Quarterly Status Report on
Plutonium-238 Space Electric Power
Fuel Development Program (U)
July 1-September 30, 1968

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AEC RESEARCH AND DEVELOPMENT REPORT
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Plutonium-238 Space Electric Power
Fuel Development Program (U)

July 1-September 30, 1968

to

Space Isotopic Fuels and Materials Branch
Space Electric Power Office
Division of Space Nuclear Systems
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 has 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 those 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 PuO₂ is reduced.

In addition to these possible advantages, the process for making solid solution fuels is relatively economical. It consists of simply blending unshaped PuO₂ 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 PuO₂ 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 economies, 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 ²³⁸Pu 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 ²³⁸Pu specimens

A. Hexam 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 ¹⁸O
   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 (ZrO₂ and ThO₂) are being carried forward in the program.

2. Synthesis and fabrication of properties specimens: 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 0.060 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, PuO₂-ZrO₂.*

*The ZrO₂ used in this work contains 4.8 percent by weight of stabilizer
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 $^{239}$PuO$_2$–ZrO$_2$ discs has been started.
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. Typical fabrication conditions are
as follows:

- **Powder particle size (mmd)**: 1.5–2.5 μm
- **Pressing pressure**: 7.5–20 tsi
  (with preslugging; large discs pressed with
  paraffin binder)
- **Sintering Atmosphere**: CO$_2$
- **Sintering Time**: 6 hr
- **Sintering Temperature**: 1625°C

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 compo-
   sition, as indicated in Figure 5. The uniform change in
   lattice parameter with PuO$_2$ concentration shown for the
   ZrO$_2$–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 $^{239}$PuO$_2$ and
   $^{238}$PuO$_2$ structures shown in Figure 6 are typical of
those previously experienced at this Laboratory. 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 composi-
tions 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 standard ceramic engineering relations-
   ships (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. Densities ranging from 70 percent to 96 percent of
   theoretical have been produced.

E. **Thermal Analysis**: The melting curves for
   PuO$_2$–ThO$_2$ and PuO$_2$–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 PuO$_2$–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
PuO$_2$–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 pure solid solution oxides can be estimated quite
   well from results obtained with PuO$_2$, ZrO$_2$, and ThO$_2$.
   Because of the known degree of compatibility between
PuO$_2$ and Mo, TZM (99.4% Mo, 0.5% Ti, 0.08% Zr,
0.02% C) alloy was chosen as the possible cladding
material to be first investigated. The maximum safe
long-term operating temperature for the furnaces
immediately available is 1000°C, so 900°C was chosen
as a suitable temperature for investigation. Inconel
718 was selected as a material suitable for containing
materials under test. One inconel 718 test capsule (SCC-1) was loaded with TZM and tested for 355 hours at 900°C. Metallographic examinations subsequent to this exposure revealed no reaction, therefore the primary test array has been standardized as follows:

a. The containment tube is of inconel 718 (nominal analysis Ni-53, Cr-18, Fe-18.5, Nb + Ta-5.0, Mo-3.2, Ti-0.9, Al-0.4, Si-0.3), 0.350 in. O.D., 0.020 in. wall, approximately 2-1/2 in. long; ends are welded cups.

b. An inner liner of 0.002 in. Mo sheet is used (in all TZM tests) to prevent contact between test pellets and side walls. A strip of 0.002 in. Ni is spot welded across the bottom of the Mo tube as a loading aid.

c. A coil spring wound from 0.030 in. Mo wire is utilized to provide initial contact and to prevent movement during handling.

These arrangements are illustrated in Fig. 11.

Five capsules have been loaded, as listed in Table IV.

Capsule SCC-2 was removed from test after 744 hours (3 900°C). After cooling, the end of the capsule was removed and the contents were vacuum impregnated with a mounting epoxy (EPON 815). The capsule was then mounted in the same epoxy and nearly half its diameter was removed by hand grinding. The mounted capsule was prepared metallographically and the TZM-ceramic interfaces were examined and photographed.

Figure 12 shows the sectioned capsule and the stacking order of the compatibility test cylinders.

