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Weapons-Grade Plutonium Dispositioning Volume 4

Plutonium Dispositioning in Light Water Reactors

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ABSTRACT

This study is in response to a request by the Reactor Panel Subcommittee of the National Academy of Sciences (NAS) Committee on International Security and Arms Control (CISAC) to evaluate the feasibility of using plutonium fuels (without uranium) for disposal in existing conventional or advanced light water reactor (LWR) designs and in low temperature/pressure LWR designs that might be developed for plutonium disposal. Three plutonium-based fuel forms (oxides, aluminum metallics, and carbides) are evaluated for neutronic performance, fabrication technology, and material and compatibility issues. For the carbides, only the fabrication technologies are addressed.

Viable plutonium oxide fuels for conventional or advanced LWRs include plutonium-zirconium-calcium oxide ($\text{PuO}_2\text{-ZrO}_2\text{-CaO}$) with the addition of thorium oxide (ThO_2) or a burnable poison such as erbium oxide (Er_2O_3) or europium oxide (Eu_2O_3) to achieve acceptable neutronic performance. Thorium will breed fissile uranium that may be unacceptable from a proliferation standpoint. Fabrication of uranium and mixed uranium-plutonium oxide fuels is well established; however, fabrication of plutonium-based oxide fuels will require further development and performance qualification.

Viable aluminum-plutonium metallic fuels for a low temperature/pressure LWR include plutonium aluminide in an aluminum matrix ($\text{PuAl}_4\text{-Al}$) with the addition of a burnable poison such as erbium (Er) or europium (Eu). Fabrication of low-enriched plutonium in aluminum-plutonium metallic fuel rods was initially established 30 years ago and will require development to recapture and adapt the technology to meet current environmental and safety regulations. Fabrication of high-enriched uranium plate fuel by the picture-frame process is a well established process, but the use of plutonium would require the process to be upgraded in the United States to conform with current regulations and minimize the waste streams.

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SUMMARY

Changing world conditions will result in significant reductions in the number of nuclear warheads in superpower arsenals. The Secretary of Energy has been charged by the United States Congress to provide recommendations and options for disposition of excess weapons-grade plutonium resulting from downsizing of the world arsenals. The Secretary of Energy has chartered the National Academy of Sciences (NAS) Committee on International Security and Arms Control (CISAC) to review and compare the relative merits of plutonium disposal options ranging from simple storage through extraterrestrial disposal to consumption in reactors or accelerators. The CISAC Reactor Panel is tasked with examination of plutonium disposal options using existing light water reactor (LWR) designs for plutonium burning.

The Idaho National Engineering Laboratory (INEL) staff is supporting the committee's work by providing technical analyses in three specific areas identified by the Reactor Panel. The three areas of focus are the following:

1. Provide a preconceptual analysis for a reactor specifically designed for destruction of weapons-grade plutonium.
2. Evaluate the feasibility of using plutonium fuels (without uranium) for disposal in existing conventional or advanced LWRs.
3. Assist in evaluation of proposals submitted by sponsors of reactor and accelerator concepts by providing a basis from which objective comparisons can be made.

This study addresses the second area of focus; the first and third areas are addressed in companion volumes.

Use of plutonium fuels in existing conventional or advanced LWR plant designs is attractive, because it enables maximum exploitation of existing technology and infrastructure. The potential exists for weapons-grade plutonium dis-

position with minimal development costs and risk, and reduced schedule. Plutonium fuels without uranium or thorium are most desirable because production of additional weapons materials can be avoided and the plutonium destruction rate is maximized. Unfortunately, the absence of fertile materials generally results in unacceptable (positive) temperature coefficients of reactivity for the range of plutonium rod mass loadings of interest in a standard PWR fuel assembly. Acceptable temperature coefficients can probably be obtained with other resonance absorbers. The rare-earth elements gadolinium, erbium, and europium are attractive candidates.

Three categories of plutonium fuels are considered for use in conventional or advanced LWR designs: plutonium oxide fuels, aluminum-plutonium metallic fuels, and plutonium carbide fuels. Preliminary evaluations of the neutronic performance of the first two fuel types have been completed. Important neutronic performance characteristics examined include plutonium mass loading, resulting cycle length, prompt fuel temperature reactivity coefficients, isothermal temperature coefficients, and plutonium isotopic compositions. In general, reactivity coefficients are examined only at Beginning-of-Cycle (BOC). Fabrication issues have been examined for all three fuel categories and performance issues have been addressed for oxide and metallic fuels.

A number of oxide fuel compositions using weapons-grade plutonium are considered. The compositions examined include $\text{PuO}_2(\text{ZrO}_2)$ and $\text{PuO}_2(\text{ZrO}_2)$ containing small quantities of Gd_2O_3 , Er_2O_3 or Eu_2O_3 . A representative low enrichment (3.2 wt% ^{235}U) uranium oxide fuel form is examined to serve as a benchmark. Mixed oxide fuels, employing both reactor-grade and weapons-grade plutonium, and fuels containing thorium [$\text{PuO}_2(\text{ThO}_2)$, $\text{PuO}_2(\text{ZrO}_2)(\text{ThO}_2)$, and $\text{PuO}_2(\text{ThO}_2)(\text{Gd}_2\text{O}_3)$] are also examined. Fuel compositions containing significant volume fractions of zirconium oxide may also contain calcium oxide to thermally stabilize the fuel. Although not explicitly modeled, the addition of

CaO should not significantly alter the results of these analyses.

The plutonium mass loadings obtainable in the fuel forms containing only $\text{PuO}_2(\text{ZrO}_2)$ are unacceptably low and the prompt temperature coefficients of reactivity are positive. Acceptable plutonium mass loadings and negative reactivity coefficients can be obtained with plutonium fuels containing thorium, but the proliferation potential of ^{233}U production is comparable to that posed by a uranium-plutonium fuel cycle. High plutonium mass loadings and negative prompt temperature coefficients are obtained with any of the three rare-earth additives considered. For the LWR lattice configuration and compositions examined, acceptable isothermal temperature coefficients are obtained with erbium or europium as additives. Positive isothermal coefficients are obtained with gadolinium. With europium as an additive, the isothermal temperature coefficient is negative over the entire operational temperature range. At low europium mass loadings, the isothermal temperature coefficient is positive at low temperatures, but may still be acceptable. In general, use of $\text{PuO}_2(\text{ZrO}_2)$ fuel forms can result in a controllable LWR with use of these additives.

Fabrication processes for traditional mixed uranium-plutonium oxide fuels are well established and believed adaptable to fabrication of zirconium-plutonium oxide fuels containing rare-earth additives. The use of ZrO_2 as a diluent for PuO_2 creates a potential problem in obtaining a sufficiently homogeneous fuel form. Some development work would be required regardless of the process selected. Three powder preparation techniques are in current use for mixed oxide fuels. They are the coconversion process using thermal microwave denitration, the integrated dry route using mechanical blending, and the coprecipitation process. The latter two are the currently favored processes, but the integrated dry route process is unsuitable if fuel reprocessing is ultimately required to achieve the desired burnup. Conventional fabrication techniques can be adapted to manufacture pellets from the mixed oxide powders. The preferred technique will depend on the powder fabrication method used

and on the desired fuel pellet properties and performance characteristics.

