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Non-fertile Fuels Development for Plutonium and High-Enriched Uranium Dispositioning in Water Cooled Reactors

C. S. Olsen

Idaho National Engineering Laboratory
P. O. Box 1625
Idaho Falls, Idaho 83415-3890

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Abstract

As a result of dismantling the bomb, there is about 100 MT of excess weapons grade plutonium in the United States and about 150 MT in the Commonwealth of Independent States. In addition, there is another 1000 MT of plutonium in commercial spent fuel that may be used as degraded weapons material. One means to disposition weapons grade plutonium is by irradiating the fuel in light water reactors (LWRs) using a non-fertile fuel based on plutonia dispersed in an oxide mixture of zirconia stabilized with calcia or yttria as a solid solution. Plutonium dispersed in a zirconia matrix offers the potential to achieve very high burnups while maintaining mechanical integrity.

A potential improvement is based on replacing the calcia with yttria and reducing the yttria content to form a partially stabilized zirconia that may have a higher resistance to cracking. A rare-earth element is also added as a burnable poison to enhance the lifetime of the fuel and the neutronic characteristics. Yttria lowers the tetragonal to monoclinic transformation temperature to 275 °C compared with 850 °C for calcia. In addition, yttria does not significantly reduce the melting point of the solid soluton from that of zirconia near 2700 °C. However, if the mechanical properties of partially stabilized zirconia with yttria proves favorable, the yttria content may be reduced resulting in higher thermal conductivity of the ternary fuel.

The use of urania-zirconia-calcia fuels with high uranium concentration in three reactors during the 1970s and 1980s established a basis for the development of a plutonia-zirconia-calcia fuel and a urania-zirconia-calcia fuel with lower concentrations of uranium than that previously used. The existing data on phase equilibria of the plutonia-zirconia-calcia or yttria and the urania-zirconia-calcia or -yttria systems were obtained and evaluated for feasible fissile concentrations and concentrations of the matrix materials. Based on the urania ternary fuels and neutronic calculations, the composition of the ternary fuel containing plutonia is 8.3 wt% plutonia, 80.4 wt% zirconia, 9.7 wt% calcia, and 1.6% erbia. For yttria replacing calcia, the same fissile and erbia contents are retained, and the yttria content varies from 9.9 wt% to 30.4 wt% with the zirconia varying from 80.2 to 59.7 wt%.

Since the melting point of plutonia (about 2350 °C) is lower than that of ZrO_2 , the addition of zirconia increases the melting point of the fuel mixture about 125 °C. The ternary phase diagram for either the urania or plutonia based fuels using yttria in place of calcia could not be derived since the urania-yttria and the plutonia-yttria phase diagrams are needed and are not available. In addition, the plutonia-zirconia-calcia phase diagram could not be derived because the plutonia-calcia phase diagram is not available. Experimental determinations would have to be performed to obtain these phase diagrams. Although the phase diagrams are incomplete, sufficient data was available to indicate that plutonia may be better than even urania in forming a complete solid solution with zirconia.

A model to calculate density of a mixture of the constituents was developed for the addition of urania or plutonia to a stabilized zirconia mixture. Because the creation of anion vacancies from the addition of burnable poisons or stabilizing agents to zirconia, density estimates based on Vegard's law result in 20% higher values of density estimates than measured densities. The densities or lattice constants for the binary mixture of ZrO_2 with calcia or one of the rare earth oxides is within 5% of the measured values, indicating the applicability of the model to binary mixtures of alkaline earth or rare earth oxides with zirconia. The results of adding urania or plutonia to binary mixtures of zirconia and calcia are not quite as good as those of the binary mixtures (7% compared with 5%).

A theory has been developed for predicting transformation strengthening of partially stabilized zirconia (PSZ), and although the theory has been substantiated for zirconia stabilized with yttria, it

has not been verified in all systems such as zirconia mixed with alumina. This increase in mechanical properties arises from improved microcracking resistance resulting from the blunting of cracks by the transformation of the tetragonal phase to the monoclinic phase. The use of yttria to stabilize zirconia instead of calcia appears to be a beneficial step because of the additional constraint that yttria offers and the lower transformation temperature. Although data are not available for the reduction of microcracking of fissile loaded zirconia-yttria alloys, the available data indicates that yttria will be a substantial improvement over calcia stabilized zirconia fuel matrix.

The mechanical integrity of the fuel matrix is enhanced by the selection of materials with low cross sections that will have a low propensity to irradiation damage. For this reason the selection of zirconia, calcia, or yttria all exhibit good irradiation resistance. On the other hand, inspite of its good thermal conductivity, alumina is extensively damaged by fission fragments when surrounded by a fissile material.

Literature values for the diffusion rates of noble gases in non-fertile matrix material indicates that the rate controlling step is diffusion through cation vacancies as is the case with urania-based fuels. These diffusion rates, which are about two orders of magnitude higher than those of urania, were used in the FASTGRASS code to predict fission gas release as a function of temperature. Although the fission gas releases were slightly less than those of UO_2 at low temperatures, the release exceeded those of UO_2 at high temperatures. Fuel performance based on the non-fertile fuel design and using UO_2 properties show fission gas releases less than 6%, cladding strains less than the 1% NRC limit, and internal fuel rod pressures remaining less than the coolant pressures.

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1.0 Introduction

As a result of dismantling the bomb, there is about 100 MT of excess weapons grade plutonium in the United States and about 150 MT in the Commonwealth of Independent States. In addition, there is another 1000 MT of plutonium in commercial spent fuel that may be used as degraded weapons material. Nuclear Weapons in both the United States and Commonwealth of Independent States (CIS) will be dismantled as a result of recent nuclear arms reduction agreements,^[1,2] and plutonium removed from these weapons must be dispositioned in a manner that will prevent future use for hostile purposes.

Of the various methods proposed for denaturing or annihilating the surplus plutonium stock pile possessed by the United States, one means to disposition weapons grade or reactor grade plutonium is by irradiating the fuel in light water reactor (LWR) using a non-fertile fuel based on plutonia dispersed in an oxide mixture of zirconia stabilized with calcia or yttria as a solid solution. Plutonium dispersed in a zirconia matrix offers the potential to achieve very high burnups while maintaining mechanical integrity. A basis for this fuel has already been established in which zirconia has been used with UO_2 fuels for the Power Burst Facility, the Savannah River Reactor, and a light-water breeder reactor^[3]. A potential improvement is based on replacing the calcia with yttria and reducing the yttria content to form a partially stabilized zirconia that may have a higher resistance to cracking. A rare-earth element is also added as a burnable poison to enhance the lifetime of the fuel and the neutronic characteristics.