Figure 13 shows photomicrographs of the three TZM-ceramic interfaces. Examinations revealed no evidence of reaction between the materials.

Additional compatibility tests are scheduled wherein other potential clads may be evaluated. Orders have been placed for T-Ill, T-222, W-25 Re, Pt-20 Rh, and Pt-40 Rh. High temperature compatibility studies also are scheduled.

4. Additional properties with 239Pu 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 235PuO2-ZrO2 solid solution material shown in Table VI have been fabricated and shipped to Battelle Pacific Northwest Laboratory for thermal diffusivity measurements. In addition, two 100%, 235PuO2 and 233PuO2-ThO2 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.

D. Solubility in Dilute Acid: The solution rates of 235PuO2-ThO2 (1.7 watts/cc) and plasma torch microspheres were compared in the following experiment. Ten milligrams of 235PuO2 microspheres and one 0.25 in. dia by 0.25 in. tall 235PuO2-ThO2 solid solution pellet were rinsed with water, then each was placed in contact with 200 ml of 0.1 N H2SO4. After stirring continuously, a portion of each acid solution was assayed for plutonium. The solubility rate was 1.6 mg Pu/hr/g sample for the microspheres, and 0.0023 mg Pu/hr/g sample for the solid solution. Hence the rate of solution of microspheres was 700 times that of the solid solution, on a sample weight (not on a wattage) basis. If this were referred to the relative surface areas of the two fuel forms, this would correspond to 6.2 x 10⁻⁴ mg Pu/sq. mm/hr for the microspheres, and 0.25 x 10⁻⁴ mg Pu/sq. mm/hr for the solid solution. On this basis, the microsphere solution rate was 25 times that of the solid solution form.

5. Calculated and estimated properties: Data sheets have been prepared for the PuO2-ZrO2 and the PuO2-ThO2 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 UO₂, PuO₂, ZrO₂, UO₂-ZrO₂ solid solutions, and PuO₂-ThO₂ solid solutions. These conductivities were used to calculate the radial thermal gradient in a stack of 2.3 inch diameter discs.
Maximum gradients were 100° and 200°C in the first and 3.5 watts/cc ThO₂ diluent, respectively. If the ZrO₂ diluent were used, the gradients would be 112° and 300°C, respectively. Thus higher conductivity and a higher melting point is possible in the PuO₂-ThO₂ system.

B. External Radiation; The Feasibility of Using Enriched Pu: When ⁹⁵⁵Pu metal is oxidized to ²³⁵PuO₂ in air, the increase in neutron emission rate is 9700 n/sec - g Pu. This is caused by the reactions ¹⁵⁵O(α, n) Ne²⁰ and ¹⁵⁰O(α, n) Ne²¹. These reactions also increase the neutron emission rates. These increases can be eliminated if pure ¹⁵⁵O is used to prepare ²³⁵PuO₂. However, the basic emission rate (from spontaneous fission and neutron self-multiplication) of about 3000 n/sec - g Pu cannot be reduced. Experience has shown that ²³⁵PuO₂ powders received at this Laboratory can emit 45,000 - 100,000 n/sec - g Pu, because of (α, n) reactions on light element impurities.¹⁵

Conventional ²³⁵Pu also contains about 1.2 ppm ²³⁶Pu, which decays to ¹²⁵Pb and ¹⁰⁸Th 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 ²³⁵Pu to ²³⁴U by alpha decay. Since the UO₂-ZrO₂-CaO system is a solid solution system,⁵ and since UO₂-PuO₂ also form a continuous series of solid solutions, the ²³⁴U 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 ²³⁵PuO₂.⁶ Chemical changes caused by decay of other isotopes such as ²³⁶Pu should be insignificant. The effect of He accumulation in the fuel lattice is not predictable at this time for any ²³⁶PuO₂ 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 ²³⁵PuO₂-ZrO₂ discs have been fabricated in the 0.5 in. thickness.

In addition, two large 0.25 in. thick ²³⁵PuO₂-ZrO₂ discs have been fabricated. Each disc has a power of 21 watts. The first attempt to press the ²³⁵PuO₂-ZrO₂ 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 14.