Aluminum-plutonium metallic fuels are examined for use in a low temperature and low pressure LWR. The fuel consists of weapons-grade plutonium (PuAl_4 intermetallic) in an aluminum matrix. Additives of gadolinium, erbium, or europium are explored to achieve negative temperature coefficients. Plutonium mass loadings are slightly higher than for the pure $\text{PuO}_2(\text{ZrO}_2)$ fuel form, but still unacceptably low. The prompt temperature coefficients are small but negative for weapons-grade plutonium. The isothermal temperature coefficient is strongly positive. High plutonium mass loadings are obtained with any of the three rare-earth additives considered. Prompt fuel temperature coefficients are negative for both erbium and europium. The isothermal temperature coefficients are strongly negative for erbium. The BOC isothermal temperature coefficient with europium as an additive is slightly positive for the cases examined. In general, use of PuAl_4 fuel forms can result in a controllable LWR with use of these additives.

A number of Pu-Al fuel forms and fabrication techniques were developed or explored during plutonium recycle studies about 30 years ago. Fabrication techniques vary depending on the Pu-Al composition. The eutectic composition is approximately 2 at% (15.64 wt%) plutonium. Compositions with plutonium content lower than the eutectic composition are reasonably ductile and can be formed by rolling or extrusion. Compositions with higher plutonium content tend to be brittle and difficult to form. Low plutonium content alloys suitable for use in a plutonium-burning LWR have been fabricated in several forms. Successful techniques included hot extrusion of Pu-Al alloy fuel cores for insertion into zircaloy tubes, coextrusion of Pu-Al fuel cores with aluminum cladding, cylindrical-shaped aluminum clad plates, and plates fabricated using the picture-frame technique. Fabrication of high plutonium content alloys is more difficult. If high plutonium content alloys were necessary, the composition ductility could be improved by the addition of nickel, zirconium, or titanium. High plutonium content alloys have

been successfully fabricated into plate fuels. Fabrication processes would require more automation than previously employed to meet as low as reasonably achievable (ALARA) requirements and to minimize wastes.

Uranium-plutonium carbide fuels are considered because they have higher thermal conductivity and lower operating temperatures than the oxide fuels. Because of the limited plutonium car-

bide fabrication experience base, fabricability must be assessed based on existing experience with the uranium carbide fuels. Two fuel forms are believed to be suitable, one where carbide pellets are contained in a metal jacket and the other consisting of carbide particles dispersed in a graphite matrix. Although this appears to be a reasonable extension of uranium carbide experience, substantial development would be required.

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ACRONYMS

ABH	Amouyal, Benoist, and Horowitz thermal disadvantage factor method	Eu ₂ O ₃	europium oxide or europia
Al	aluminum	FIMA	fissions per initial metal atoms
ALARA	as low as reasonably achievable	g	gram
at%	atom percent	g/rod	gram per fuel rod
ATR	Advanced Test Reactor	Gd	gadolinium
B	boron	Gd ₂ O ₃	gadolinium oxide or gadolinia
BISO	multilayered non-SiC coated spherical particles	GTA	gas tungsten arc
BOC	Beginning-of-Cycle	GWD/MT	gigawatt day per metric ton
BWR	Boiling Water Reactor	H	hydrogen
CF	capacity factor	HFIR	High Flux Isotope Reactor
CaO	calcium oxide	HMTA	hexamethylenetetramine
CIS	Commonwealth of Independent States	HTGR	High Temperature Gas Reactor
CISAC	Committee on International Security and Arms Control	HWR	Heavy Water Reactor
COMBINE	Neutron spectrum and cross-section generation computer code	IFR	Integral Fast Reactor
CVD	chemical vapor deposition	INEL	Idaho National Engineering Laboratory
DBTT	Ductile to Brittle Transition Temperature	K	Kelvin
EB	electron beam	LWR	Light Water Reactor
EBWR	Experimental Boiling Water Reactor	MCNP	Monte Carlo Neutron Photon code
EOC	End-of-Cycle	Mo	molybdenum
Er	erbium	MOX	mixed oxide
Er ₂ O ₃	erbium oxide or erbia	MT	metric ton
Eu	europium	MTA	methylenetetramine
		MTHM	metric ton of heavy metal
		MTR	Materials Test Reactor
		MW(e)	megawatt electrical power

MW(t)	megawatt thermal power	Th	thorium
mV	millivolt	ThO ₂	thorium oxide
NAS	National Academy of Sciences	TRISO	multilayered (4) coated spherical particles: buffer, IPyC, SiC, OPyC
pcm	percent milli (10^{-5})	U	uranium
PM	powder metallurgy	UC	uranium carbide
PNL	Pacific Northwest Laboratory	UO ₂	uranium oxide
PRTR	Plutonium Recycle Test Reactor	VAC	vacuum arc melting
Pu	plutonium	VF	volume fraction
PuAl ₄	plutonium aluminide	w	fuel rod volume fraction of burnable poison (Gd ₂ O ₃ , Er ₂ O ₃ , Eu ₂ O ₃)
PuC	plutonium carbide	W	tungsten
PuO ₂	plutonium oxide	wt%	weight percent
PWR	Pressurized Water Reactor	x	fuel rod volume fraction of PuO ₂
Si	silicon	y	fuel rod volume fraction of ThO ₂
SRL	Savannah River Laboratory	z	fuel rod volume fraction of ZrO ₂
Ta	tantalum	Zr	zirconium
TCE	trichloroethylene	ZrO ₂	zirconium oxide
TD	theoretical density		

1. INTRODUCTION

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. Plutonium removed from these weapons must be dispositioned in a manner that will prevent future use for hostile purposes. Various methods have been proposed for denaturing or annihilating the surplus plutonium stockpile possessed by the United States. The Secretary of the Department of Energy requested the National Academy of Sciences (NAS) Committee on International Security and Arms Control (CISAC) to evaluate disposition options.

The Idaho National Engineering Laboratory (INEL) staff is supporting the CISAC Reactor Panel by providing technical analysis in three specific areas:

1. Provide a preconceptual analysis for a reactor specifically designed for destruction of weapons-grade plutonium.
2. Evaluate the feasibility of using plutonium fuels (without uranium) for disposal in existing conventional or advanced light water reactors (LWRs).
3. Assist in evaluation of proposals submitted by sponsors of reactor and accelerator concepts by providing a basis from which objective comparisons can be made.

This volume presents the results of the activities in the second area. Separate volumes address the other two areas. This volume examines three types of fuels—plutonium-based oxide fuels, aluminum-plutonium metallic fuels, and plutonium-based carbide fuels for plutonium disposition in LWR designs. Neutronic analysis, fuel fabrication, and fuel performance are discussed for the oxide and metallic fuels. Only fuel fabrication is discussed for the carbide fuels.

Neutronic performance characteristics of weapons-grade plutonium oxide (PuO_2) fuel compositions are explored for use in a conven-

tional or advanced LWR. The familiar oxide fuel form was selected primarily because the developmental risk is expected to be small relative to other fuel forms not in commercial use today.