Because a fertile material such as ^{238}U is not required this fuel may also use high-enriched uranium (HEU) with 93% enriched ^{235}U instead of plutonia.

The characteristics of this non-fertile fuel is discussed with regard to its fuel performance behavior. The neutronic behavior has been documented in a separate publication.^[4] A strategy for developing this fuel is also presented.

The fuel is designed for a PWR 17 x 17 fuel design and a BWR 8 x 8 fuel design (Table 1). The fuel is based on 8.3 wt% PuO_2 which could also be the same content of UO_2 containing high-enriched-uranium (HEU).

Table 1. Composition of stabilized solid solution using calcia

Parameter	PWR	BWR
Cladding	Zircaloy-2	Zircaloy-4
Outside Diameter (cm)	0.9498	1.2258
Inside Diameter (cm)	0.8354	1.0643
Fuel Diameter	0.8189	1.0434
Radial Gas Gap	0.00826	0.0104
Pitch (cm)	1.25	1.6256
Composition (wt %)		
PuO_2	8.3	8.3
ZrO_2	80.4	80.4
CaO	9.7	8.3
Er_2O_3	1.6	1.6

This composition ensures a completely stabilized zirconia with 20 mole% calcia resulting in a cubic solid solution. An improved fuel design may be developed by substituting calcia with yttria. The tentative composition for this fuel is shown in Table 2 for completely stabilized cubic solid solution

containing 20.4 wt% yttria (20.6 mole%) and partially stabilized zirconia (PSZ) containing as low as 9.9 wt% yttria (6.0 mole% yttria). The basis for the partially stabilized structure is described below under mechanical integrity.

Table 2. Composition of stabilized and partially stabilized solid solution using yttria

<u>Parameter</u>	<u>PWR</u>	<u>BWR</u>
Cladding	Zircaloy-2	Zircaloy-4
Outside Diameter (cm)	0.9498	1.2258
Inside Diameter (cm)	0.8354	1.0643
Fuel Diameter	0.190	1.0434
Radial Gas Gap	0.00826	0.0104
Pitch (cm)	1.25	1.6256
Composition (wt %)		
PuO ₂	8.3	8.3
ZrO ₂	80.2 to 59.7	80.2 to 59.7
Y ₂ O ₃	9.9 to 30.4	9.9 to 30.4
Er ₂ O ₃	1.6	1.6

2.0 Zirconia-Based Fuels Phase Equilibria

At atmospheric pressure, ZrO_2 undergoes phase changes from monoclinic to tetragonal between 950 and 1150 °C and from tetragonal to cubic (fluorite structure) at about 2300 °C. The monoclinic to tetragonal transformation exhibits a substantial amount of hysteresis and a large 3% volume change between heating and cooling. The transformation is diffusionless (martensitic), and the origin of the large hysteresis is explained by strain energy considerations in the transforming crystal lattice. The large volume change associated with the transformation gives rise to internal stresses upon heating and cooling. The monoclinic to tetragonal transformation is particularly physically deleterious to the ceramic structure.^[5] Doping of ZrO_2 with small additions of CaO , MgO , or rare earths such as Y_2O_3 can be used to lower the two transition temperatures in ZrO_2 and stabilize the cubic fluorite structure at high temperatures and eliminate the large volume changes during phase changes.

In a parallel fashion to the development of ternary $\text{UO}_2\text{-ZrO}_2\text{-CaO}$ fuels, PuO_2 may be substituted for UO_2 in order to achieve high burnup fuel capability (7.45×10^{20} fissions/cm³) and still retain structural integrity. Although burnable poisons such as erbia or gadolinia may be used to stabilize a cubic structure, large quantities of burnable poisons require large amounts of plutonium to compensate for reactivity. The plutonium will not be completely burned and would therefore require fuel reprocessing. However, small amounts of the rare earths may be added to enhance the neutronic performance and contribute to stabilizing the structure.

For the $\text{UO}_2\text{-ZrO}_2\text{-CaO}$ fuel system, the pseudo binary phase diagrams required to support this system are the $\text{UO}_2\text{-ZrO}_2$, $\text{UO}_2\text{-CaO}$, and the $\text{ZrO}_2\text{-CaO}$ phase diagrams shown in Figures 1, 2 and 3.^[6-9] These diagrams along with experimental measurements identifies the composition range to achieve the stabilized, single phase solid solution range for a ternary fuel. This region used for solid solution ternary fuels is shown in Figure 4.^[5]

From the $\text{ZrO}_2\text{-CaO}$ phase diagram shown in Figure 3, about 15 mole% calcia is required to stabilize the cubic structure, but in considering the ternary phase diagram, the calcia content has to be increased to 9.7 wt% (20.1 mole% calcia) and the zirconia content correspondingly decreased to maintain the single-phase, cubic solid solution. This composition is assumed to be the same composition for plutonia ternary fuels.

The pseudo binary as well as the ternary diagrams assume stoichiometric phases. The urania-zirconia phase diagram (Figure 1) exhibits a two phase structure, a low-urania cubic structure and a high zirconia tetragonal to monoclinic structure. The liquidus temperature for the binary system with about 80 mole% zirconia is about 2500 °C, 240 °C lower than the melting point of urania. The addition of about 15 mole% calcia (Figure 3) stabilizes the tetragonal zirconia structure in the cubic fluorite structure. The zirconia-calcia phase diagram exhibits a tetragonal to monoclinic transformation near 850 °C.

For the plutonia-zirconia-calcia system, not all of the phase diagrams that are needed are available. The plutonia-zirconia phase diagram is shown in Figure 5.^[10] The high-zirconia region exhibits the monoclinic structure of zirconia at concentrations greater than 77 mole%. The addition of zirconia acts to increase the liquidus temperature to about 2425 °C compared with the 2350 °C melting point of plutonia. The zirconia-calcia phase diagram (Figure 3) indicates 15 mole% calcia is needed to stabilize the zirconia structure. The phase-diagram that is missing is the plutonia-calcia phase diagram.

