-238 Isotopic Fuels and Heat Source
Program Review

U. S. A. E. C. Headquarters

October 29-30, 1968

Prepared by the Los Alamos Scientific Laboratory,
University of California

(Work sponsored by Isotopes and Materials Branch, SEPO/SNS)

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission

A Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights, or

B Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

leg

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.

CONTENTS

- I. Introductory
 - A. Properties of solid solutions and possible advantages
 - B. The overall program
- II. Short-term accelerated survey
 - A. Objectives
 - B. Results and current status
 - 1. Synthesis and fabrication
 - (a) specimens for properties
 - (b) specimens for safety evaluation
 - (c) large disc fabrication
 - 2. Properties
 - (a) Measured
 - (b) Calculated
 - 3. Tests in progress
- III. Future plans
- IV. Data sheets for Solid Solution Fuels (Appendix)

I. INTRODUCTION

A. Properties of solid solutions and possible advantages

In order to gain some insight into what is meant by a solid solution fuel, it would be helpful to describe its structure.

Consider a simple crystallographic lattice array of plutonium and oxygen atoms. In the case of PuO_2 , the plutonium atoms are located in a face-centered cubic array. A plutonium atom can be removed from the crystal lattice, and its position can be filled by substituting a diluent atom such as zirconium or thorium. This substitution can be continued until a large fraction of the plutonium atoms have been replaced. The diluent atom will be larger or smaller than the plutonium atom, so some expansion or contraction of the crystallographic unit cell will occur. However, as long as the crystal habit remains unchanged, one has a solid solution of the diluent atom oxide in PuO_2 . In some systems there is only limited solubility, while in others the solubility is very extensive.

For this application diluents that have very high solubilities were selected. Moreover, the diluents were chosen to enhance the properties of the PuO_2 . For example, diluents having oxides that are more stable than PuO_2 were selected so that the resulting solid solution would be more stable than PuO_2 . The free energies of formation of these diluents are compared to that of PuO_2 in Table I. The following properties of such solid solutions may be predicted on the basis of known thermodynamic correlations:

1. The thermal stability of the PuO_2 is increased. Thus the tendency for PuO_2 to dissociate or vaporize is reduced. Moreover, the melting point can be increased.

2. The power density of a given fuel body can be varied over a significant range with minimal change in fuel properties.
3. By judicious choice of diluent the reactivity of PuO_2 with water and with container materials can be reduced.
4. The specific radioactivity of a given size respirable particle of PuO_2 is reduced.

In addition to these possible advantages, the process for making solid solution fuels is relatively economical. It consists of simply blending unshaped PuO_2 and diluent oxide powders, followed by cold pressing and sintering. It should be noted that it is not necessary to melt the fuel in order to prepare a solid solution; the solution is formed by a solid state diffusion during the sintering process.

B. The overall program

The first task in the program was to conduct an accelerated short-term development phase to provide a technical basis for estimating the performance of $^{238}\text{PuO}_2$ solid solution fuels by November, 1968. This included process chemistry development, fabrication development, properties measurements, and theoretical estimates of performance of various fuel compositions and various power densities.

The second task involves follow-on fabrication and properties work with the preferred fuel composition for the purpose of establishing the capability for producing a limited number of large specimens for use as heat sources.

The later tasks in the program are directed towards defining production methods and economics, and to provide assistance to the Commission and its contractors in order to establish a reliable commercial capability.

II. SHORT-TERM ACCELERATED SURVEY

A. Objectives

1. Select fuel composition and power density
2. Develop synthesis and fabrication procedures
3. Prepare small ^{239}Pu pellets and make the following screening measurements:
 - A. Crystallography
 - B. Microstructure
 - C. Chemical composition, purity, and uniformity
 - D. Density
 - E. Thermal analysis
 - F. Preliminary "long term" compatibility at 900°C , and short term overtests.
4. Measure additional properties with ^{238}Pu specimens
 - A. Helium migration (700°C to 1400°C)
 - B. Prepare samples for thermal diffusivity measurements
 - C. Prepare samples for sea water solubility measurements
5. Calculate and estimate properties
 - A. Thermal conductivity (use thermal diffusivity data, if available)
 - B. Long term compatibility
 - C. External radiation; the feasibility of using enriched ^{18}O
 - D. Radiochemical changes in fuel over lifetime, and their effects
 - E. Basic thermodynamic properties
6. Demonstrate fabrication of discs (about 2 in. diam x 0.5 in. tall) and demonstrate individual disc encapsulation, if required.