Weapons-grade plutonium fuel compositions considered in the neutronic analyses include plutonium-zirconium oxides with thorium and/or burnable poison additives: gadolinium, erbium, and europium. A typical pressurized water reactor (PWR) uranium oxide (UO_2) fuel is also analyzed as a reference case for comparison purposes. The specific fuel compositions analyzed include the following:

- UO_2 (3.2 wt% ^{235}U , reference case).
- $\text{PuO}_2(\text{ZrO}_2)$
- $\text{PuO}_2(\text{ZrO}_2)(\text{ThO}_2)$
- $\text{PuO}_2(\text{ThO}_2)$
- $\text{PuO}_2(\text{ThO}_2)(\text{Gd}_2\text{O}_3)$
- $\text{PuO}_2(\text{ZrO}_2)(\text{Gd}_2\text{O}_3)$
- $\text{PuO}_2(\text{ZrO}_2)(\text{Er}_2\text{O}_3)$
- $\text{PuO}_2(\text{ZrO}_2)(\text{Eu}_2\text{O}_3)$.

Plutonium fuel compositions containing uranium are explicitly not included; the primary intent and goal of this study is to explore pure plutonium fuels that do not breed ^{239}Pu (via ^{238}U) and whose usage would expedite the consumption of the nuclear weapons plutonium stockpile. Isotopic compositions for reactor and weapons-grade plutonium in mixed oxide (MOX) fuels are included for comparison purposes.

The three fabrication processes reviewed for oxide fuel production as powders were coconversion (also known as thermal microwave denitration), integrated dry route (mechanical blending), and coprecipitation. Three important processes for the production of pellets include the integrated dry route process, wet conversion, and dry con-

version. Four significant factors considered during manufacturing of pellets are (1) control of specific area of powder, (2) control of green density, (3) mixing of different amount of powder, and (4) sintering time, temperature, and atmosphere.

Neutronic performance characteristics of weapons-grade, aluminum-plutonium fuel compositions are explored for use in a non-commercial, low-pressure, low-temperature, nonelectricity-producing LWR. This option was specifically requested by NAS to provide a baseline for comparison to other plutonium burning options. The aluminum-plutonium neutronic analyses are very similar to the plutonium oxide neutronic analyses.

Weapons-grade aluminum-plutonium fuel compositions considered in the neutronic analyses include aluminum-plutonium with the burnable poison additives: gadolinium, erbium, and europium. Specific fuel compositions analyzed include the following:

- $\text{PuAl}_4(\text{Al})$
- $\text{PuAl}_4(\text{Al})(\text{Gd})$
- $\text{PuAl}_4(\text{Al})(\text{Er})$
- $\text{PuAl}_4(\text{Al})(\text{Eu})$.

The following plutonium-zirconium with zirconium hydride fuel compositions were also analyzed to assess the effects of hydrides on temperature feedback coefficients:

- $\text{PuZr}(\text{ZrH}_{1.6})$

- $\text{Pu}(\text{ZrH}_{1.6})$.

Several forms of the metallic aluminum-plutonium alloys have been fabricated, including zircaloy encapsulated aluminum-plutonium rods, aluminum clad wires, cylindrical shaped aluminum clad plate fuels, and aluminum-clad plate fuels fabricated by the frame technique. The fabrication process will need to be more automated than previously used because of as low as reasonably achievable (ALARA) requirements and the minimization of mixed wastes (mixture of hazardous chemicals and radioactive materials).

The fabrication of mixed uranium-plutonium carbide fuels, analogous to the mixed oxide fuels of uranium and plutonium (MOX fuels), are discussed. In addition, potential fuels of plutonium carbide with other metal carbides such as niobium and zirconium carbide are discussed. These fuels are candidates for plutonium burning because they have higher thermal conductivity and lower operating temperatures than oxide fuels. The carbide fuels also have a higher density that allows an increase in fissile density. Because there is a limited PuC fuels experience base, fabrication details for PuC fuels are not available, but are formulated from those of uranium carbide (UC) fuels based on the similarity in their chemistries.

In order to perform the analyses and evaluations, assumptions and general requirements are necessary. These are presented in Section 2. Three categories of fuels were considered: oxide fuels, aluminum-plutonium metallic fuels, and carbide fuels. The neutronic analysis, fuel fabrication, and performance behavior for each fuel type are presented in Sections 3, 4, and 5, respectively. The conclusions are presented in Section 6.

2. ASSUMPTIONS AND REQUIREMENTS

In evaluating potential fuel forms for burning plutonium, a number of assumptions and requirements were imposed by NAS on the evaluation. These assumptions and requirements are summarized below:

- This study focuses on weapons-grade plutonium fuels specifically for use in light water thermal reactors.
- Fuel optimization for the production of electricity or commercial steam supply is not a requirement.
- Fuel optimization with respect to economic concerns is also not a requirement.
- Fuel types to be evaluated for performance and fabrication include plutonium oxides, aluminum-plutonium metallics, and plutonium carbides.
- Plutonium oxide fuel compositions will not include the addition of uranium.
- Weapons-grade plutonium isotopic content (atom percent) is assumed to be:
 - 95.5% ^{239}Pu
 - 4.0% ^{240}Pu
 - 0.5% ^{241}Pu .
- The weapons-grade plutonium stockpile is 50 metric tons (MT).

3. OXIDE FUELS

3.1 Neutronic Analysis

3.1.1 Introduction. This section describes the neutronic performance characteristics of oxide fuel compositions containing weapons-grade plutonium. The familiar oxide fuel form is considered to be a leading candidate fuel form because of its relatively low developmental risk and potential use in a conventional or advanced LWR.

Plutonium oxide fuel compositions considered in the neutronic analyses include plutonium-zirconium oxides with thorium and/or burnable poison additives: gadolinium, erbium, and europium. A standard PWR uranium oxide (UO_2) fuel is also analyzed as a reference case for comparison purposes. The specific fuel compositions analyzed include:

- UO_2 (reference case)
- $\text{PuO}_2(\text{ZrO}_2)$
- $\text{PuO}_2(\text{ZrO}_2)(\text{ThO}_2)$
- $\text{PuO}_2(\text{ThO}_2)$
- $\text{PuO}_2(\text{ThO}_2)(\text{Gd}_2\text{O}_3)$
- $\text{PuO}_2(\text{ZrO}_2)(\text{Gd}_2\text{O}_3)$
- $\text{PuO}_2(\text{ZrO}_2)(\text{Er}_2\text{O}_3)$
- $\text{PuO}_2(\text{ZrO}_2)(\text{Eu}_2\text{O}_3)$.

Plutonium oxide fuel compositions containing uranium were excluded from the task by the CISAC Reactor Panel. The primary intent and goal of this study is to explore pure plutonium fuels that do not breed ^{239}Pu (via ^{238}U) and whose usage would expedite the consumption of the nuclear weapons plutonium stockpile. MOX isotopics for reactor and weapons-grade plutonium are included for comparison purposes.

Fuel compositions containing significant volume fractions of the diluent zirconium oxide (ZrO_2), which includes most oxide fuel composi-

tions analyzed in this document, may be required to contain calcium oxide (CaO) in order to thermally stabilize and improve the thermal conductivity of the fuel. Although CaO was not explicitly considered in the neutronic analyses, the substitution of CaO for ZrO_2 should not have a significant impact on the neutronic results. The CaO diluent would typically account for only 5–10 wt% of the fuel composition. Neutron cross sections for calcium and zirconium are similar with calcium having a slightly larger thermal absorption cross section.