1. Face-centered cubic solid solution
2. Tetragonal solid solution
3. Monoclinic solid solution
4. Monoclinic solid solution + tetragonal solid solution
5. Face-centered solid solution + tetragonal solid solution
6. Face-centered solid solution + monoclinic solution

Z518 c90-1294-01

Figure 1 Urania-Zirconia Pseudo binary Phase Diagram

Figure 2 Urania-Calcia Pseudo binary Phase Diagram

Z516 cso-1294-03

Figure 3 Zirconia-Calcia Pseudo binary Phase Diagram

Z516 cso-1294-04

Z516 cso-0195-05

Figure 4 Urania-Zirconia-Calcia Pseudo binary Phase Diagram

Figure 5 Plutonia-Zirconia Pseudo binary Phase Diagram

Z516 cso-1294-02

The substitution of yttria for calcia lowers the tetragonal to monoclinic transformation temperature to 275 °C compared with 850 °C for the zirconia-calcia system (Figure 6).^[11] Although yttria in the amount of about 20 mole% (30.4 wt%) stabilizes the fluorite cubic structure, smaller amounts (6 mole%, 9.9 wt% yttria) that yield a partially stabilized structure may offer improved cracking resistance by the transformation of a smaller amount of tetragonal transformation to the monoclinic structure. The phase diagrams that are needed for the urania and plutonia systems are the urania-yttria and the plutonia-yttria phase diagrams.

Figure 6 Zirconia-Yttria Phase Diagram

3.0 Density Estimates of Advanced Ternary Fuels

Because the components have different crystallographic structures at room temperatures, a method is discussed to estimate the density of binary mixtures of zirconia with other stabilizing oxides, then the density of these structures with the addition of urania, and finally with the additions of plutonia replacing the urania is estimated.

3.1 Defect Structure

The addition of calcia or yttria to zirconia results in a lattice defect structure in order to maintain charge neutrality from the addition of the +2 calcium cation or the +3 yttrium (or other rare earth) cation. These additions could result in the creation of cation interstitials or oxygen vacancies. For the fluorite structure, a comparison of measured versus calculated densities shows the creation of oxygen vacancies according to Equations 1 and 2 for calcia and yttria, respectively.,

The oxygen deficiency through oxygen vacancies (O_v) in the lattice lowers the density compared with that predicted from a perfect crystal with all of the lattice positions filled. The defect structure is another reason beside the different crystal structures why the rule of mixtures over predicts the density of these structures.

A model was developed^[12] that is based on the crystallographic structure of CaF_2 , fluorite (Figure 7). Cubic zirconia exhibits the same structure with differing amounts of stabilizing elements. The density model assumes spherical packing of ions and utilizes the calculated mean number of anion vacancies per unit cell. In conjunction with this model, an equation was developed for the calculation of the theoretical density of stabilized ZrO_2 cubic solid solution based on a substitutional model which takes into account the vacancies formed by stabilizers with valences different than Zr^{+4} .

Figure 7 Fluorite structure of CaF_2 , ZrO_2 , and UO_2

The density (mass/volume) is derived from the size of the unit cell which yields the volume of the crystal structure and then the appropriate atomic masses of the elements are used to calculate the mass in the density equation.

The equation to calculate the lattice constant for ZrO_2 stabilized by different amounts of elements follows:

$$d_O = 0.1A \left[R_{Zr} + R_O + \frac{\sum (P_k M_k \Delta R_k)}{100 + \sum M_k (P_k - 1)} \right] \quad (3)$$

The sum is over all the stabilizing elements where R_{Zr} and R_O are the ionic radii of Zr^{+4} and O^{-2} , respectively, R_k is the ionic radius of the k th stabilizer ionic, and M_k is the mole percentage of the k th stabilizer. The term P_k is the number of ions per unit cell of each stabilizing element in the oxide. The constant A is based on the geometry of the unit cell of the fluorite structure, i.e.

$$A = \frac{4}{\sqrt{3}} = 2.3094 \quad (4)$$

Using the dimension of the unit cell give by Equation 3, the density of the solid solution of a stabilizing oxide with zirconia is given by:

$$\rho = \left[A_{Zr} + 2A_O + \frac{\sum P_k M_k (\Delta A_k + \{(P_{Ok} / P_k) - 2\} A_O)}{100 + \sum M_k (P_k - 1)} \right] \times \left\{ \frac{Z}{10^{-24} N d_O^3} \right\} \quad (5)$$

where A_{Zr} is the gram atomic weight of zirconium

A_O is the gram atomic weight of oxygen

ΔA_k is the difference between the gram atomic weight of the k th stabilizing element and that of Zr

N is Avogadro's number $6.023 \times 10^{23} \text{ mol}^{-1}$

Z is the number of molecules per unit cell

P_k is the number of ions per molecule of the stabilizing element

P_{Ok} is the number of oxygen ions per molecule in the stabilizer.

d_O is the lattice constant from Equation 3.

3.2 Density of Zirconia with the Addition of Stabilizing Oxides Calcia or Rare Earth Elements

The density of zirconia mixed with calcia or with one of the rare earth elements (Y, Er, or Gd) listed below is obtained from Equation 3 for the lattice parameter and Equation 5 for the density. The appropriate ionic radii and atomic masses for yttrium, erbium, gadolinium, zirconium, calcium, and oxygen are given in Table 3.^[13]

Table 3 Stabilizing Elements and Their Properties

<u>Element</u>	<u>Ionic Radius</u> <u>(nm)</u>	<u>Atomic Mass</u> <u>(g/mole)</u>
Zirconium	0.0800	91.230
Oxygen	0.1400	15.999
Calcium	0.0990	40.320
Yttrium	0.0980	88.920
Erbium	0.0881	167.280
Gadolinium	0.0938	157.270

For the binary mixtures of zirconia with the alkaline earth calcium oxide ($\text{ZrO}_2\text{-CaO}$), the calculated values of the lattice constant and the density are shown in Table 4. The number of ions per molecule in the calcium oxide stabilizer is 1. The number of oxygen ions per molecule is also 1 for the calcia stabilizer. The measured densities of calcia in zirconia are between 3 and 5% lower than the calculated values. This may be due to a smaller contraction of the lattice from the +2 ions compared with the +4 ions in the zirconium matrix or uncertainties in the ionic radii values. Experimental measurements of the lattice constant are not available.

Table 4 Comparison of Density for $\text{ZrO}_2\text{-CaO}$ Mixtures

<u>CaO</u> <u>(mole %)</u>	<u>Lattice Constant</u> <u>Calculated (nm)</u>	<u>Density (kg/m³)</u>		<u>Density</u> <u>Deviation (%)</u>
		<u>Calculated</u>	<u>Measured</u>	
10.0	0.5125	5820.4	5530.0	5.25%
15.0	0.5146	5621.6	5360.0	4.88%
20.0	0.5168	5427.3	5235.0	3.67%
22.2	0.5178	5343.2	5118.0	4.40%

For the binary mixtures of zirconia with a rare-earth element (erbium, yttrium, or gadolinium oxide), the calculated values of the lattice constant and the density are listed for yttria in Table 5, for erbia in Table 6, and for gadolina in Table 7.^[12] From the general formula M_2O_3 , the number of cations per molecule of these stabilizers is 2, and the number of oxygen ions per molecule is 3.