7. Additional requirements for SEPO/SNS Safety Evaluation

- A. Arc tunnel tests (pellets)
- B. Impact tests (discs)
- C. Unspecified tests

B. Results and current status

1. Fuel selection: It has not been possible to select a given fuel composition and power density for near term applications. Therefore, three reference power densities (1.7, 3.5, and 4.4 watts/cc) and two diluents (ZrO_2 and ThO_2) are being carried forward in the program.
2. Synthesis and fabrication: The following types of specimens have been fabricated by the process shown in Figure 1:
 - (a) Pellets, 0.254 in. dia x 0.35 in. long with axial hole 0.060 in. dia x 0.080 in. deep
 - (b) Pellets, as above, except 0.25 in. long
 - (c) Pellets, as above, without axial hole
 - (d) Thin wafers, 0.250 in. dia x 0.035 in. thick
 - (e) Large discs, nominally 2 in. dia x 0.5 in. thick
 - (f) Same as (e), except 0.25 in. thick

All of the above specimens have been fabricated with the first reference fuel composition, $\text{PuO}_2\text{-ZrO}_2$,* at a plutonium concentration that corresponds to a power density of 1.7 watts/cc. In addition, compositions equivalent to 3.5 and 4.4 watts/cc have been fabricated. Specimens that have been prepared during this phase of the program are shown in Table II. In addition, the fabrication of large $^{238}\text{PuO}_2\text{-ZrO}_2$ discs has been started.

* The ZrO_2 used in this work contains 4.8 percent by weight CaO stabilizer

Typical fabricated specimens are shown in Figures 2, 3, and 4.

Experience has indicated that both the ZrO_2 - and the ThO_2 - diluent fuels can be fabricated directly in any of the reference power densities.

The overall yield of PuO_2 in producing the large discs is 98 percent.

3. Screening measurements:

- A. Crystallography: All of the reference fuel systems have been shown to be face-centered cubic (fluorite) structure over the complete range of composition, as indicated in Figure 5. The uniform change in lattice parameter with PuO_2 concentration shown for the $\text{ZrO}_2|\text{CaO}|$, ThO_2 , and CeO_2 diluents indicate that these form complete solid solution systems with PuO_2 . On the other hand, there is a limit in the solubility of PuO_2 in unstabilized ZrO_2 ; the fcc solid solution region extends only to 77 mole percent ZrO_2 (at room temperature), and monoclinic ZrO_2 is in equilibrium with the saturated fcc structure at higher ZrO_2 concentrations.
- B. Microstructure: Typical microstructures are shown in Figures 6, 7, and 8. The $^{239}\text{PuO}_2$ and $^{238}\text{PuO}_2$ structures shown in Figure 6 are typical of those previously experienced at this Laboratory.⁽¹⁾ The PuO_2 - ZrO_2 structures reflect the Si, Al, and Fe impurities that are present in commercial grade ZrO_2 (see next section). These elements appear in the grey grain boundary phases. As the effects of such impurity phases are not yet known, no attempt has been made to eliminate them from the starting ZrO_2 powder. The PuO_2 - ThO_2 microstructure shown in Figure 8 does not

show any evidence of impurity phases.

Alpha radioautographs of the 1.7 and 4.4 watts/cc compositions indicate uniform power densities, as shown in Figure 9.

- C. Chemical Composition: The chemical compositions of the solid solution materials are essentially identical to those of the starting powders. A small amount of iron is picked up in powder milling steps. Chemical purities are shown in Table III.
- D. Density: During the accelerated phase of the program the the standard ceramic engineering relationships (density as a function of pressing pressures, sintering temperature, etc.) were not studied. Instead the desired densities were obtained by pressing and sintering the specimens under conditions that were generated in earlier work with PuO_2 powders.⁽¹⁾ Densities ranging from 70 percent to 96 percent of theoretical have been produced.
- E. Thermal Analysis: The melting point curves for $\text{PuO}_2\text{-ThO}_2$ and $\text{PuO}_2\text{-ZrO}_2$ (unstabilized) appear in the literature, and are reproduced in Figure 10. Also shown in this figure are melting points obtained by high temperature differential thermal analysis of the solid solution fuels. When the 39 m/o $\text{PuO}_2\text{-ZrO}_2$ (1.7 watt/cc) composition was cycled thermally to the melting point, no transitions were indicated until melting occurred at 2400°C (4350°F). The 40 m/o $\text{PuO}_2\text{-ThO}_2$ did not display any transition up to the melting point. The solidus temperature was 2725°C (4950°F); the liquidus temperature was 2925°C (5300°F).

F. Compatibility: In general, the compatibility of the pure solid solution oxides can be estimated quite well from compatibility results obtained with PuO_2 , ZrO_2 , and ThO_2 . In addition, the compatibility of solid solution fuels, (including ^{238}Pu compositions) with TZM at 900°C is being investigated in preliminary tests. The experimental array is shown in Table IV; the compatibility capsule design is shown schematically in Figure 11. This design brackets the solid solution fuel sample with the individual components.