The neutronic analyses are preliminary investigations and cursory in nature, providing general insights into important reactor physics parameters and trends for the plutonium fuel compositions considered. Neutronic analyses in this study show oxide fuel compositions with the greatest potential for use in conventional or advanced light water power reactors include the plutonium-zirconium oxide with erbium, europium, or thorium oxide additives. Thorium, however, breeds fissile ^{233}U (potential weapons material) and may not be desirable from this standpoint.

3.1.1.1 Methodology. In general, the analytical design, development, and evaluation of a new fuel composition are dependent on reactor design requirements. One key design requirement, the fuel cycle length, is needed in the fuel development process. Fuel cycle length determines the minimum mass loading of fissile and fertile heavy metals required to sustain a power level for the cycle duration. From the initial mass loadings, depletion calculations over the fuel cycle length can be performed to determine reactivity and isotopic compositions. Once an acceptable loading is obtained, fuel performance characteristics, such as temperature coefficients, control rod worths, and power distributions, can be calculated at different points in the fuel cycle. Only after iteratively adjusting the mass loadings (adding poisons as necessary) and recalculating the fuel performance characteristics over the fuel cycle, one can ultimately develop a fuel composition with a

specific mass loading for a given lattice geometry and fuel cycle length.

The plutonium fuel evaluation methodology used in this study is a simplified process because specific reactor design requirements (e.g., fuel cycle length) have yet to be determined. A PWR lattice geometry is assumed and an approximate goal range of 1–3 years for a fuel cycle length is used. A minimum fuel cycle length of 1 year was chosen because this is approximately the current time duration between core reloads for 3-year commercial reactor fuel cycles. Power reactor fuel cycle lengths of less than 1 year would tend to degrade the reactor capacity factor and in turn would adversely impact the plutonium dispositioning schedule.

The first step in the simplified evaluation process is the parametric determination of fuel rod mass loadings for a fixed Beginning-of-Cycle (BOC) reactivity level at room temperature (300 K). This is done primarily because the calculation is not limited to a fixed specified fuel cycle length. The BOC reactivity level is arbitrarily based on the standard PWR UO_2 fuel composition. The assumption is that the UO_2 BOC excess reactivity would be sufficient for a plutonium fuel composition to overcome similar reactivity effects from fission product poisoning, temperature, density changes, control rods, etc., in an LWR core environment. Because the analysis is not bound by specifying a fuel cycle length, plutonium burnup times can be adjusted by simply increasing the plutonium rod mass loading while maintaining the same BOC reactivity level.

The second step is to evaluate each fuel composition with selected mass loadings against the following performance characteristics:

- Plutonium burnup time [100% fissions per initial metal atoms (FIMA), constant power]
- Prompt fuel Doppler temperature coefficient
- Isothermal temperature coefficient

- Plutonium/poison isotopics.

A plutonium fuel composition can be eliminated if any of the performance characteristics are deficient. For example, the plutonium mass loading should achieve a minimum mass quantity per rod to burn for at least 1 year at a specified average rod power and the prompt fuel temperature coefficients should be negative.

The third step is to evaluate plutonium oxide fuel composition constituents for compatibility and fabricability, and identify any potential developmental risks. This is the subject of Sections 3.2 and 3.3.

3.1.1.2 Neutronic Assumptions. The following neutronic assumptions were made:

- Neutronic calculations use the Evaluated Nuclear Data File Version 5 (ENDF/B-5).
- Neutronic models are based on a commercial Westinghouse 17×17 PWR fuel assembly and are expected to be applicable to a boiling water reactor (BWR) as well.
- No attempt has been made to optimize the lattice geometry to ensure every plutonium composition and rod mass loading is optimally moderated.
- The effect of soluble poisons (^{10}B) in the coolant is not included in the isothermal temperature coefficient evaluations.
- The reactivity effects of fuel thermal expansion are not included in the temperature coefficient evaluations.

3.1.1.3 Computer Codes. The neutronic analyses use three computer codes—the Monte Carlo Neutron Photon (MCNP) code,¹ the COMBINE code,² and the ORIGEN2 code.³

The MCNP code is a general purpose, continuous energy, generalized geometry, coupled neutron-photon Monte Carlo transport code. Infinite media unit cell models are constructed in MCNP geometry format for the calculation of

k-infinity and the determination of rod mass loadings.

The COMBINE code is a 166-multigroup deterministic neutron spectrum code based on the B_N approximation to the Boltzman transport equation. Solution methodology options include the Nordheim method for resolved resonance shielding and the Amouyal, Benoist, and Horowitz (ABH) method for unit cell thermal self-shielding. The k-infinity is calculated for a unit cell as a function of temperature to determine the prompt fuel Doppler and isothermal temperature coefficients of reactivity.

The ORIGEN2 code is a zero-dimensional, one-group code for calculating the buildup, decay, and processing of radioactive materials.

The code is specifically used to perform plutonium depletion calculations in order to determine approximate plutonium isotopic content in a fuel composition at End-of-Cycle (EOC) conditions (33 GWD/MT).

3.1.1.4 Unit Cell Model Description.

Neutronic calculations are based on a two-dimensional infinite array of lattice cells or unit cells with dimensions based on a typical commercial PWR fuel assembly. The unit cell is described by a central cylindrical fuel rod, fuel gap, cladding, and an encompassing square water region as shown on Figure 1. In order to represent an infinite media of unit cells, mirror boundaries are applied to all four sides of the square water region and on top and bottom of the unit cell.

$$r_1 = 0.4095 \text{ cm (rod)}$$

$$r_2 = 0.4177 \text{ cm (gap)}$$

$$r_3 = 0.4749 \text{ cm (clad)}$$

Figure 1. Typical PWR unit cell lattice geometry.

The fuel composition in a unit cell fuel rod is plutonium oxide (PuO_2) with a zirconium oxide diluent (ZrO_2). Fuel additives include thorium oxide (ThO_2) and burnable poisons such as gadolinium oxide (Gd_2O_3), erbium oxide (Er_2O_3), and europium oxide (Eu_2O_3), or gadolinia, erbia, europia, respectively. The fuel gap is assumed to be a void, the cladding is zircaloy metal, and the moderator/coolant is light water (H_2O).

Redesign of the PWR fuel assembly was not considered in this study because of time constraints. However, based on the results of this study, future work will be required to ensure that the ultimate fuel assembly design is always in an undermoderated configuration for a given plutonium mass loading.

3.1.1.5 K-Infinity Determination. Fuel rod mass loadings and material volume fractions are based on a unit cell k-infinity that is characteristic of a typical PWR lattice cell with a 3.2 wt% enriched ^{235}U uranium oxide (UO_2) fuel rod at BOC conditions and 300 K. The PWR unit cell model produces a k-infinity value of approximately 1.40. In the parametric studies, mass loadings are selected to achieve k-infinity values of approximately 1.40.

3.1.2 Discussion. This section presents the neutron physics and the calculated performance parameters for the plutonium oxide fuel compositions. In addition, the discussion provides insight and reasons for selection of fuel additives.

High-enriched, weapons-grade plutonium fuel in a light water thermal reactor is very reactive primarily because of the large thermal neutron fission cross section of ^{239}Pu . At 0.01 eV, the ^{239}Pu fission cross section is approximately 1,000 barns and monotonically decreases to 500 barns at 0.1 eV. Above 0.1 eV, the fission cross section rises sharply into the only ^{239}Pu thermal resonance that has a maximum peak value of >3,000 barns at 0.3 eV.