Table 5 Comparison of Density for $\text{ZrO}_2\text{-Y}_2\text{O}_3$ Mixtures

<u>Yttria</u> <u>(mole %)</u>	<u>Lattice</u> <u>Calculated</u>	<u>Constant</u> <u>(nm)</u> <u>Measured</u>	<u>Density</u> <u>Calculated</u>	<u>(kg/m³)</u> <u>Measured</u>	<u>Density</u> <u>Deviation (%)</u>
35.	0.5300		5438.2	5543.0	-1.89%
31.2	0.5278		5511.7	5603.0	-1.63%
26.3	0.5254		5595.6	5655.0	-1.05%
20.0	0.5219		5716.4	5760.0	-0.76%
19.8	0.5218		5720.5	5800.0	-1.37%
17.9	0.5207	0.5162	5760.3	5826.0	-1.13%
16.5	0.5198		5790.7	5810.0	-0.33%
12.1	0.5170	0.5146	5892.8	5932.0	-0.66%
11.1	0.5164	0.5145	5917.4	5945.0	-0.46%
10.0	0.5156		5945.2	5950.0	-0.08%
9.0	0.5149	0.5150	5971.1	5980.0	-0.15%
8.0	0.5142	0.5128	5997.6	5990.0	0.13%
6.9	0.5134	0.5126	6027.6	6008.0	0.33%

Table 6 Comparison of Lattice Parameter for ZrO₂-Er₂O₃ Mixture

Er ₂ O ₃ (Mole %)	Lattice Constant (nm)		Density (kg/m ³)	
	Calculated	Measured	Calculated	Lattice Deviation (%)
6.7	0.5104	0.5131	6627.1	-0.52%
9.0	0.5111	0.5135	6745.4	-0.46%
10.0	0.5115	0.5140	6798.6	-0.49%
13.5	0.5125	0.5155	6967.4	-0.58%
20.0	0.5143	0.5165	7249.7	-0.43%
25.0	0.5156	0.5177	7443.1	-0.42%

The measured densities of yttria in zirconia are up to 1.9% higher than the calculated values. Measured densities of erbia in zirconia are not available, but the measured lattice constant is about 0.5% higher than the calculated values. Calculated values for the gadolinia additions cannot be compared with experimental values since experimental data are not available.

3.3 Density of Stabilized Zirconia with Urania

The model was revised for the additions of urania or plutonia to the lattice. Urania and plutonia are assumed to each have a valence of +4 so that they do not contribute to the creation or destruction of oxygen vacancies in the lattice. Further, since these cations are slightly larger than that of zirconium, the ionic radius of each cation are mass averaged in the lattice. Since erbia is considered for a burnable poison in the weapons-grade plutonium fuel, equations for the lattice constant (Equation 7) and for the density (Equation 8) include erbia.

Table 7 Density of ZrO₂-Gd₂O₃ Mixtures

Gd ₂ O ₃ (mole %)	Calculated Lattice Constant (nm)	Calculated Density (kg/m ³)
35.9	0.5249	7257.7
31.2	0.5232	7166.3
26.3	0.5213	7061.1
20.0	0.5187	6908.5
19.8	0.5186	6903.3
17.9	0.5177	6852.5
16.5	0.5171	6813.7
12.1	0.5149	6682.7
11.1	0.5144	6650.9
10.0	0.5139	6615.0
9.0	0.5133	6581.5
8.0	0.5128	6547.0
6.9	0.5122	6508.1

$$d_o^{F-Zr-Ca} = 2.3094 \left\{ \left((100-M_F)(0.08+0.14) + M_F(R_F+0.14) \right) + \frac{(1*M_{Ca}*(0.099-0.08) + 2*M_{Er}*(0.098-0.08))}{[100+M_{Ca}*(1-1) + M_{Er}*(2-1)]} \right\} \quad (6)$$

$$\rho_{F-Ca-Er} = \left\{ \frac{4}{(10^{-21} * 6.023 * 10^{24} * d_o^3)} \right\} \quad (7)$$

$$\left\{ (100-M_F)((91.23+2*15.994) + (M_F)((A_F+2*15.994) + \frac{(1*M_{Ca}*(40.08-91.23) + 2*M_{Er}*(88.92-91.23) + ((1/1)+(3/2)-2)*15.994)}{100+M_{Ca}*(1-1) + M_{Er}*(2-1)}) \right\} * 1000$$

Using Equations 6 and 7, the lattice parameter is presented in Table 8 and the density is presented in Table 9 for $\text{UO}_2\text{-ZrO}_2\text{-CaO}$ fuel mixtures for fuel compositions given by Boltax et al.^[1] for the Special Water Reactor (SWR), the Bettis light-water breeder reactor, and for BR-3 tests with the SWR fuel. Also included is the estimated density for the ternary fuel used in the Power Burst Facility (PBF).^[14] The theoretical density for the SWR fuel was given as approximately 6000 kg/m^3 although the method of estimating the theoretical density was not given. The densities for the other fuel mixtures were also not given.

Table 8 Lattice Constant for mixtures of UO_2 with ZrO_2 and CaO

<u>Fuel Type</u>	<u>UO₂ Fertile Composition (mole %)</u>	<u>CaO Composition (mole %)</u>	<u>Lattice Constant (nm)</u>
Bettis	20.24	10.25	0.5186
BR-3	11.83	14.77	0.5181
SWR	6.69	14.8	0.5166
PBF	13.78	12.82	0.5179

Table 9 Density for mixtures of UO_2 with ZrO_2 and CaO

<u>Fuel Type</u>	<u>UO₂ Fertile Composition (mole %)</u>	<u>CaO Composition (mole %)</u>	<u>Density (kg/m³)</u>
Bettis	20.24	10.25	7034.1
BR-	11.83	14.77	6356.3
SWR	6.69	14.8	6048.8
PBF	13.78	12.82	6547.9

Lattice parameters were measured for mixtures of UO_2 and ZrO_2 with sufficient additions of CaO to stabilize the cubic structure at high temperatures^[15] by X-ray diffraction and are shown in Table 10. The measured and calculated values from Equation 6 agree within about 0.5%.