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 ²³⁵PuO₂-ZrO₂ 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. FUNDAMENTAL STUDIES OF HELIUM RELEASE

A. Transmission electron microscopy:
Thin films of five actinide oxides have been examined by transmission electron microscopy during and after in situ annealing. Specimens have been prepared in three ways: by vacuum deposition of all five oxides onto copper substrates; by cleaving polycrystalline air-fired bulk ThO₂ and PuO₂; and by oxidation of electrochemically thinned thorium metal and delta plutonium alloy. For purposes of this report only results from the deposition preparation method will be discussed. (Within the physical limitations of the sample type, however, all specimens behaved similarly.)

Films about 1000Å in thickness were prepared by evaporation of the oxide from a resistance heated tungsten basket onto an electro-polished copper target maintained at room temperature. The oxide was deposited at the rate of ~5Å/sec under a background pressure of ~10⁻⁶ Torr. The oxide films were floated off the copper substrates in a 30% by volume HNO₃ in CH₂CH₂OH
mixture, washed and mounted on grids.

As deposited, the oxides were randomly oriented and the grains were less than 100 Å in diameter. Annealing, by use of an unapertured electron beam, caused growth of the grains to final diameters of ~2 μm, with grain diameter to foil thickness ratios approximating 10:1 (Figure 15). Initial grain growth was found to occur at temperatures as low as 500°C for AmO₂, and 1000°C for UO₂; however, to obtain large grains in PuO₂, NpO₂ and ThO₂ temperatures between 1300 and 1500°C were required.

During annealing, the following features were observed in the films:

1) In ThO₂, NpO₂ and PuO₂ extensive microwinning was observed by electron diffraction as well as microscopy (Figure 16). This feature was universal in well-annealed grains of ThO₂ and NpO₂ and was frequently present in PuO₂. However, only an occasional twin was seen in UO₂, and none in AmO₂.

2) During preparation, 2 or more layers of the original frequently overlapped. Heating caused sintering together of these layers. Grains formed from such regions contained large numbers of cavities (Figure 17), but this feature was never observed in grains grown from single layers of evaporated foil. During annealing, the high temperature produced grooving at grain boundaries and triple points and when these grooves were trapped inside the single final layer formed by the sintering of the multiple thicknesses cavities were the result. This feature appeared in all five of the oxides although in UO₂ and AmO₂ they were less distinctly geometric (Figure 18) and in both these oxides they annealed out easily upon further heating.

3) The edges of fully annealed grains maintained distinctly geometric shapes (Figure 19). This effect was especially marked in ThO₂ and NpO₂, less so for PuO₂ and UO₂ (Figure 20), and was almost absent in AmO₂.

4) Another aspect of the sintering behavior was the tendency for cracks in the film to bridge and heal themselves by growth of grains from the edges of the crack (Figure 21). This effect was most common in the AmO₂, UO₂ and PuO₂. For NpO₂ and ThO₂ the process rarely completed the healing of the crack. However, when bridged, subsequent grain growth obliterated all trace of the original crack in the final fully annealed structure.

Electron diffraction was used to index a large number of grains of ThO₂ and PuO₂. The results are listed in Table IX.

Microtwins usually were found to be parallel to the <110> or <135>. These two orientations were also common for the edges of the cavities and the geometric edges of the annealed foils.

The distinctness and heat stability of the three features observed (microtwin, cavities and edges) were greatest for ThO₂ and NpO₂. In PuO₂ the cavities were often rounded and material surface diffusion greater (bridging of cracks). In UO₂ and AmO₂ no twins were seen, the cavities filled in or annealed out easily and edges only suggested geometric forms. It is obvious that the relative melting points of those materials affect the observed features, but quantitative statements are not yet possible.

B. Helium bubble formation

An investigation is presently under way to determine the relation of helium bubble formation to structural defects in actinide metal oxides. Thus far, a device has been constructed to allow deposition of helium atoms (in the form of alpha particles) just beneath the surface of oxide samples, and metallographic procedures have been developed for examination of the resulting structures.