High temperature tests also are programmed, including the molten fuel compatibility. In previous work it was shown that there is no reaction between PuO_2 and Mo after 6 hr. at 1650°C in an Ar atmosphere.⁽³⁾

4. Additional properties with ^{238}Pu specimens:

- A. Helium Migration: The 0.25 in. dia x 0.25 in. tall pellets that have been put in storage to accumulate He from alpha decay are shown in Table V.
- B. Thermal Diffusivity: The four wafers of $^{238}\text{PuO}_2\text{-ZrO}_2$ solid solution material shown in Table VI have been fabricated and shipped to Batelle Pacific Northwest Laboratory for thermal diffusivity measurements. In addition, two 100% $^{238}\text{PuO}_2$ specimens are being prepared.
- C. Sea Water Solubility: The sixteen samples listed in Table VII have been fabricated and shipped to the Naval Radiological Defense Laboratory at San Francisco for solubility tests. One pellet of each power density was equipped with a 0.060 in. dia blind axial hole for thermocouple insertion.

5. Calculated and estimated properties: Data sheets have been prepared for the $\text{PuO}_2\text{-ZrO}_2$ and the $\text{PuO}_2\text{-ThO}_2$ fuels (see appendix).

A. Thermal Conductivity: The thermal conductivity for the 1.7 and 3.5 watt/cc compositions have been estimated from literature citations of the thermal conductivities of UO_2 , PuO_2 , ZrO_2 , $\text{UO}_2\text{-ZrO}_2$ solid solutions, and $\text{UO}_2\text{-ThO}_2$ solid solutions. The results are summarized in Figure 12. This graph shows the radial temperature drop as a function of power density and thermal conductivity, using the estimated values of thermal conductivity (see data sheets). The $\text{PuO}_2\text{-ThO}_2$ system has the lowest calculated temperature gradient, i. e., less than 100°C at a power density of 1.7 watts/cc, and 250°C at a power density of 3.5 watts/cc.

This graph was based on a fuel geometry of 2.3 inch diameter discs, stacked to an infinite height. Any end losses will reduce these calculated gradients.

B. External Radiation; The Feasibility of Using Enriched ^{16}O : When ^{238}Pu metal is oxidized to $^{238}\text{PuO}_2$ in air, the increase in neutron emission rate is 9700 n/sec - gPu. This is caused by the reactions $^{17}\text{O}(\alpha, n) \text{Ne}^{20}$ and $^{18}\text{O}(\alpha, n) \text{Ne}^{21}$. These reactions also increase the photon emission rates. These increases can be eliminated if pure ^{16}O is used to prepare $^{238}\text{PuO}_2$.¹⁶ However, the basic emission rate (from spontaneous fission and neutron self-multiplication) cannot be reduced. Experience has shown that $^{238}\text{PuO}_2$ powders received at this Laboratory can emit 45,000 - 100,000 n/sec - gPu, because of (α, n) reactions on light element impurities.⁽⁴⁾

Conventional ^{238}Pu also contains about 1.2 ppm ^{236}Pu , which

decays to ^{212}Pb and ^{208}Tl daughters that produce intense penetrating gamma radiation. Dose rate contributions can be calculated directly once the system geometry is defined.

- C. Radiochemical Changes in Fuel: The major change in the conversion of ^{238}Pu to ^{234}U by alpha decay. Since the $\text{UO}_2\text{-ZrO}_2\text{-CaO}$ system is a solid solution system,⁽⁵⁾ and since $\text{UO}_2\text{-PuO}_2$ also form a continuous series of solid solutions, the ^{234}U should also be in solution as it is produced. While lattice vacancies and new interstitial locations occur at room temperature because of alpha decay, these dislocations anneal out at higher temperature in $^{238}\text{PuO}_2$.⁽⁶⁾ Chemical changes caused by decay of other isotopes such as ^{236}Pu should be insignificant. The effect of He accumulation in the fuel lattice is not predictable at this time for any $^{238}\text{PuO}_2$ fuel forms. However, experimental work is in progress.

- D. Basic Thermodynamic Properties: (See Data Sheets in Appendix)

6. Demonstrate Fabrication of Discs

As shown in Table II and Figure 4, large $^{238}\text{PuO}_2\text{-ZrO}_2$ discs have been fabricated in the 0.5 in. thickness.

In addition, two large 0.25 in. thick $^{238}\text{PuO}_2\text{-ZrO}_2$ discs have been fabricated. The first attempt to press the $^{238}\text{PuO}_2\text{-ZrO}_2$ powders was only partially successful, and the unfired specimen had several edge defects. However, sintering this specimen showed that no detrimental effects were to be expected during the firing steps. After slight procedural changes, the second disc was pressed and sintered to form a satisfactory product, as shown in Figure 13.

7. Additional SEPO/SNS Safety Requirements

- A. Pellets for ARC Tunnel Tests

The samples that have been sent to Sandia Laboratories are

listed in Table VIII.