Densities (Table 11) were calculated from direct measurements and weights of the machined and cleaned specimens. Porosity values were calculated from the bulk, apparent, and true volume relationships. The apparent volume was determined by CCl_4 immersion, while the true volume was calculated from the theoretical densities of the compositions. The calculated density is consistently about 7 % higher than the measured density. Some of this difference may be due to difference assumed in the uranium isotopes. Further evaluation is needed in order to improve the model. The densities calculated from Vegard's law are higher by about 20% than both the calculated densities based on lattice parameters or the measured values demonstrating the erroneous approach using the rule of mixtures.

Table 10 Comparison of Measured and Calculated Lattice Parameter for Mixtures of UO_2 and ZrO_2 Stabilized with CaO

Fuel Type	UO ₂ Fertile Composition (mole %)	CaO Composition (mole %)	Lattice Constant (nm)		Lattice Deviation (%)
			Calculated	Measured	
B-1	8.39	12.03	0.5159	0.5158	-0.01%
B-2	21.45	12.15	0.5198	0.5230	0.60%
B-3	36.68	12.32	0.5245	0.5270	0.48%
BL-3	36.68	12.32	0.5245	0.5270	0.48%

Table 11 Comparison of Measured and Calculated Density for Mixtures of UO_2 and ZrO_2 Stabilized with CaO

Fuel Type	UO ₂ Fertile Composition (mole %)	CaO Composition (mole %)	Calculated Density (kg/m ³)	Density based on Mixtures	Measured Density (kg/m ³)	Density Deviation (%)
B-1	8.39	12.03	6262.8	7469.0	5860	-6.87%
B-2	21.45	12.15	7023.7	6703.6	6580	-6.74%
B-3	36.68	12.32	7863.6	7066.5	7380	-6.55%
BL-3	36.68	12.32	7863.6	7066.5	7380	-6.55%

The lattice parameters of a mixture of plutonia in zirconia stabilized with calcia obtained from Equation 6 are listed in Table 12. Experimental measurements of the lattice parameter have not been found. Again, these values are based on Pu^{+4} without any Pu^{+3} in the mixture.

Table 12 Lattice Parameter for mixtures of PuO_2 with ZrO_2 and CaO

PuO ₂ Fertile Composition (mole %)	CaO Composition (mole %)	Lattice Constant (nm)
1.78	12.03	0.5140
2.66	12.15	0.5143
3.80	14.27	0.5155
4.44	12.32	0.5148

The density of a mixture of plutonia in zirconia stabilized with calcia is listed in Table 13. These densities were obtained from Equation 7 using the calculated lattice parameter in Table 12.

Table 13 Density for mixtures of PuO_2 with ZrO_2 and CaO

PuO ₂ Fertile Composition (mole %)	CaO Composition (mole %)	Density (Kg/m ³)
1.78	12.03	5921.0
2.66	12.15	5972.3
3.80	14.37	5960.2
4.44	12.32	6078.4

4.0 Thermal Conductivity of PuO₂ (or UO₂)-Stabilized ZrO₂ Mixtures Using CaO or Y₂O₃

In a parallel fashion to the development of ternary UO₂-ZrO₂-CaO fuels, PuO₂ may be substituted for UO₂ in order to achieve high burnup fuel capability (7.45×10^{20} fissions/cm³) and still retain structural integrity. Small amounts of the rare earths may be added to enhance the neutronic performance and contribute to stabilizing the cubic structure. Therefore, a ZrO₂-CaO matrix is selected as the primary choice for the matrix, with the potential to replace calcia with yttria to enhance fuel performance. The thermal conduction of UO₂-ZrO₂, UO₂-ZrO₂-CaO, ZrO₂-CaO, and ZrO₂-Y₂O₃ mixtures is presented as a basis for the thermal conductivity of UO₂-ZrO₂-CaO, UO₂-ZrO₂-Y₂O₃, PuO₂-ZrO₂-CaO, and PuO₂-ZrO₂-Y₂O₃ ternary fuels.

4.1 Thermal Conduction of UO₂-ZrO₂ mixtures

Thermal diffusivity^[15] of different binary UO₂-ZrO₂ fuels is shown in Figure 7. As the amount of urania decreases, the thermal diffusivity of the ZrO₂-UO₂ mixtures increases. An anomaly appears to occur when only 6% zirconia is added to urania resulting in a substantial increase in thermal diffusivity. The data for high concentrations of UO₂ show a consistant decrease in thermal conductivity with incresing urania contents.

The data in Figure 7 were converted to thermal conductivity values using the density and heat capacity of these materials.^[16] The thermal conductivity of the mixtures with different amounts of UO₂ decreases with increasing temperature as with diffusivity (Figure 8). For comparison, the thermal conductivity of UO₂ derived from a large data base of UO₂ thermal conductivities is also shown in Figure 8.^[16] Since the thermal conductivity of urania with 5 wt% plutonia is coincident with the curve for pure UO₂, the binary mixture of plutonia with zirconia and the ternary mixture of plutonia with zirconia and calcia or yttria are expected to be nearly the same as that of the similar alloys with urania. At low temperatures, the thermal conductivity of the binary fuel mixture is about a factor of two below that of pure UO₂, but at temperatures near the operating centerline temperatures of the fuel, the thermal conductivity is about 25% lower than that of UO₂.

In order to stabilize the face-centered-cubic structure of UO₂ and ZrO₂ at high temperature, calcia is added as one of the stabilizing agent. The thermal conductivity of ternary ZrO₂-UO₂ mixtures with calcia as a stabilizing agent is shown in Figure 9. The thermal conductivity of the ternary mixture with large concentrations of UO₂ is even lower than that of the binary mixture, up to a two fold reduction from that of pure UO₂. The reduced thermal conductivity arises from the generation of oxygen vacancies from the introduction of the +2 calcium cation that reduces the mean free path of the photons in the lattice. The low urania or plutonia concentrations in the non-fertile fuels will enhance the thermal conductivity of these ternary fuels.

From the data in Figure 8, the thermal conductivity changes very little for urania concentrations between 4 and 20 mole%. Since this data covers the fissile concentration range for the non-fertile fuel, a least squares fit of the date for urania concentrations indicates thermal conductivity decreasing with increasing temperature as shown by the following equation:

$$k = 2.0976 - 2.0101 \times 10^{-4} T$$

where T = temperature (C)

Thermal Diffusivity

Binary Urania-Zirconia Alloys

Figure 7 Thermal diffusivity of $\text{UO}_2\text{-ZrO}_2$ mixtures

Thermal Conductivity

Binary Zirconia-Calcia Alloys

Figure 8 Thermal Conductivity of ZrO₂-UO₂ mixtures

Thermal Conductivity

Ternary Urania-Zirconia-Calcia Alloys

Figure 9 Thermal conductivity of UO₂-ZrO₂-CaO mixtures

4.2 Thermal Conductivity of ZrO_2 Binary Mixtures

The thermal conductivity of a ZrO_2 -CaO mixture without a fissile material is shown in Figure 10.[13] The thermal conductivity decreases with an increase in calcia content up to about 10 mole percent calcia. Then additional calcia appears to have no further effect. The thermal conductivity of yttria behaves similar to that of calcia.[17] Although about 20 % yttria is required to stabilize the cubic structure in zirconia, the thermal conductivity of a solution containing less than 10 mole% yttria yields a partially stabilized structure (PSZ) which may have superior mechanical properties to that of a calcia stabilized structure and is expected to have a higher thermal conductivity because of its lower concentration in PSZ.