A schematic drawing of the alpha bombardment test chamber is shown in the accompanying Figure 22. Alpha particles are accelerated to 9 MeV in a tandem Van de Graaff accelerator, and enter the device at the right. As the beam proceeds to the left, it passes through a focusing aperture, a valve (to allow isolation of radioactive samples from the accelerator), another focusing aperture, and a 1/2-mil Havar foil window, before reaching the target area. The Havar (a cobalt-iron-chromium-nickel alloy) serves the dual purpose of degrading the beam energy to the desired 5 MeV and of isolating radioactive samples. Beam divergence
problems require that the foil be kept close to the sample.

The movable aperture just in front of the target contains an aperture hole, a ZnS disk, and a quartz disk. The disks will luminesce when struck by the beam of alpha particles, and are present for alignment purposes. After final beam alignment, the aperture hole is swung into place to allow the 1/8-in. dia. beam to strike the oxide target. A -300 V bias is applied to the aperture plate to control electron emission from the sample.

The oxide specimen is mounted on a water-cooled copper plate. The number of alpha particles deposited is determined by monitoring the electrons which flow to the sample (through the plate) to neutralize the helium ions.

An alpha particle deposition energy of 5 MeV was chosen because it duplicates the energy of alpha decay in plutonium, and because higher energies might lead to fission of the actinide atoms with resultant severe lattice damage. Calculations show that 5 MeV alpha particles will be deposited in a narrow band about 10 microns beneath the sample surface. As deposited, the helium will be present as individual atoms. Subsequent heating will cause agglomeration into helium bubbles, and these will be examined microscopically. Bubble behavior will be evaluated as a function of annealing temperature, annealing time, and will be correlated with crystal defects such as grain boundaries and voids.

Initial studies will be carried out on ThO₂, an essentially non-radioactive compound of fluorite structure. Special metallographic mounting and polishing procedures have been developed to allow examination of this ceramic at high magnification without difficulty from edge rounding. After bombardment and handling procedures have been worked out, studies will be made on ²³³PuO₂, which is similar in many ways to ThO₂.

C. X-ray line broadening analyses:

The changes in crystallite size and strain in the lattice of PuO₂ as a function of time of self-irradiation will be studied through the technique of x-ray line broadening analysis. Other items of interest that might be obtained from the x-ray examination are changes in lattice parameters, stacking fault probabilities, strains as a function of distance perpendicular to kkl planes and twinning probabilities.

A material that has a large crystalline size and no lattice strain or other faults or defects will, in general, yield a quite sharp powder pattern line upon x-ray diffraction examination. A broadened x-ray line occurs when some physical operation changes the crystallite size from large to small and/or introduces large strains in the lattice. By comparing the broadened x-ray line with the sharp line through the use of a rather detailed mathematical procedure called "deconvolution" estimates of the small crystallite size and large strains can be made.

A computer program has been written to assist in the analysis of the data. Its general philosophy of operation and the evaluation of the results obtained will be described below. There are three methods used for the determination of crystallite size and strain; the obtaining of the integral breadth of the line profile, the examination of Fourier coefficients describing the shape of a line, and the evaluation of the second moment of the line profile about its centroid. All three methods are incorporated in the computer program.

REFERENCES


TABLES

Table I

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<th>Element</th>
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<td>ZrO₂</td>
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Table II

LIST OF SPECIMENS PREPARED AS OF OCTOBER 20, 1968

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Table III

Chemical Composition of Typical Powders

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<tr>
<td>Mn</td>
<td>500</td>
</tr>
<tr>
<td>Fe</td>
<td>0.1%</td>
</tr>
<tr>
<td>Co</td>
<td>&lt; 30</td>
</tr>
<tr>
<td>Ni</td>
<td>100</td>
</tr>
<tr>
<td>Cu</td>
<td>30</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt; 30</td>
</tr>
<tr>
<td>Nb</td>
<td>&lt; 300</td>
</tr>
<tr>
<td>Mo</td>
<td>&lt; 100</td>
</tr>
<tr>
<td>Sn</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Hf</td>
<td>2%</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt; 30</td>
</tr>
<tr>
<td>Bi</td>
<td>&lt; 10</td>
</tr>
</tbody>
</table>