The high reactivity associated with ^{239}Pu in a thermal neutron spectrum leads to relatively small plutonium mass loadings per rod if a fertile

isotope or burnable poison is not used. Without the fertile material or burnable poison, the low plutonium mass rods will tend to burn out in a relatively short period of time and limit the reactor to relatively short fuel cycles. Short fuel cycles would, in turn, lead to a degraded capacity factor and reduce the consumption rate of the plutonium stockpile.

Calculated burnup time estimates (full power years) are based on a simple linear relationship where the average rod power times the burnup time equals the total plutonium fission energy available in a given fuel rod loading. Time estimates are intended only as a convenient measure to estimate a maximum possible in-core exposure for a plutonium fuel rod or assembly at a constant power level. The average rod power chosen, 58.88 kW/rod, is arbitrarily based on a 3,000 MW(t) PWR reactor with 193 fuel assemblies and 264 fuel rods per assembly. In an actual reactor, complete burnup of the plutonium (100% FIMA) would be unrealistic; however, with an innovative fuel management scheme high plutonium burnups (>80% FIMA) should be achievable.

The prompt fuel Doppler temperature coefficient results primarily from the resonance absorption behavior of heavy metal fuel isotopes or poisons. A weapons-grade plutonium fuel without a fertile material or resonance absorber poisons is somewhat unique in that its resonance behavior is dominated by the ^{239}Pu isotope. All the ^{239}Pu resolved resonances have both a capture and a fission width associated with each resonance. In general, the capture and fission widths are of comparable magnitude and any negative temperature feedback from Doppler broadened capture resonances would tend to be offset by fission resonances. Therefore, one might expect a weapons-grade plutonium fuel to exhibit a small temperature feedback contribution—either positive or negative. Resonance absorbers, such as thorium and burnable poisons with resonance behavior, can be mixed into the fuel to ensure the prompt coefficient is sufficiently negative for use in an LWR.

The prompt coefficients calculated for the different fuel compositions are derived from

k-infinity values calculated at discrete fuel temperatures over the temperature range of 600–2400 K with a fixed moderator temperature of 600 K. This temperature range envelopes typical PWR operational fuel temperatures, where the maximum fuel temperature is approximately 2061 K and the average moderator temperature is approximately 589 K at 2,200 psia.

The isothermal temperature coefficient is a measure of the combined thermal reactivity feedback response to uniform heating of both the light water moderator and the fuel. The isothermal temperature coefficients calculated in this study include feedback mechanisms from (a) Doppler broadened resonances (prompt feedback), (b) moderator thermal neutron spectral shift with temperature, and (c) water moderator density reduction with increasing water temperature (approximately 0.7 g/cc at 589 K and 2,200 psia saturation conditions). Fuel rod dimensional changes due to thermal expansion are not included. Isothermal temperature coefficients are evaluated over the temperature range of 300–600 K.

The thermal neutron peak in an LWR lies below the ^{239}Pu 0.3 eV thermal resonance. For a moderator temperature increase, the thermal neutron peak will spectrally shift upward in energy (harden) and allow a greater number of thermal neutrons to encounter the ^{239}Pu thermal resonance. The result is an increase in the capture-to-fission ratio in the ^{239}Pu resonance that would in general allow the moderator temperature coefficient to become more negative. However, the standard PWR lattice considered in this study is in some cases overmoderated (low plutonium rod mass loadings) and can lead to a positive reactivity increase with increasing moderator temperature. A carefully selected burnable poison with a thermal absorption resonance in the vicinity of the ^{239}Pu 0.3 eV resonance can be used to further enhance the plutonium capture-to-fission ratio.

The ideal burnable poison will be required to hold down excess reactivity, provide resonance absorption, and possess unique spectral absorp-

tion properties. The following burnable poisons are considered:

- Gadolinium
- Erbium
- Europium.

The burnable poison (oxide form) is assumed to be homogeneously mixed in the plutonium oxide fuel composition.

Gadolinium has a large thermal cross section and can provide significant holddown reactivity to allow greater plutonium rod mass loadings. In addition, the seven natural isotopes of gadolinium are all good resonance absorbers and tend to transmute progressively up into higher mass natural gadolinium isotopes and, thereby, replenish depleted isotopes.

Boron (^{10}B) could be used in place of the gadolinium to provide holddown reactivity. However, the ^{10}B isotope would not provide resonance absorption to improve the prompt fuel temperature coefficient and because of its $1/v$ absorption cross section could provide a positive contribution to the isothermal temperature coefficient. In addition, boron in the oxide fuel matrix may be undesirable because of helium gas generation and the potential for increased fuel swelling and rod pressure. Hence, boron is not considered in the analysis.

Erbium (^{167}Er) and europium (^{151}Eu) were specifically selected for their unique spectral absorption properties relative to ^{239}Pu , in addition to reactivity holddown capabilities. These two isotopic poisons each have two low energy thermal absorption resonances in the vicinity of the 0.3 eV ^{239}Pu fission/capture thermal resonance as shown below:

Isotope	Resonance energy
^{167}Er	0.460 eV
^{167}Er	0.584 eV
^{151}Eu	0.321 eV
^{151}Eu	0.461 eV

The resonance overlap between the poison resonances and the 0.3 eV ^{239}Pu resonance tends to hold down the ^{239}Pu reactivity both at steady-state operational temperature and during moderator temperature rises in which the thermal neutron peak (approximately 0.07 eV) spectrally shifts upward in energy.

The three burnable poisons and their natural companion isotopes are good resonance absorbers that additionally contribute negative temperature feedback reactivity and improve the prompt temperature coefficient. The poisons also have significant thermal neutron absorption cross sections that provide holddown reactivity and allow for increased plutonium rod mass loadings to support extended fuel cycle burnup times and improve the Pu/H ratio for improved fuel assembly moderation. Erbium has an added favorable feature because its $1/v$ absorption cross-section tail is relatively flat at very low thermal energies; this cross section feature inhibits reactivity increases for moderator temperature spectral shifts.

The unit cell neutronic analyses in this study focus on the standard 17×17 PWR lattice without consideration for redesign to achieve optimal moderation. In general, low plutonium mass loadings per fuel rod produce an overmoderation condition using this standard lattice. However, future analyses can draw upon several redesign options for unit cell moderation optimization:

- Cladding thickness increase
- Lattice pitch decrease
- Fuel rod diameter increase.

Other innovative ideas requiring further analysis that could improve plutonium fuel assembly temperature coefficients and moderation include spray coating of the fuel pellets or cladding with resonance materials, or the use of resonance cladding materials such as tungsten-rhenium.

The unit cell calculations for k-infinity and the subsequent translation to temperature coefficient values miss what could be important contribu-

tions to the temperature behavior of the overall reactor system. For example, optimally moderated fuel assemblies with burnable poison rods interspersed in the lattice could make the coefficients more negative, as could a fuel assembly with both PuO_2 and UO_2 fuel rods. A reactor core dominated by UO_2 fuel assemblies may exhibit acceptable temperature coefficient behavior for a minimum number of PuO_2 assemblies (e.g., a quarter core load of PuO_2 fuel assemblies). In addition, a core model calculation could account for thermal leakage effects that would also make the temperature coefficient more negative. More sophisticated fuel assembly and core models are needed to calculate these contributions and are part of the future work effort of Section 3.1.5.