4.3 Fuel Temperatures

Higher fuel temperatures resulting from a lower thermal conductivity may be mitigated by using pellets fabricated with an annulus. Steady-state fuel temperatures based on UO_2 thermal conductivity were calculated for both the PWR and BWR fuel designs at 196.85 W/cm (6 kW/ft) and 393.7 W/cm (12 kW/ft). Central holes of with diameters of 5%, 7.5%, and 10% of the fuel pellet diameter and a coolant temperature of 310 °C were assumed. Since these calculations were to examine the effect of a central hole on the centerline temperature, the use of the UO_2 thermal conductivity is an adequate assumption, recognizing that the fuel temperatures for a binary or ternary mixture would be higher. The results are shown in Table 14.

Table 14 Fuel temperatures for various annular hole sizes for PWR fuel pellets

Centerline Hole Diameter (cm)	Ratio Hole Size to Fuel Diameter (%)	196.85 W/cm Power		393.7 W/cm Power	
		Centerline Temperature (K)	Temperature Drop Compared to Solid Pellet (K)	Centerline Temperature (K)	Temperature Drop Compared to Solid Pellet (K)
0	0	1071.7	0	1822	0
0.0409	5	1050	21.7	1759	63
0.0464	5.66	1045.3	26.4	1745.5	76.5
0.06141	7.5	1031.2	40.5	1704.3	117.7
0.08188	10	1010.1	61.6	1642.4	179.6

For the PWR fuel design, a central hole 5% of the pellet diameter results in a 21.7 °C drop in the centerline temperature at 196.85 W/cm (6.0 kW/ft) power level and 63.0 °C at 393.7 W/cm. Increasing the hole diameter to 10% of the pellet diameter results in 61.6 °C drop at 196.85 W/cm and 179.6 °C at 393.7 W/cm. Thus an annular hole is effective in reducing the centerline temperature as well as providing free space for fission gas release.

Thermal Conductivity

Binary Zirconia-Calcia Alloys

Figure 10 Effect of calcia on ZrO_2 conductivity

Table 15 Fuel temperatures for various annular hole sizes for BWR fuel pellets

Centerline Hole Diameter (cm)	Ratio Hole Size to Fuel Diameter (%)	196.85 (W/cm) Power		393.7 W/cm Power	
		Centerline Temperature (K)	Temperature Drop Compared to Solid Pellet (K)	Centerline Temperature (K)	Temperature Drop Compared to Solid Pellet (K)
0.0000	0.0	1058.1	0.0	1784.1	0.0
0.05217	5.0	1037.1	21.0	1723.1	61.0
0.07826	7.5	1019.1	39.0	1669.2	114.9
0.10434	10.0	998.7	59.3	1610.3	173.8

For the BWR fuel design, a central hole 5% of the pellet diameter results in a 20.9 °C drop in the centerline temperature at 196.85 W/cm (6.0 kW/ft) power level and 61.0 °C at 393.7 W/cm. Increasing the hole diameter to 10% of the pellet diameter results in 59.3 °C drop at 196.85 W/cm and 173.8 °C at 393.7 W/cm. Thus an annular hole is also effective in reducing the centerline temperature for a BWR fuel pellet as well as providing free space for fission gas release. The fuel temperatures are lower for the BWR fuel pellet than the PWR fuel pellet because of the larger diameter fuel and the same linear power level.

5.0 Mechanical Behavior of Partially Stabilized Zirconia (PSZ)

Although a number of oxides may be used to stabilize the cubic structure of zirconia such as calcia or magnesia, yttria offers the potential to strengthen zirconia by increasing the resistance to microcracking by the transformation of a small amount of the tetragonal phase to the monoclinic phase in a partially stabilized zirconia (PSZ). Although in pure zirconia, the 3% expansion during the phase shift is sufficient to severely weaken and fracture the zirconia, zirconia that is only partially stabilized, exhibits higher strength than the zirconia that is completely stabilized to the cubic fluorite structure.

Retention of the tetragonal structure is the key factor for fabricating a tougher material based on the transformation-toughening concept.^[18] In brittle materials, the transformation usually occurs as the polycrystalline body is cooled through its transformation temperature; this produces a highly microcracked body. Stresses that arise from the shape change associated with the transformation cause these microcracks. Retention of the tetragonal phase is viewed in terms of constraint of this shape change. Constraint can arise from two sources. First, if the polycrystalline body were single phase, neighboring grains, each with a different crystallographic orientation, could constrain the anisotropic shape change of one another. Second, if a particle of the material were surrounded by a matrix of another material, the matrix material could constrain the particle shape change. If the transformation were to take place, stresses that arise from the constraint would alter the transformation thermodynamics from the familiar, unconstrained case. These stresses can also cause microcrack development which must be avoided to maintain the constraint.

The critical stress intensity factor based upon the constraint is given by:

$$K_C = \left[K_o^2 + \frac{2k\left(\frac{\Delta V}{V}\right)^2 E_c V_p R}{3(1 - \nu_c^2)} \right]^{\frac{1}{2}} \quad (8)$$

The contribution of the stress-induced fracture toughness will depend on the elastic constraining factor, k , the shape change associated with the transformation, $\frac{\Delta V}{V}$, the elastic constants of the constraining material, E_c , the volume fraction of the metastable phase, V_p , and the radius of the process zone, R . K_C for zirconia partially stabilized by yttria as a function of the volume fraction of tetragonal zirconia is shown in Figure 12 for values of the various parameters shown in the figure. Nearly perfect agreement is obtained for zirconia stabilized with yttria although not as good agreement was obtained with zirconia and alumina.