Table IV

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

<table>
<thead>
<tr>
<th>Material</th>
<th>Concentration, ppm by wt. or %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂</td>
<td>&lt; 30</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>Be</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>Na</td>
<td>300</td>
</tr>
<tr>
<td>Mg</td>
<td>500</td>
</tr>
<tr>
<td>Al</td>
<td>0.4%</td>
</tr>
<tr>
<td>Si</td>
<td>0.2%</td>
</tr>
<tr>
<td>Ca</td>
<td>3</td>
</tr>
<tr>
<td>Ti</td>
<td>0.3</td>
</tr>
<tr>
<td>V</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Cr</td>
<td>0.5</td>
</tr>
<tr>
<td>Mn</td>
<td>500</td>
</tr>
<tr>
<td>Fe</td>
<td>0.1%</td>
</tr>
<tr>
<td>Co</td>
<td>&lt; 30</td>
</tr>
<tr>
<td>Ni</td>
<td>100</td>
</tr>
<tr>
<td>Cu</td>
<td>30</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt; 30</td>
</tr>
<tr>
<td>Nb</td>
<td>&lt; 300</td>
</tr>
<tr>
<td>Mo</td>
<td>&lt; 100</td>
</tr>
<tr>
<td>Sn</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Hf</td>
<td>2%</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt; 30</td>
</tr>
<tr>
<td>Bi</td>
<td>&lt; 10</td>
</tr>
</tbody>
</table>

Total 137
### Table V
PELLETS IN STORAGE FOR HE RELEASE MEASUREMENTS
(AS OF OCTOBER 20, 1968)

<table>
<thead>
<tr>
<th>Type Test</th>
<th>No. of Specimens</th>
<th>Material</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small tunnel(1)</td>
<td>3</td>
<td>PuO₂ - ZrO₂[X]</td>
<td>standard</td>
</tr>
<tr>
<td>Small tunnel</td>
<td>3</td>
<td>PuO₂ - ZrO₂[X]</td>
<td>standard</td>
</tr>
<tr>
<td>Small tunnel</td>
<td>4</td>
<td>ZrO₂[Y]</td>
<td>standard</td>
</tr>
<tr>
<td>Large tunnel(2)</td>
<td>1</td>
<td>&quot;</td>
<td>spinning</td>
</tr>
<tr>
<td>Large tunnel</td>
<td>1</td>
<td>&quot;</td>
<td>edge-on</td>
</tr>
<tr>
<td>Large tunnel</td>
<td>1</td>
<td>&quot;</td>
<td>face-on</td>
</tr>
<tr>
<td>Large tunnel</td>
<td>10</td>
<td>ZrO₂[Y]</td>
<td>spinning</td>
</tr>
<tr>
<td>Impact(1)</td>
<td>2</td>
<td>&quot;</td>
<td>face-on</td>
</tr>
<tr>
<td>Small tunnel</td>
<td>5</td>
<td>&quot;</td>
<td>standard</td>
</tr>
</tbody>
</table>

Notes:
(1) Standard specimen for small tunnel test:
- 0.25 in. dia x 0.26 in. long; axial hole 0.060 in. dia x 0.060 in. deep
- 0.25 in. dia x 0.26 in. long; axial hole 0.060 in. dia x 0.060 in. deep
(2) Standard specimen for large tunnel test and for impact:
- 2 in. dia x 0.8 in. thick
- (spinning type has 3/16 in. dia diametral hole through)
- (edge-on type has 1/8 in. dia blind diametral hole)
- (face-on specimen and impact type have no holes)

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

<table>
<thead>
<tr>
<th>Composition</th>
<th>Number</th>
<th>Power Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>239PuO₂-ZrO₂</td>
<td>2</td>
<td>1.7 watts/cc</td>
</tr>
<tr>
<td>233PuO₂-ZrO₂</td>
<td>2</td>
<td>3.5 watts/cc</td>
</tr>
</tbody>
</table>