B. Specimens for Impact Tests

The samples that have been sent to Sandia Laboratories for impact testing are shown in Table VIII. In addition, two large $^{239}\text{PuO}_2\text{-ZrO}_2$ discs were in storage at LASL on October 18 for these tests.

C. Unspecified Tests

As shown in Table II, numerous pellets, discs, and powders are available for test.

III. FUTURE PLANS

The most immediate program requirement is to reach a capability for producing discs that have diameters in the 2.0 to 2.5 inch range. Present fabrication equipment is limited to a 2 inch diameter. A larger press and sintering furnace has been ordered, and the enclosure designs are complete. These new units should be available during the third quarter of FY 1969.

Parametric studies of the reference fuel processing operations will be done, including establishing dimensional tolerance capabilities. (Experience with many pellets of $\text{PuO}_2\text{-ZrO}_2$ has indicated that good dimensional control is possible by this process.)

Tests now in progress will be evaluated, and in some cases (particularly compatibility and safety evaluation) these tests will be extended.

Fuel properties, including geometries, will be continuously extended as a parallel development task for scheduled mission applications. If required, fuel discs for a few 500 watt heat sources will be produced.

REFERENCES

1. "Studies on the Formation of Pu_2O_3 in the Sintering of PuO_2 ," W. C. Pritchard and R. L. Nance, Los Alamos Scientific Laboratory Report No. LA-3493 (1966).
2. "Plutonium-Uranium Mixed Oxides," N. H. Brett, J. D. L. Harrison, and L. E. Russell, Plutonium 1960 p. 492, Cleaver-Hume Press, Ltd., London (1961).
3. "Compaction and Sintering of PuO_2 -Mo Powder Mixtures," W. C. Pritchard, K. A. Johnson, J. A. Leary, and W. J. Maraman, Los Alamos Scientific Laboratory Report No. LA-2621 (1961).
4. "Preparation and Evaluation of Refined Plutonium-238," Document CMB-1458 (July 17, 1968) Annual Report for the Period July 1, 1967 - June 30, 1968, by Los Alamos Scientific Laboratory; Work Sponsored by the Division of Isotopes Development, U. S. A. E. C.
5. "Thermal Properties of Compositions in the System UO_2 - ZrO_2 - CaO ," R. S. Kern and R. J. Beals, Ceram. Bull. 46, 1154 (1967).
6. "Self-Irradiation Damage in Plutonium Ceramics," C. W. Bjorklund, R. M. Douglass and J. A. Leary, Bull. Amer. Ceram. Soc. 46, 901 (1967).

Table I
GIBBS STANDARD FREE ENERGIES OF FORMATION
(kcal/g - atom of oxygen)

	$-\Delta G_f^\circ$	
	<u>1000°K</u>	<u>2000°K</u>
PuO ₂	105	85
ZrO ₂	108	86
ThO ₂	124	102
CaO	127	98

Table II

LIST OF SPECIMENS PREPARED AS OF OCTOBER 20, 1968

<u>Composition</u>	<u>Type</u>	<u>Number</u>
$^{239}\text{PuO}_2 - \text{ZrO}_2 \text{Y} $	Pellets	29
" "	Small discs	3
$^{239}\text{PuO}_2 - \text{ZrO}_2 \text{X} $	Pellets	12
$^{239}\text{PuO}_2 - \text{ThO}_2$	Pellets	9
$^{239}\text{PuO}_2 - \text{ZrO}_2 \text{Y} $	Large discs	4
$^{238}\text{PuO}_2 - \text{ZrO}_2 \text{Y} $	Pellets	36
" "	Small discs	7
100% $^{238}\text{PuO}_2$	Pellets	14
$^{238}\text{PuO}_2 - \text{ThO}_2$	Pellets	12
$\text{ZrO}_2 \text{Y} $	Pellets	3
ThO_2	Pellets	<u>3</u>
Total		135

Table III
Chemical Composition of Typical Powders

Element	Concentration, ppm by wt., or %			
	ZrO ₂ X	ZrO ₂ Y	ThO ₂	PuO ₂
Li	< 30		< 0.5	< 0.2
Be	< 1	< 1	< 0.5	< 0.1
B	< 3	< 3	0.5	3
Na	300	200	20	< 10
Mg	500	50	2	< 10
Al	0.4%	0.1%	20	15
Si	0.1%	0.5%	10	45
Ca	3	3	10	10
Ti	0.3	100		
V	< 10	50	< 100	
Cr	10	50	2	10
Mn	500	50	< 1	< 1
Fe	0.1%	400	20	20
Co	< 30	< 30	< 5	< 10
Ni	100	10	< 2	< 5
Cu	30	30	2	5
Zn	< 30	< 30		< 10
Nb	< 300	< 300		
Mo	< 100	< 100		
Sn	< 10	< 30		2
Hf	2%	2%		
Pb	< 30	< 30	2	< 1
Bi	< 10	< 3		< 1