Figure 11 Fracture strength of partially stabilized zirconia with yttria

6.0 Irradiation Behavior

In addition to the need to have high mechanical strength and resistance to microcracking discussed above, the retention of mechanical integrity is based on the dispersion of a fissile material (uranium or plutonium) in a matrix which itself does not deteriorate under neutron irradiation which implies materials with low neutron cross sections. An example of a deteriorating matrix is the use of carbide fuels dispersed in a graphite matrix for space applications. Fission fragment damage occurred to the graphite matrix by the surrounding fissile materials. An analogous case is the potential limitation to high burnups in PWR and BWR fuels from the absorption of neutrons and the resultant damage to the U-238 matrix containing fissile U-235 fuel.

A number of materials may be selected for the matrix material for dispersing urania or plutonia, such as alumina (Al_2O_3), BeO, zirconia, calcia, or yttria. Because of the previous development of the urania-zirconia-calcia fuels, zirconia-calcia was selected as the matrix material from which to expand the technology to plutonia substituted for urania. Alumina has been suggested as a matrix material^[20] because of its high thermal conductivity, but significant swelling of Al_2O_3 irradiated at high temperature is attributable to the unfauling of interstitial dislocation loops and the formation of networks which serve as efficient sinks for conversion of interstitial point defects to lattice atoms. Anisotropic growth of polycrystalline alumina can cause microcracking which limits the usefulness of this ceramic in high-temperature, high-dose applications.^[21]

$\text{ZrO}_2\text{-UO}_2$ plate-type fuel elements with a wide range of UO_2 loadings were tested in pressurized water loops over a range of surface heat flux values.^[22, 23] The ZrO_2 -base fuels were found to be extremely plastic during irradiation and to undergo densification to essentially 100% theoretical density very shortly after irradiation began. Irradiation-induced phase changes were observed by X-ray diffraction, with multiphase compositions homogenizing into a single metastable phase with the fluorite-type structure. Fission gas precipitates internally as bubbles, beginning at an early stage of irradiation. The in-pile fuel swelling is linear with exposure, after correction for initial densification, up to 40×10^{20} fissions/cc and was determined to be 0.7% $\Delta V/V$ per 10^{20} fissions/cc for compositions between 25 and 46 wt% UO_2 and temperatures between 704 and 1260 °C.

Postirradiation measurements had been made at 700 to 1500 °C of the release of ^{133}Xe recoiled into single-crystal Al_2O_3 , BeO, MgO, and ZrO_2 crystals during neutron irradiation in contact with UO_2 powder.^[24] Diffusion coefficients for ^{133}Xe have been calculated from the slope of the release curve following the initial release. The activation energy for ^{133}Xe release from Al_2O_3 above 1100 °C was 65 kcal/g-mole. The xenon release behavior had been compared to anion diffusion in these oxides.

For most oxides there are two release processes, an initial rapid release which persists for several minutes only, and slower release over hours during which the accumulative fraction of xenon released is linear with the square root of the heating time. The mechanism of the initial rapid release has not been determined. Diffusion coefficients calculated from the slope of the release curve during the slower release agree in magnitude with anion diffusion coefficients measured for the same oxides over the temperature range of 1100 °C to 1500 °C. The activation energy of 64 kcal/g-mole is reported for an extrinsic or impurity controlled diffusion process.

The fused, pure zirconia specimens gave release behavior similar to alumina. The initial rapid process was observed for both first and second heat treatments of these samples, and after several minutes of heating, the accumulative fractional release was linear with the square root of heating

time. The release curves for single heating of fused calcia-stabilized zirconia showed an initial rapid release followed by a fractional release which was linear with the square root of the heating time with no evidence of an initial rapid process. The single crystal zirconia samples, both pure and yttria stabilized had release curves similar to alumina, initial rapid process evident in both first and second heating with subsequent accumulative fraction release being linear with the square root of the heating time. The magnitudes of the diffusion coefficients above 1100 °C for Al_2O_3 , BeO and MgO were nearly the same whereas the diffusion coefficients in ZrO_2 were ten to a hundred times larger than that of alumina.

Although the measurements discussed above indicated diffusion through the anion vacancies as the rate controlling mechanism, preponderance of other measurements similar to those discussed above and shown in Table 16 indicate that rate controlling mechanism is diffusion through the cation vacancies as evidenced by the high activation energy which is the similar process in UO_2 .^[25-28] All the measurements but two are in the range from 89 to 99 kcal/mole. The highest is for hafnia-erbium system which is expected to be similar to that of zirconia-based alloys and the lowest is for a zirconia-calcia-yttria system which must be regarded as an outlier. Because the composition is similar to that for the non-fertile fuels, the values for D_0 and Q of 8.3×10^{-2} and 99 kcal/mole respectively for the composition $1\text{UO}_2\text{-}1\text{Y}_2\text{O}_3\text{-}1\text{ZrO}_2$ were used to revise the FASTGRASS code^[29] as a mechanistic model for fission product release. These values correspond to a diffusion rate that is about two orders of magnitude higher than that of urania. Minor changes were also made for the atom volume based on the density of the non-fertile fuel and fission product yields for plutonium in addition to those for uranium.

Table 16 Measured Diffusion Coefficients for Cation Diffusion

System	D_0 (cm^2/sec)	Q (kcal/mole)	Species	Reference
$1\text{UO}_2\text{-}1.5\text{Y}_2\text{O}_3$	7.2×10^{-3}	89	Xenon	25
$4\text{UO}_2\text{-}1\text{Y}_2\text{O}_3$	$1/6 \times 10^{-2}$	96	Xenon	25
$1\text{UO}_2\text{-}1\text{Y}_2\text{O}_3\text{-}1\text{ZrO}_2$	8.3×10^{-2}	99	Xenon	25
$\text{HfO}_2\text{-Er}_2\text{O}_3$		185 - 153		26
$\text{ZrO}_2\text{-CaO-Y}_2\text{O}_3$	8.5×10^{-8}	42	Xenon	27
$\text{ZrO}_2\text{-UO}_2$	15	92	Xenon	28

Fission product releases were calculated for the noble fission gases, tellurium, iodine, cesium, barium, and strontium as a function of centerline fuel temperatures corresponding to different power densities in the fuel. These calculations were performed for both BWR and PWR fuel designs to determine fission gas behavior in non-fertile fuel and in UO_2 as a reference case. Since the effect of temperature was of primary importance, the temperature gradient was set to a small value of 3 °C.

The results of the FASTGRASS calculations are shown in Figure 13 for the PWR case. The BWR case exhibited similar behavior, but the temperatures are slightly lower because of the lower volumetric power density. At low fuel temperatures, the release from UO_2 -based fuels are slightly higher than those for the non-fertile fuels, but as the temperature increases, the release from the non-fertile fuel exceeds that of UO_2 -based fuels. From the standpoint of being able to retain fission products, the non-fertile fuel is not as good as the UO_2 fuels, but more importantly is maintaining the cladding strain below the 1% maximum allowed by NRC. In this sense, enhanced fission product release is desirable. Qualification testing would quantify the better approach; retention versus release of the fission products.