3.1.3 Results. This section presents the analytical neutronic fuel performance results for each of the candidate plutonium oxide fuel compositions.

3.1.3.1 Uranium Oxide (UO_2) Reference Case. A typical PWR unit cell with a UO_2 fuel rod (3.2 wt% ^{235}U) was chosen as the reference case from which neutronic characteristic comparisons are made for the plutonium fuel compositions. The unit cell k-infinity value at BOC conditions and 300 K (room temperature) is calculated to be approximately 1.40 and is used as a basis to achieve appropriate mass loadings of plutonium, thorium, and burnable poisons for the proposed plutonium fuel compositions. In addition, the UO_2 reference case temperature coefficients, both prompt and isothermal, are calculated and used for comparison purposes.

The reference UO_2 unit cell fuel rod contains approximately 60.0 g/rod ^{235}U and 1,810.0 g/rod ^{238}U assuming a 12-ft fuel rod length. The prompt temperature coefficient at BOC is negative, -2.75 to -1.81 pcm/K, over the fuel temperature range of 600–2400 K. Table 1 and Figure 2 show the prompt fuel temperature coefficient data and comparative curves. The isothermal temperature coefficients at BOC are also strongly negative, -7.0 to -38.0 pcm/K, over the temperature range of 300–600 K. Figure 3 shows the isothermal temperature coefficient as a function of temperature.

Table 1. Prompt fuel Doppler temperature coefficient comparison for the different plutonium oxide fuel compositions.

Fuel composition	Mod. temp. (K)	Fuel temp. (K)	K-infinity	Temp. (K)	Temp. coeff. (pcm/K)
UO ₂ (3.2% wt U-235)	600	600	1.2790337	800	-2.756
	600	1,000	1.2612513	1,300	-2.204
	600	1,600	1.2405598	2,000	-1.809
	600	2,400	1.2186687		
PuO ₂ (Th ₂ O ₂) (x = 0.044, y = 0.956)	600	600	1.2736674	800	-3.769
	600	1,000	1.2496693	1,300	-2.786
	600	1,600	1.2240983	2,000	-2.091
	600	2,400	1.1995316		
PuO ₂ (Th ₂ O ₂)(Gd ₂ O ₃) (x = 0.105, y = 0.8943, w = 0.0007)	600	600	1.3250388	800	-3.258
	600	1,000	1.3025446	1,300	-2.388
	600	1,600	1.2786850	2,000	-1.776
	600	2,400	1.2558713		
PuO ₂ (ZrO ₂)(Er ₂ O ₃) (x = 0.05, z = 0.924, w = 0.026)	600	600	1.2998449	800	-0.749
	600	1,000	1.2947996	1,300	-0.521
	600	1,600	1.2895832	2,000	-0.372
	600	2,400	1.2846514		
PuO ₂ (ZrO ₂)(Eu ₂ O ₃) (x = 0.05, z = 0.94690, w = 0.0031)	600	600	1.3959711	800	-0.426
	600	1,000	1.3926622	1,300	-0.321
	600	1,600	1.3889325	2,000	-0.242
	600	2,400	1.3852102		
PuO ₂ (ZrO ₂)(Gd ₂ O ₃) (x = 0.05, z = 0.949135, w = 0.000865)	600	600	1.4781316	800	-0.390
	600	1,000	1.4747275	1,300	-0.332
	600	1,600	1.4704116	2,000	-0.259
	600	2,400	1.4659479		
PuO ₂ (ZrO ₂) 4% ²⁴⁰ Pu (x = 0.004, z = 0.996)	600	600	1.5121108	800	+0.0528
	600	1,000	1.5125939	1,300	~0.0000
	600	1,600	1.5124991	2,000	-0.0167
	600	2,400	1.5121942		
PuO ₂ (ZrO ₂) 18% ²⁴⁰ Pu (x = 0.0058, z = 0.9942)	600	600	1.4519977	800	-0.244
	600	1,000	1.4499409	1,300	-0.229
	600	1,600	1.4470587	2,000	-0.186
	600	2,400	1.4439542		

Note: x, y, z, w = fuel volume fraction of PuO₂, ThO₂, ZrO₂, Xx₂O₃ poison, respectively.

Figure 2. Prompt fuel Doppler temperature coefficient comparison for the different plutonium fuel compositions (moderator temperature equals 600 K).

Figure 3. Isothermal temperature coefficient for a typical UO_2 (3.2 wt% ^{235}U enrichment) PWR fuel composition.

Plutonium isotopic compositions⁴ at BOC and EOC for a UO₂ (low-enriched PWR fuel) fuel and a MOX (reactor-grade plutonium) fuel are shown in Table 2. The UO₂ fuel is subjected to a burnup of 33 GWD/MT (typical current PWR fuel exposure) followed by a 10-year storage period (some ²⁴¹Pu decay) prior to reprocessing.

Table 2. Approximate plutonium isotopic composition for a UO₂ and a MOX fuel.

Isotope	UO ₂		MOX	
	BOC	EOC	BOC	EOC
Pu-238	0.0	0.013	0.013	0.019
Pu-239	0.0	0.603	0.603	0.404
Pu-240	0.0	0.243	0.243	0.321
Pu-241	0.0	0.091	0.091	0.178
Pu-242	0.0	0.050	0.050	0.078

The BOC MOX plutonium feed is plutonium recovered from UO₂ spent fuel, so the plutonium isotopics are identical for the UO₂ EOC and MOX BOC conditions. The MOX fuel has a 3.64% fissile plutonium content at BOC and is also subjected to an exposure of 33 GWD/MT. The MOX EOC isotopics also include a 10-year storage period prior to reprocessing.

3.1.3.2 Plutonium Mass Loading [PuO₂(ZrO₂)]. Unit cell calculations were performed to determine the plutonium mass loading that would result in a calculated k-infinity value of 1.40 for a PuO₂(ZrO₂) fuel. Using the calculated atom densities and assuming a 12-ft rod length, the unit cell k-infinity of 1.40 produced a plutonium mass loading of 7.8 g/rod. This mass loading corresponds to a PuO₂ volume fraction (x) of approximately 0.4% and a corresponding ZrO₂ volume fraction (z) of 99.6%.

The plutonium mass loading of 7.8 g/rod is quite small compared to the 60.0 g/rod ²³⁵U and 1,810.0 g/rod ²³⁸U loading in a comparable rod containing 3.2 wt% ²³⁵U uranium oxide. However, in the uranium oxide fuel rod, when the fertile ²³⁸U is removed, only 10.5 g of ²³⁵U per rod is required to achieve a k-infinity of 1.40. Because the plutonium isotopic composition is primarily fissile ²³⁹Pu and only 4.0% fertile

²⁴⁰Pu, the two mass loadings would be expected to be similar, and indeed this is the case. The plutonium mass loading is slightly less than the ²³⁵U loading in part because ²³⁹Pu has a larger thermal fission cross section than ²³⁵U and a higher number of neutrons emitted per fission.