Table IV

COMPATIBILITY TESTS IN PROGRESS AS OF OCTOBER 27, 1968
(900°C TESTS)

<u>Capsule</u>	<u>Alloy</u>	<u>Fuel Materials</u>		
A	TZM	$\text{ZrO}_2 \text{X} $,	$\text{PuO}_2\text{-ZrO}_2 \text{X} $,	PuO_2
B	"	"	"	"
			(1.7 watt/cc)	(4.4 watt/cc)
C	TZM	$\text{ZrO}_2 \text{Y} $,	* $\text{PuO}_2\text{-ZrO}_2 \text{Y} $.	* $\text{PuO}_2\text{-ZrO}_2 \text{Y} $
D	"	"	"	"
			(1.7 watt/cc)	(3.5 watt/cc)
E	TZM	ThO_2 ,	$\text{PuO}_2\text{-ThO}_2$,	PuO_2
			(1.7 watt/cc)	(4.4 watt/cc)

* = ^{238}Pu , all others ^{239}Pu

Table V

PELLETS IN STORAGE FOR He RELEASE MEASUREMENTS
(AS OF OCTOBER 20, 1968)

$^{238}\text{PuO}_2$	4.4 watts/cc
$^{238}\text{PuO}_2\text{-ZrO}_2$	3.5 watts/cc
$^{239}\text{PuO}_2\text{-ZrO}_2$	1.7 watts/cc
$^{238}\text{PuO}_2\text{-ThO}_2$	1.7 watts/cc

Table VI
THERMAL DIFFUSIVITY SAMPLES
(0.25 in. dia x 0.030 in. thick)

<u>Composition</u>	<u>Number</u>	<u>Power Density</u>
$^{238}\text{PuO}_2\text{-ZrO}_2$	2	1.7 watts/cc
$^{238}\text{PuO}_2\text{-ZrO}_2$	2	3.5 watts/cc

Table VII

$^{238}\text{PuO}_2\text{-ZrO}_2$ SAMPLES SHIPPED TO NRDL FOR SOLUBILITY TESTS
(0.25 in. dia x 0.25 in. tall)

<u>Date Shipped</u>	<u>No. of Pellets</u>	<u>Power Density watts/cc</u>
August 28	4, one with axial hole	4.4
September 24	4, " " " "	1.6
October 9	4, " " " "	3.5
October 15	4, " " " "	1.7

Table VIII
SAMPLES SENT TO SANDIA LABORATORIES

<u>Type Test</u>	<u>No. of Specimens</u>	<u>Material</u>	<u>Type</u>
Small tunnel ⁽¹⁾	3	PuO ₂ - ZrO ₂ X (1.7 watt/cc)	standard
Small tunnel	3	PuO ₂ - ZrO ₂ X (2.2 watt/cc)	standard
Small tunnel	4	ZrO ₂ Y	standard
Large tunnel ⁽²⁾	2	"	spinning
Large tunnel	2	"	edge-on
Large tunnel	2	"	face-on
Large tunnel	10	ZrO ₂ Y	spinning
Impact ⁽²⁾	2	"	face-on
Small tunnel	<u>2</u>	"	standard
	30		

Notes: (1) standard specimen for small tunnel test:

0.25 in. dia x 0.35 in. long; axial hole 0.060 in. dia x 0.080 in. deep

(2) standard specimen for large tunnel test and for impact:

2 in. dia x 0.5 in. thick

(spinning type has 3/16 in. dia diametral hole through)

(edge-on type has 1/4 in. dia blind diametral hole)

(face-on and impact types have no holes)

Figure 1
SOLID SOLUTION FUEL FLOWSHEET

Figure 2. $^{239}\text{PuO}_2\text{-ZrO}_2$ Pellets, 0.25 in. dia x 0.25 in. tall
(39 m/o PuO_2 , 1.7 watts/cc conc.)

LOS ALAMOS
PHOTO LABORATORY

NEG.
NO.

688406

PLEASE RE-ORDER
BY ABOVE NUMBER

Figure 3. $\text{PuO}_2\text{-ZrO}_2$ Solid Solution Developmental Discs (0.25 in. dia, 0.027 in., 0.039 in., and 0.050 in. thick), on top of metal columns. Scale markings are 1/64 in. each.

LOS ALAMOS
PHOTO LABORATORY

NEG.
NO.