### Table VII
SAMPLES SENT TO SANDIA LABORATORIES

<table>
<thead>
<tr>
<th>No. of Pellets</th>
<th>Power Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>4, one with axial hole</td>
<td>4.4</td>
</tr>
<tr>
<td>4</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td>3.5</td>
</tr>
<tr>
<td>4</td>
<td>1.7</td>
</tr>
</tbody>
</table>

### Table VIII
SCHEDULED FOR SOLUBILITY TESTS
(0.25 in. dia x 0.36 in. tall)

<table>
<thead>
<tr>
<th>Date Shipped</th>
<th>Power Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>August 28</td>
<td>4.4</td>
</tr>
<tr>
<td>September 24</td>
<td>1.6</td>
</tr>
<tr>
<td>October 9</td>
<td>3.5</td>
</tr>
<tr>
<td>October 15</td>
<td>1.7</td>
</tr>
</tbody>
</table>
SOLID SOLUTION FUEL FLOWSHEET

Figure 1

Figure 2. 239PuO2-ZrO2 pellets, 0.25 in. dia x 0.25 in. tall
(39 m/o PuO2, 1.7 watts/cc conc.)
Figure 3. PuO$_2$-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.

Figure 4. Large $^{239}$PuO$_2$-ZrO$_2$ solid solution disc (39 m/o PuO$_2$, 2 in. dia x 0.5 in. tall)

Figure 5. Lattice parameters of PuO$_2$ solid solutions as a function of composition.
Figure 6. Microstructures of PuO₂ specimens, 500X (dark areas are pores)

**PuO₂ (11.1 g/cc)**

**As Polished**

**PuO₂ (10.2 g/cc)**

**Hot Acid Etch**

(HCl, HBr, HF)

Figure 7. Microstructure of PuO₂-ZrO₂ solid solution, 500X (7.04 g/cc, 39 m/o PuO₂, gray areas are high in Fe, Al, and Si)
Figure 8. Microstructure of PuO₂-ThO₂ Solid Solution, 750X
(9.7 g/cc, 40 m/o PuO₂)

ALPHA PARTICLE AUTORADIOGRAPHS
PuO₂ AND PuO₂-ZrO₂[S]
(MAGNIFICATION: 14 X)

Figure 9

4.4 WATTS/cc
100% PuO₂

1.7 WATTS/cc
39 m/o PuO₂
Figure 10. Melting Temperatures of \( \text{PuO}_2 \) Solid Solutions

Curves from Plutonium Handbook

Figure 11. Typical Solid Solution Compatibility Capsule for Test at 900°C

Scale: 2 x 1

Figure 12. Compatibility test capsule SCC-2 sectioned after testing. 1.5X

Figure 13. TZM-ceramic interfaces, SCC-2

Figure 14. Large \( ^{238}\text{PuO}_2-ZrO_2 \) solid solution disc (39 m/o \( \text{PuO}_2 \), 2 in. dia x 0.25 in. thick)
(a) As-deposited ThO₂

(b) Early grain growth in PuO₂

Figure 15. Typical appearance of as-deposited and partially annealed actinide oxide foils together with their diffraction patterns (50,000X)

Figure 16. Fully annealed grain PuO₂ showing microtwins (55,000X)
Figure 17. Geometric cavities in NpO₂. (50,000X)

Figure 18. Geometric cavities in UO₂. (62,000X)
Figure 19. Geometric edges of annealed ThO$_2$.
(72,000X)

Figure 20. Edges of annealed UO$_2$.
(50,000X)
Figure 21. Crack healing in PuO₂ evaporated films (78, 000X)
PLUTONIUM DIOXIDE-ZIRCONIUM DIOXIDE SOLID SOLUTION DATA SHEETS

1. Composition
PuO₂ and CaO stabilized ZrO₂ form a continuous series of solid solutions. Therefore the composition can vary from 0 to 100% PuO₂ depending on the power density required.

2. Specific Power
PuO₂-ZrO₂ solid solutions can be varied from 0 to 0.402 w/g.

3. Power Density
The power density is a function of ²³⁸Pu concentration which in turn is a function of ZrO₂ concentration and porosity, as shown in Figure A1.

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 PuO₂ and ZrO₂.