For a 17 × 17 PWR fuel assembly with 264 fuel rods per assembly, approximately 2.0 kg of plutonium can be loaded at BOC in each assembly. For a 3,000 MW(t) PWR with 193 fuel assemblies and assuming one quarter or 48 assemblies are designated as plutonium assemblies, 96 kg of plutonium could be loaded in the PWR core. The total 50,000 kg plutonium stockpile would then translate into approximately 520 core loads.

Because the plutonium mass per rod is so low, the plutonium fuel rods/assemblies would burn out after no more than one-third of a year in a 3,000 MW(t) PWR with an average rod power of 58.88 kW (Table 3). The fuel rod mass loading must be increased in order to extend the burnup time to at least 1 year.

In addition, the PuO₂(ZrO₂) fuel rod with only 7.8 g/rod plutonium has a large ZrO₂ volume fraction (99.6%) that is virtually solid ZrO₂. Although zirconium oxide has very good neutronic properties (low neutron absorption) and is chemically compatible as a fuel diluent, it has a relatively low thermal conductivity that would inhibit pin heat removal by conduction and could lead to fuel temperatures higher than the current maximum fuel temperatures in a UO₂ PWR fuel rod. However, with the inclusion of CaO in the PuO₂(ZrO₂) fuel composition, the thermal conductivity will be greatly improved.

Another consideration of low plutonium mass loading is fuel assembly overmoderation. Partial loss of reactor coolant or moderator density reduction would increase the reactivity of a fuel rod or assembly and lead to an increase in rod power. Preliminary results show that a fuel rod with only 7.8 g/rod plutonium cannot be configured on a PWR rod pitch that will result in an undermoderated configuration. Other alternatives, such as increasing the cladding or fuel rod diameters, would also probably not result in an

Table 3. Summary of rod mass loadings and estimated plutonium burnup times.

Fuel composition	PuO ₂ VF (x)	ThO ₂ VF (y)	ZrO ₂ VF (z)	Xx ₂ O ₃ VF (w)	Pu (g/rod)	Th (g/rod)	ZrO ₂ (g/rod)	Xx ₂ O ₃ (g/rod)	Pu Mass (kg/assembly)	Burnup time (yr)
PuO ₂ (ZrO ₂) - 0%Pu-240 4%Pu-240 8%Pu-240 12%Pu-240 18%Pu-240	0.0034	0.0000	0.9966	0	6.6	0	1246	0	1.75	0.29
	0.0040	0.0000	0.9960	0	7.8	0	1245	0	2.06	0.34
	0.0043	0.0000	0.9957	0	8.4	0	1245	0	2.21	0.36
	0.0049	0.0000	0.9951	0	9.5	0	1244	0	2.52	0.42
	0.0058	0.0000	0.9942	0	11.3	0	1243	0	2.98	0.49
PuO ₂ (ThO ₂)(ZrO ₂)	0.0040	0.0000	0.9960	0	7.8	0	1245	0	2.06	0.34
	0.0055	0.0750	0.8700	0	10.7	125	1088	0	2.83	0.47
	0.0065	0.1220	0.8715	0	12.7	204	1090	0	3.34	0.55
	0.0075	0.1600	0.8325	0	14.6	267	1041	0	3.80	0.64
	0.0100	0.2590	0.7310	0	19.5	433	914	0	5.15	0.85
	0.0150	0.4220	0.5630	0	29.2	705	704	0	7.72	1.27
	0.0200	0.5500	0.4300	0	39.0	919	538	0	10.29	1.69
	0.0440	0.9560	0	0	85.8	1597	0	0	22.64	3.73
PuO ₂ (ThO ₂)(Gd ₂ O ₃)	0.0440	0.9560	0	0	85.8	1597	0	0	22.64	3.73
	0.1000	0.8994	0	0.00060	194.9	1503	0	0.86	51.45	8.47
	0.1050	0.8943	0	0.00070	204.6	1494	0	1.00	54.02	8.90
	0.1500	0.8483	0	0.00170	292.3	1417	0	2.43	77.18	12.71
	0.2000	0.7958	0	0.00420	389.8	1330	0	5.99	102.90	16.94
	0.2500	0.7427	0	0.00730	487.2	1241	0	10.42	128.63	21.18
	0.3000	0.5725	0	0.01275	584.7	957	0	18.20	154.35	25.41
	0.0040	0	0.996000	0.00000	7.8	0	1245	0.00	2.06	0.34
PuO ₂ (ZrO ₂)(Gd ₂ O ₃)	0.0100	0	0.989920	0.00008	19.5	0	1238	0.11	5.15	0.85
	0.0150	0	0.984840	0.00016	29.2	0	1231	0.23	7.72	1.27
	0.0200	0	0.979760	0.00024	39.0	0	1225	0.34	10.29	1.69
	0.0500	0	0.949135	0.00087	97.4	0	1187	1.23	25.73	4.24
	0.0040	0	0.9960	0.0000	7.8	0	1245	0.00	2.06	0.34
PuO ₂ (ZrO ₂)(Er ₂ O ₃)	0.0200	0	0.9786	0.0135	39.0	0	1223	22.48	10.29	1.69
	0.0500	0	0.9240	0.0260	97.4	0	1155	43.29	25.73	4.24
	0.0040	0	0.9960	0.0000	7.8	0	1245	0.00	2.06	0.34
PuO ₂ (ZrO ₂)(Eu ₂ O ₃)	0.0200	0	0.9786	0.0014	39.0	0	1223	2.00	10.29	1.69
	0.0500	0	0.9469	0.0031	97.4	0	1184	4.43	25.73	4.24

K-infinity = 1.40

PWR @ 3,000 MW(t) with 264 fuel rods/assembly and 193 fuel assemblies

Single rod volume = 192.69 cm³

Fuel rod length = 12.0 ft

Fuel rod radius = 0.4095 cm

Average fuel rod power = 58.88 kW/rod

VF = volume fraction of the fuel

x = volume fraction of WPuO₂ in the fuely = volume fraction of ThO₂ in the fuelz = volume fraction of ZrO₂ in the fuel

w = volume fraction of burnable poison in the fuel

Xx = burnable poison (Gd, Er, Eu)

undermoderated configuration. One solution is to increase the plutonium rod mass loading with poison additives and then optimize the assembly design to achieve optimum moderation. Another solution might be to increase the parasitic absorption of the lattice through the use of an absorbing cladding, such as stainless steel.

3.1.3.3 Pu-240 Enrichment [$\text{PuO}_2(\text{ZrO}_2)$]. Increasing the ^{240}Pu isotopic content in the weapons-grade plutonium effectively reduces the k-infinity value and allows for increased plutonium mass loading in a fuel rod. Parametric studies were performed with 0, 4, 8, 12, and 18 at% ^{240}Pu to understand the behavior of k-infinity as a function of plutonium mass loading. Figure 4 shows k-infinity as a function of plutonium mass and Table 3 provides the mass loadings, volume fractions, and corresponding burnup times.

From Figure 4, it is apparent that as the ^{240}Pu atom percent increases, the plutonium mass loading per rod also increases, but only slightly. For

example, the plutonium mass loading at 4% ^{240}Pu is approximately 7.8 g/rod, and at 18% ^{240}Pu enrichment is approximately 11.0 g/rod (i.e., a 40% increase). The plutonium mass loading at 18%, however, is still so low that the plutonium fuel rods/assemblies would burn out in less than half a year in a 3,000 MW(t) PWR with an average rod power of 58.88 kW (Table 3).