688511

PLEASE RE-ORDER
BY ABOVE NUMBER

Figure 4. Large $^{239}\text{PuO}_2\text{-ZrO}_2$ Solid Solution Disc
(39 m/o PuO_2 , 2 in. dia x 0.5 in. tall)

Figure 5

Figure 6. Microstructures of PuO_2 Specimens, 500X
(dark areas are pores)

$^{239}\text{PuO}_2$
(11.1 g/cc)

$^{238}\text{PuO}_2$
(10.2 g/cc)

Figure 7. Microstructure of $\text{PuO}_2\text{-ZrO}_2$ Solid Solution, 500X
(7.04 g/cc, 39 m/o PuO_2 , gray areas are high in Fe,
Al, and Si)

As Polished

Hot Acid Etch
(HCl, HBr, HF)

Figure 8. Microstructure of PuO_2 - ThO_2 Solid Solution, 750 X
(9.7 g/cc, 40 m/o PuO_2)

Figure 9

ALPHA PARTICLE AUTORADIOGRAPHS

PuO_2 AND $\text{PuO}_2\text{-ZrO}_2\text{[S]}$

(MAGNIFICATION: 14 X)

4.4 WATTS/cc
100% PuO_2

1.7 WATTS/cc
39m/o PuO_2

MELTING TEMPERATURES OF PuO_2 SOLID SOLUTIONS
(CURVES FROM PLUTONIUM HANDBOOK)

Figure 10

FIGURE II

TYPICAL SOLID SOLUTION COMPATIBILITY CAPSULE FOR TEST AT 900°C

SCALE : 2 = 1

Figure 12

Figure 13. Large $^{238}\text{PuO}_2\text{-ZrO}_2$ Solid Solution Disc
(39 m/o PuO_2 , 2 in. dia x 0.25 in. thick)

APPENDIX

PLUTONIUM DIOXIDE - ZIRCONIUM DIOXIDE SOLID SOLUTION DATA SHEETS1. Composition

PuO_2 and CaO stabilized ZrO_2^* form a continuous series of solid solutions. Therefore the composition can vary from 0 to 100% PuO_2 depending on the power density required.

2. Specific Power

$\text{PuO}_2\text{-ZrO}_2$ solid solutions can be varied from 0 to 0.402 w/g.

3. Power Density

The power density is a function of ^{238}Pu concentration which in turn is a function of ZrO_2 concentration and porosity, as shown in Figure 1.

4. Physical Properties: Since very little has been measured on the solid solutions, most of the properties have been estimated using the reported properties for PuO_2 and ZrO_2 .

a. Density (measured by x-ray diffraction) See Figure 1.

b. Average Linear Thermal Expansion Coefficient**

$$10.8 \times 10^{-6}/^{\circ}\text{C} \text{ (298-1273}^{\circ}\text{K)}$$

c. Heat Capacity

See Table I

d. Enthalpy

See Table I

* " ZrO_2 " in these data sheets refer to $\text{ZrO}_2 - 4.8 \text{ w/o CaO}$

** Estimated

e. Temperature of Phase Transformation

100 m/o PuO_2	melting point	2400°C (pure PuO_2 in sealed capsule)
40 m/o PuO_2 - 60 m/o ZrO_2		2400°C (in argon atmosphere)

No other phase transformations below the melting point were observed.

f. Latent Heat of Melting*

100 m/o PuO_2	16.8 kcal/mole
80 m/o PuO_2 - 20 m/o ZrO_2	17.6
40 m/o PuO_2 - 60 m/o ZrO_2	19.2
100 m/o ZrO_2	20.8

g. Vapor Pressures

At temperature of 2300°K ,

	<u>Pure $\text{PuO}_2^\dagger$</u>	<u>80 m/o PuO_2</u>	<u>40 m/o PuO_2</u>	<u>Pure ZrO_2</u>
PuO_2 :	$2.3 \times 10^{-5} \text{ atm.}$	$1.8 \times 10^{-5} \text{ atm.}$	$0.9 \times 10^{-5} \text{ atm.}$	—
ZrO_2 :	—	$1.4 \times 10^{-8} \text{ atm.}$	$4.2 \times 10^{-8} \text{ atm.}$	$7.0 \times 10^{-8} \text{ atm.}$

PuO_2 pressure at $1400^\circ\text{K} = 1.5 \times 10^{-13} \text{ atm.}$

† Pressure for $\text{PuO}_{1.87}$ which is congruent composition

h. Thermal Conductivity ($\text{cal}/(\text{cm}^\circ\text{C sec})$, at 100% density)*

<u>Temp.</u>	<u>80 m/o PuO_2 - 20 m/o ZrO_2</u>	<u>40 m/o PuO_2 - 60 m/o ZrO_2</u>
973°K (700°C)	7.9×10^{-3}	5.7×10^{-3}
1473°K (1200°C)	6.4×10^{-3}	3.3×10^{-3}

i. Thermal Diffusivity for Pressed and Sintered Pellets*

(cm^2/sec , 95% density)

<u>Temp.</u>	<u>80 m/o PuO_2 - 20 m/o ZrO_2</u>	<u>40 m/o PuO_2 - 60 m/o ZrO_2</u>
973°K (700°C)	9.0×10^{-3}	6.6×10^{-3}
1473°K (1200°C)	7.2×10^{-3}	3.7×10^{-3}

* Estimated

j. Viscosity

Not available

k. Surface Tension

Not available

l. Spectral Emissivity

Not available

m. Crystallography

FCC Structure (fluorite)

Space Group Fm3m

Lattice Constant varies linearly from

100 m/o PuO_2 = 5.3954 Å to 100 m/o ZrO_2 = 5.138 Å

n. Solubilities

PuO_2 - ZrO_2 solid solutions are more stable than PuO_2 itself (see Table I). Therefore the solubility of the Pu from solid solutions would be expected to be lower than for PuO_2 itself.

o. Diffusion Rates

Not available

p. Selected Thermodynamics Functions are shown in Table I.