Fission Product Release

Figure 12 Comparison of Fission Gas release between UO_2 and non-fertile fuel

FRAPCON^[30] calculations were performed for the non-fertile fuel design but using UO_2 as a reference case for a low power case with average power levels at 229 W/cm for beginning of life (BOL) and decreasing to 164 W/cm at end of life (EOL). A high-power case was also performed with average power levels at 312 W/cm for BOL and decreasing to 246 W/cm at EOL. The PWR fuel rod was prepressurized to 345 psi with a 2200 psi external coolant pressure.

For the high-power case, the peak fuel temperatures at BOL was 2051 K and 1495 at EOL. The radial gas gap closed increasing the gap conductance and lowering the free void volume in the fuel rod. As a result the fission gas pressure inside the rod reached 1900 psi. The cladding hoop strain was still in compression because of the higher 2200 psi coolant pressure. Fission gas release was 6.1%.

For the low-power case, the peak fuel temperatures at BOL was 1680 K and 1163 at EOL. The radial gas gap closed increasing the gap conductance and lowering the free void volume in the fuel rod. As a result the fission gas pressure inside the rod reached 1800 psi. The cladding hoop strain was still in compression. Fission gas release was 3.9% consistent with the lower fuel temperatures.

Similar results were obtained for the BWR fuel design using UO_2 . The fuel temperatures were higher than that of the PWR fuel although the volumetric power density was less because the radial gas gap did not close. The fission product release was slightly lower 2.5% and the fission gas pressure was substantially reduced because of maintaining the void volume in the radial gas gap. Because of the gas gap the internal pressure was reduced to 168 psi.

7.0 Fuel Qualification

Based upon the fuel development and testing plans developed for the Space Exploration Initiative (SEI)^[31], a non-fertile fuel could be ready for qualification testing in a commercial reactor in about four years. Initial fuel qualification will require testing small fuel samples prepared by different processes and exhibiting different characteristics to determine the optimum fuel fabrication process and validate the expected fuel performance. Further testing will involve testing individual small fuel rod segments or bundles of segments to further expand the fuels performance data base for the non-fertile fuel. Because statistical testing requires a very large number of samples and irradiation facilities are extremely expensive, the approach is to minimize the nuclear testing and to establish the confidence limits by establishing failure mechanisms and models for these mechanisms with their uncertainties. A statistical failure rate for this fuel can then be established. Validation of the fuel performance is done by testing a large number of fuel rods in a commercial reactor.

8.0 Conclusions

The use of urania-zirconia-calcia fuels with high uranium concentration in three reactors during the 1970s and 1980s established a basis for the development of a plutonia-zirconia-calcia fuel and a urania-zirconia-calcia fuel with lower concentrations of uranium than that previously used. The existing data on phase equilibria of the plutonia-zirconia-calcia or yttria and the urania-zirconia-calcia or -yttria systems were obtained and evaluated for feasible fissile concentrations and concentrations of the matrix materials. Based on the urania ternary fuels and neutronic calculations, the composition of the ternary fuel containing urania or plutonia is 8.3 wt% urania or plutonia, 80.4 wt% zirconia, 9.7 wt% calcia, and 1.6% erbia. For yttria replacing calcia, the same fissile and erbia contents are retained, and the yttria content varies from 9.9 wt% to 30.4 wt% with the zirconia varying from 80.2 to 59.7 wt%.

Since the melting point of plutonia (about 2350 °C) is lower than that of ZrO_2 , the addition of zirconia increases the melting point of the fuel mixture about 125 K. Ternary phase diagram for either the urania or plutonia based fuels using yttria in place of calcia could not be derived since the urania-yttria and the plutonia-yttria phase diagrams are needed and are not available. In addition, the plutonia-zirconia-calcia phase diagram could not be derived because the plutonia-calcia phase diagram is not available. Experimental determinations would have to be performed for these phase diagrams. Although the phase diagrams are incomplete, sufficient data was available to indicate that plutonia may be better than even urania in forming a complete solid solution with zirconia.

A potential improvement in the HEU or plutonia fuels is the substitution of yttria for calcia. Yttria lowers the tetragonal to monoclinic transformation temperature from 850 °C for calcia to 275 °C for yttria. In addition, yttria does not lower the liquidus temperature from the melting point of zirconia near 2700 °C. However, if the mechanical properties of partially stabilized zirconia with yttria proves favorable, the yttria content may be reduced resulting in higher thermal conductivity of the ternary fuel.

A model to calculate density of a mixture of the constituents was developed for the addition of urania or plutonia to a stabilized zirconia mixture. Because the creation of anion vacancies from the addition of burnable poisons or stabilizing agents to zirconia, density estimates based on Vegard's law result in unusually 20% higher values of density estimates than measured densities. The densities or lattice constants for the binary mixture of ZrO_2 with calcia or one of the rare earth oxides is within 5% of the measured values, indicating the applicability of the model to binary mixtures of alkaline earth or rare earth oxides with zirconia.

The results of adding urania or plutonia to binary mixtures of zirconia and calcia are not as good as those of the binary mixtures (7% compared with 5%), but at this point in developing advanced fuels based on these ternary mixtures, the 7% error is acceptable. Experimental data on the densities and lattice parameters are needed for the various isotopic mixtures and different oxidation states of the fuel.

A theory has been developed for predicting transformation strengthening of partially stabilized zirconia, and although the theory has been substantiated for zirconia stabilized with yttria, it has not been verified in all systems such as zirconia mixed with alumina. This increase in mechanical properties arises from improved microcracking resistance resulting from the blunting of cracks by the transformation of the tetragonal phase to the monoclinic phase. The use of yttria to stabilize zirconia instead of calcia appears to be a beneficial step because of the additional constraint that yttria offers and the lower transformation temperature. Although data are not available for the reduction of microcracking of fissile loaded zirconia-yttria alloys, the available data indicates that yttria will be a substantial improvement over calcia stabilized zirconia fuel matrix.

The mechanical integrity of the fuel matrix is enhanced by the selection of materials with low cross sections that will not be damaged by irradiation. For this reason the selection of zirconia, calcia, or yttria all exhibit good irradiation resistance. On the other hand, inspite of its good thermal conductivity, alumina is extensively damaged by fission fragments when surrounded by a fissile material.

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