*a"ZrO₂" in these data sheets refer to ZrO₂ - 4.8 w/o CaO

a. Density (measured by x-ray diffraction). See Figure A1.
b. Average Linear Thermal Expansion Coefficient*
   \(10.8 \times 10^{-6}/°C (298-1273°K)\)
c. Heat Capacity. See Table A1
d. Enthalpy. See Table A1
e. Temperature of Phase Transformation
   100 m/o PuO₂ melting point 2400°C (pure PuO₂ in sealed capsule)
   40 m/o PuO₂ - 60 m/o ZrO₂ 2400°C (in argon atmosphere)
   No other phase transformations below the melting point were observed.
f. Latent Heat of Melting*
   100 m/o PuO₂ 16.8 kcal/mole
   80 m/o PuO₂ - 20 m/o ZrO₂ 17.6
   40 m/o PuO₂ - 60 m/o ZrO₂ 19.2
   100 m/o ZrO₂ 20.8
g. Vapor Pressures
   At temperature of 2300°K,
   \(\frac{\text{Pure PuO₂}}{\text{PuO₂}}: \frac{2.3 \times 10^{-8} \text{atm.}}{1.8 \times 10^{-8} \text{atm.}}\)
   \(\frac{\text{ZrO₂}}{\text{ZrO₂}}: \frac{1.4 \times 10^{-8} \text{atm.}}{7.0 \times 10^{-8} \text{atm.}}\)
   \(\frac{40 \text{ m/o PuO₂}}{\text{PuO₂}}: \frac{0.9 \times 10^{-8} \text{atm.}}{7.0 \times 10^{-8} \text{atm.}}\)
   \(\frac{\text{Pure ZrO₂}}{\text{ZrO₂}}: \frac{4.2 \times 10^{-8} \text{atm.}}{7.0 \times 10^{-8} \text{atm.}}\)

PuO₂ pressure at 1400°K = 1.5 \times 10^{-13} atm.
\* Pressure for PuO₁.₈ which is congruent composition

h. Thermal Conductivity (cal/(cm°C sec), at 100% density)*

\[
\begin{array}{c|c|c}
\text{Temp.} & 80 \text{ m/o PuO₂} - 20 \text{ m/o ZrO₂} & 1473°K (1200°C) \\
973°K (700°C) & 7.9 \times 10^{-3} & 6.4 \times 10^{-3} \\
1473°K (1200°C) & 3.3 \times 10^{-3} & 3.3 \times 10^{-3} \\
\end{array}
\]

i. Thermal Diffusivity for Pressed and Sintered
Pellets* (cm²/sec, 95% density)

\[
\begin{array}{c|c|c}
\text{Temp.} & 80 \text{ m/o PuO₂} - 20 \text{ m/o ZrO₂} & 1473°K (1200°C) \\
973°K (700°C) & 9.0 \times 10^{-3} & 9.0 \times 10^{-3} \\
1473°K (1200°C) & 7.2 \times 10^{-3} & 7.2 \times 10^{-3} \\
\end{array}
\]

---

Figure A1
of the PuO₂-ZrO₂ 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


PLUTONIUM DIOXIDE-THORIUM DIOXIDE SOLID SOLUTION DATA SHEETS

1. Composition

PuO₂ and ThO₂ form a continuous series of solid solutions. Therefore the composition can vary from 0 to 100% PuO₂ depending on the power density required.

2. Specific Power

PuO₂-ThO₂ solid solutions can be varied from 0 to 0.402 w/g.

3. Power Density

The power density is a function of ⁴²⁸Pu concentration which in turn is a function of ThO₂ concentration and porosity as shown in Figure A2.