5. Mechanical Properties*

a. Room Temperature Compressive Strength (psi)

80 m/o PuO_2 - 20 m/o ZrO_2 140,000

40 m/o PuO_2 - 60 m/o ZrO_2 220,000

b. Young's Modulus

22×10^6 psi decreasing as temperature increases

c. Shear Modulus

12×10^6 psi decreasing as temperature increases

* Estimated

6. Chemical Properties

Due to the larger negative free energy of formation of the PuO_2 - ZrO_2 solid solutions, the solid solutions should be less reactive towards metals by 3-5 kcal/mole depending on the composition and temperature.

Sources of Information Used to Estimate Properties

1. N. H. Brett and L. E. Russell, Plutonium 1960, E. Grison, W. B. H. Lord, and R. D. Fowler, (ed), Cleaver-Hume Press, Ltd., London, 1961, p. 397.
2. K. K. Kelley, Bureau of Mines Bulletin 584, 1960, p. 209.
3. ANL-7438, 1968.
4. JANAF Thermochemical Tables, the Dow Chemical Co., Midland, Mich., 1964.
5. R. N. R. Mulford and L. E. Lamar, Plutonium 1960, E. Grison, W. B. H. Lord, and R. D. Fowler, (ed), Cleaver-Hume Press, London, 1961, 411.
6. W. A. Chupka, J. Berkowitz, and M. G. Inghram, The Journal of Chemical Physics 26, 1957, 1207.
7. R. S. Kern, R. J. Beals, Ceramic Bulletin 46, 1967, p. 1154.

Table I

Calculated Thermodynamic Functions for $\text{PuO}_2\text{-ZrO}_2$ Solid Solutions

cal mole ⁻¹ deg ⁻¹				kcal mole ⁻¹		
Temp. (°K)	(Cp ^o)	(S _T ^o)	$\left[\frac{-(G_T^o - H_{298}^o)}{T} \right]$	$(H_T^o - H_{298}^o)$	(ΔH_f^o)	(ΔG_f^o)
<u>80 m/o PuO₂-20 m/o ZrO₂</u>						
298		19.2	19.2	0	- 254.8	- 242.2
900	21.0	42.0	29.0	11.7	- 254.0	- 218.4
1000	21.1	44.2	30.4	13.8	- 254.0	- 214.5
1200	21.4	48.1	33.0	18.1	- 253.4	- 206.6
1400	21.6	51.4	35.5	22.3	- 252.4	- 199.0
<u>40 m/o PuO₂-60 m/o ZrO₂</u>						
298		16.4	16.4	0	- 258.6	- 245.6
900	19.4	36.8	24.8	10.8	- 257.6	- 220.6
1000	19.6	38.8	26.0	12.8	- 257.5	- 216.5
1200	20.0	42.7	28.5	16.7	- 257.4	- 208.2
1400	20.3	45.5	30.6	20.8	- 256.7	- 200.3

Figure 1

PLUTONIUM DIOXIDE - THORIUM DIOXIDE SOLID SOLUTION DATA SHEETS1. Composition

PuO_2 and ThO_2 form a continuous series of solid solutions. Therefore the composition can vary from 0 to 100% PuO_2 depending on the power density required.

2. Specific Power

PuO_2 - ThO_2 solid solutions can be varied from 0 to 0.402 w/g.

3. Power Density

The power density is a function of ^{238}Pu concentration which in turn is a function of ThO_2 concentration and porosity as shown in Figure 1.

4. Physical Properties: Since very little has been measured, most of the properties have been estimated using the properties known for PuO_2 and ThO_2 .

a. Density (measured by x-ray diffraction) See Figure 1

b. Average Linear Thermal Expansion Coefficient*

$$10.5 \times 10^{-6}/^{\circ}\text{C} \text{ (298-1273}^{\circ}\text{K)}$$

c. Heat Capacity

See Table II

d. Enthalpy

See Table II

e. Temperature of Phase Transformation, $^{\circ}\text{C}$

100 m/o PuO_2	melting point	2400 $^{\circ}$ (pure PuO_2 in sealed capsule)
80 m/o PuO_2 - 20 m/o ThO_2		2400 $^{\circ}$ (open system)
40 m/o PuO_2 - 60 m/o ThO_2		2925 $^{\circ}$ (open system)
100 m/o ThO_2		3300 $^{\circ}$

*Estimated

f. Latent Heat of Melting*

100 m/o PuO ₂	16.8 kcal/mole
80 m/o - 20 m/o ThO ₂	17.0
40 m/o PuO ₂ - 60 m/o ThO ₂	17.5
100 m/o ThO ₂	18.0

g. Vapor Pressures

At temperature of 2300°K

	<u>Pure PuO₂†</u>	<u>80 m/o PuO₂*†</u>	<u>40 m/o PuO₂*†</u>	<u>Pure ThO₂</u>
PuO ₂	2.3×10^{-5} atm.	1.8×10^{-5}	0.9×10^{-5}	
ThO ₂	—	2×10^{-8}	7×10^{-8}	1.1×10^{-7}

† Pressure for PuO_{1.87} (the congruent composition)

PuO₂ pressure at 1400°C = 1.5×10^{-13} atm.

h. Thermal Conductivity (100% density)*

700°C	9×10^{-3} cal/cm - °C - sec
1200°C	6×10^{-3} cal/cm - °C - sec

i. Thermal Diffusivity for Pressed and Sintered Pellets*

700°C	11×10^{-3} cm ² /sec
1200°C	7×10^{-3} cm ² /sec

j. Viscosity

Not available

k. Surface Tension

Not available

l. Spectral Emissivity

Not available

* Estimated

m. Crystallography

FCC Structure (fluorite)

Space Group Fm3m

Lattice Constant varies linearly from

100 m/o PuO_2 = 5.3954 Å to 100 m/o ThO_2 = 5.598 Å

n. Solubilities

PuO_2 - ThO_2 solid solutions are more stable than PuO_2 itself (see Table II). Therefore the solubility of the Pu from solid solutions would be expected to be lower than for PuO_2 itself.

o. Diffusion Rates

Not available

p. Selected Thermodynamic Functions are shown in Table II.

5. Mechanical Properties*

a. Room Temperature Compressive Strength (psi)

150,000

b. Young's Modulus (psi)

30×10^6

c. Shear Modulus (psi)

12×10^6

6. Chemical Properties

Due to the larger negative free energy of formation of the PuO_2 - ThO_2 solid solutions, the solid solutions should be less reactive towards metals by 10-20 kcal/mole depending on the composition and temperature.

*Estimated

Sources of Information Used to Estimate Properties

1. R. N. R. Mulford and F. H. Ellinger, J. Phys. Chem. 62 (1958) 1466.
2. N. H. Brett and L. E. Russell, Plutonium 1960, E. Grison, W. B. H. Lord, and R. D. Fowler, (ed), Cleaver-Hume Press, Ltd., London (1961) 397.
3. B. Ohnysty and F. K. Rose, J. Am. Ceram. Soc. 47 (1964) 398.
4. ANL-7438, 1968.
5. A. C. Victor and T. B. Douglas, J. Res. Nat. Bur. Stds. 65 (1961) 105.
6. R. N. R. Mulford and L. E. Lamar, Plutonium 1960, E. Grison, W. B. H. Lord, and R. D. Fowler, (ed), Cleaver-Hume Press, Ltd., London (1961) 411.
7. R. J. Ackermann, E. G. Rauh, and R. J. Thorn, J. Phys. Chem. 67 (1963) 762.
8. Janaf Thermochemical Tables.
9. D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," No. 18 in Advances in Chemistry Series, American Chemical Society, Washington D. C. (1956).

Table II

Calculated Thermodynamic Functions for $\text{PuO}_2\text{-ThO}_2$ Solid Solutions

	cal mole ⁻¹ deg ⁻¹				kcal mole ⁻¹		
	Temp. (°K)	C_p^0	S_T^0	$-\left(\frac{G_T^0 - H_{298}^0}{T}\right)$	$H_T^0 - H_{298}^0$	ΔH_f^0	ΔG_f^0
80 m/o $\text{PuO}_2\text{-20 m/o ThO}_2$	298	—	19.9	19.9	0	-260.9	-248.4
	900	21.1	42.9	29.8	11.8	-260.2	-224.7
	1000	21.2	45.1	31.1	14.0	-260.2	-220.7
	1100	21.4	47.1	32.5	16.0	-260.8	-217.1
	1200	21.5	49.0	33.9	18.2	-259.8	-213.5
40 m/o $\text{PuO}_2\text{-60 m/o ThO}_2$	298	—	18.6	18.6	0	-277.0	-264.1
	900	19.7	39.4	27.1	11.1	-276.2	-239.3
	1000	19.9	41.5	28.5	13.0	-276.2	-235.1
	1100	20.1	43.4	29.7	15.1	-276.8	-231.7
	1200	20.3	45.2	31.0	17.1	-276.9	-228.4

Figure 1

DENSITY AND COMPOSITION OF $\text{PuO}_2 - \text{ThO}_2$ SOLID SOLUTIONS