4. Physical Properties: Since very little has been measured, most of the properties have been estimated using the properties known for PuO₂ and ThO₂.

a. Density (measured by x-ray diffraction). See Figure A2.

b. Average Linear Thermal Expansion Coefficient:

10.5 × 10⁻⁶/°C (298-1273°K)
c. Heat Capacity. See Table AII.
d. Enthalpy. See Table AII.
e. Temperature of Phase Transformation, °C.

\[
\begin{align*}
100 \text{ m/o PuO}_2 & \quad \text{melting point: } 2400°C \text{ (pure PuO}_2 \text{ in sealed capsule)} \\
80 \text{ m/o PuO}_2 - 20 \text{ m/o ThO}_2 & \quad 2400°C \text{ (open system)} \\
40 \text{ m/o PuO}_2 - 60 \text{ m/o ThO}_2 & \quad 2925°C \text{ (open system)} \\
100 \text{ m/o ThO}_2 & \quad 3300°C
\end{align*}
\]

f. Latent Heat of Melting*

\[
\begin{align*}
100 \text{ m/o PuO}_2 & \quad 16.8 \text{ kcal/mole} \\
80 \text{ m/o - 20 m/o ThO}_2 & \quad 17.0 \\
40 \text{ m/o - 60 m/o ThO}_2 & \quad 17.5 \\
100 \text{ m/o ThO}_2 & \quad 18.0
\end{align*}
\]

g. Vapor Pressures (2500°C)

\[
\begin{align*}
\text{Pure PuO}_2 \dagger & \quad 80 \text{ m/o PuO}_2 \ddagger \\
\text{PuO}_2: & \quad 2.3 \times 10^{-5} \text{ atm} \quad 1.8 \times 10^{-5} \\
\text{ThO}_2: & \quad 2 \times 10^{-6} \\
40 \text{ m/o PuO}_2 & \quad \text{Pure ThO}_2 \\
\text{PuO}_2: & \quad 0.9 \times 10^{-5} \\
\text{ThO}_2: & \quad 7 \times 10^{-8} \quad 1.1 \times 10^{-7}
\end{align*}
\]

\[
\dagger \text{Pressure for PuO}_2 \text{ at the congruent composition} \\
\ddagger \text{PuO}_2 \text{ pressure at } 1400°C = 1.8 \times 10^{-13} \text{ atm.}
\]

h. Thermal Conductivity (100% density)*

\[
\begin{align*}
700°C & \quad 9 \times 10^{-3} \text{ cal/cm°C-sec} \\
1200°C & \quad 6 \times 10^{-3} \text{ cal/cm°C-sec}
\end{align*}
\]

i. Thermal Diffusivity for Pressed and Sintered Pellets*

\[
\begin{align*}
700°C & \quad 11 \times 10^{-3} \text{ cm²/sec} \\
1200°C & \quad 7 \times 10^{-3} \text{ cm²/sec}
\end{align*}
\]

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 PuO₂ = 5.3964 Å to 100 m/o ThO₂ = 5.598 Å

n. Solubilities

PuO₂-ThO₂ solid solutions are more stable than PuO₂ itself (see Table AII). Therefore the solubility of the Pu from solid solutions would be expected to be lower than for PuO₂ itself.

o. Diffusion Rates. Not available

p. Selected Thermodynamic Functions are shown in Table AII.

*Estimated

\[\text{Figure A2}\]

\[\text{Table AII}\]

\[
\begin{array}{cccc}
\text{mol} & \text{mol} & \text{mol} & \text{mol} \\
& \text{g} \cdot \text{cm}^3 & \text{g} \cdot \text{cm}^3 & \text{g} \cdot \text{cm}^3 \\
\hline
100 & 19.3 & 19.3 & 0 & -762.9 & -1084.4 \\
80 & 18.1 & 18.1 & 0.8 & -746.7 & -980.6 \\
60 & 16.9 & 16.9 & 1.6 & -731.1 & -964.3 \\
40 & 15.7 & 15.7 & 2.4 & -716.7 & -948.0 \\
20 & 14.5 & 14.5 & 3.2 & -702.3 & -931.8 \\
0 & 13.3 & 13.3 & 4.0 & -688.9 & -915.5
\end{array}
\]

\[\text{Table continued}\]
5. Mechanical Properties
   a. Room Temperature Compressive Strength (psi) 150,000
   b. Young's Modulus (psi) 30 x 10^6
   c. Shear Modulus (psi) 12 x 10^6

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

SOURCES OF INFORMATION USED TO ESTIMATE PROPERTIES


*Estimated