Extracting plutonium from spent commercial LWR fuel (approximately 24 wt% ^{240}Pu) and blending it with weapons-grade plutonium can also improve the prompt fuel temperature coefficient. The prompt fuel temperature coefficient at 4% ^{240}Pu is relatively small and positive, +0.0528 to ~0.00 pcm/K, over the temperature range of 600–1600 K, and small and negative, -0.0167 pcm/K, over the temperature range of 1600–2400 K. The positive coefficient is highly undesirable and would certainly raise a licensing concern. Increasing the ^{240}Pu enrichment does improve the prompt coefficient. At 18% ^{240}Pu , the prompt temperature coefficient is still relatively small, but negative, -0.244 to -0.186 pcm/K

Figure 4. Plutonium rod mass loading relationship for different ^{240}Pu enrichments in a $\text{PuO}_2(\text{ZrO}_2)$ fuel composition.

over the entire temperature range 600–2400 K. Table 1 gives the prompt fuel temperature coefficients and Figure 2 shows a comparative plot of the coefficients.

Extracting plutonium from spent commercial LWR fuel (enriched in fertile ^{240}Pu) and blending it with weapons-grade plutonium can result in an improved (although only slightly) isothermal temperature coefficient over that of a weapons-grade $\text{PuO}_2(\text{ZrO}_2)$ fuel. The isothermal temperature coefficient of a pure weapons-grade plutonium fuel is strongly positive over the temperature range of 300–600 K (Figure 5). The isothermal temperature coefficient becomes more positive with increasing temperature and ranges from approximately +7.0 to +20.0 pcm/K between 300 and 600 K. As the ^{240}Pu isotopic content is increased, the isothermal temperature coefficient becomes less positive over the temperature range, but nevertheless remains positive for ^{240}Pu atom percentages up to 18%. Figure 5 shows the strong positive temperature coefficients for all three ^{240}Pu isotopic concentrations.

To achieve a negative isothermal temperature coefficient, a ^{240}Pu isotopic concentration much greater than 18% would be required.

3.1.3.4 Thorium Additive [$\text{PuO}_2(\text{ThO}_2)$ (ZrO_2)]. To further increase the plutonium rod mass loading and achieve negative temperature coefficients, thorium (ThO_2) was considered as an additive to the $\text{PuO}_2(\text{ZrO}_2)$ fuel. Adding ThO_2 to the $\text{PuO}_2(\text{ZrO}_2)$ fuel mixture allows for large increases in plutonium rod mass loading and consequently longer burnup times. Figure 6 shows the plutonium and thorium mass loading relationship and Table 3 provides the mass loadings, volume fractions, and corresponding burnup times.

Thorium (^{232}Th) is a fertile, threshold-fission isotope (similar to ^{240}Pu and ^{238}U) with epithermal and thermal capture resonances. Thorium would, therefore, be expected to play a similar role as ^{238}U in UO_2 fuels (i.e., provide resonance absorption to hold down reactivity, extend fuel burnup time, and produce a negative prompt fuel Doppler temperature coefficient).

Figure 5. Isothermal temperature coefficient comparison for a $\text{PuO}_2(\text{ZrO}_2)$ fuel with different ^{240}Pu enrichments.

Figure 6. Plutonium and thorium rod mass loading relationship for a $\text{PuO}_2(\text{ThO}_2)(\text{ZrO}_2)$ fuel composition.

The addition of ThO_2 at a volume fraction (y) of 55% allows for a weapons-grade plutonium loading of 39.0 g/rod. At this loading, the plutonium fuel rods/assemblies could burn for up to 1.7 years in a 3,000 MW(t) PWR with an average rod power of 58.88 kW (Table 3). This is a significant burnup time extension over both pure weapons-grade plutonium fuel (7.8 g/rod) and blending in higher ^{240}Pu isotopic concentrations (11.0 g/rod at 18% ^{240}Pu). A pure $\text{PuO}_2(\text{ThO}_2)$ fuel rod would contain 85.8 g/rod plutonium (fissile) and 1,597 g/rod thorium (fertile ^{232}Th) and result in almost a 4-year burnup time (100% FIMA) at constant rod power.

Table 1 and Figure 2 show the strongly negative prompt temperature associated with a pure $\text{PuO}_2(\text{ThO}_2)$ fuel composition relative to the $\text{PuO}_2(\text{ZrO}_2)$ fuel composition. In fact, the pure $\text{PuO}_2(\text{ThO}_2)$ prompt temperature coefficient is now comparable to the UO_2 reference case.

The isothermal temperature coefficients are compared on Figure 7 for the following three cases:

- $\text{PuO}_2(\text{ZrO}_2)$
- $\text{PuO}_2(\text{ThO}_2)(\text{ZrO}_2)$
- $\text{PuO}_2(\text{ThO}_2)$.

where x , y , and z are the PuO_2 , ThO_2 , and ZrO_2 volume fractions. The first fuel composition contains no thorium; the second is an intermediate mixture with PuO_2 , ThO_2 , and ZrO_2 ; and the third contains no ZrO_2 (all PuO_2 and ThO_2). In general, the greater the thorium volume fraction, the more negative the isothermal temperature coefficients at BOC.

The approximate plutonium isotopic content at BOC and EOC for a pure weapons-grade $\text{PuO}_2(\text{ThO}_2)$ fuel is provided in Table 4, and for comparison purposes only, the plutonium isotopic content for a weapons-grade $\text{PuO}_2(\text{UO}_2)$ fuel is also provided. Both fuels have the same initial BOC plutonium isotopics as assumed in this study; in addition, the $\text{PuO}_2(\text{UO}_2)$ fuel uses depleted uranium (0.2 wt% ^{235}U). The EOC isotopics in both cases are for a 33 GWD/MT exposure with zero storage time after exposure.

Figure 7. Isothermal temperature coefficient comparison for $\text{PuO}_2(\text{ThO}_2)$, $\text{PuO}_2(\text{ThO}_2)(\text{ZrO}_2)$, and $\text{PuO}_2(\text{ThO}_2)(\text{Gd}_2\text{O}_3)$ fuels relative to the $\text{PuO}_2(\text{ZrO}_2)$ fuel composition.

It is interesting to note the EOC isotopic similarity between these two weapons-grade plutonium fuels and the PWR UO_2 fuel (Table 2). However, the UO_2 fuel does have a higher percentage of ^{240}Pu and lower percentage of ^{241}Pu at EOC and the $\text{PuO}_2(\text{ThO}_2)$ and $\text{PuO}_2(\text{UO}_2)$ fuels never reach a 20% buildup concentration of ^{240}Pu at EOC for the 33 GWD/MT exposure.

The corresponding plutonium rod mass loadings at BOC and EOC for the $\text{PuO}_2(\text{ThO}_2)$ and $\text{PuO}_2(\text{UO}_2)$ fuel compositions are given in Table 5.

Table 4. Approximate plutonium isotopic compositions for $\text{PuO}_2(\text{ThO}_2)$ and $\text{PuO}_2(\text{UO}_2)$ fuel compositions containing weapons-grade plutonium, natural thorium, and depleted uranium.

Isotope	$\text{PuO}_2(\text{ThO}_2)$		$\text{PuO}_2(\text{UO}_2)$	
	BOC	EOC	BOC	EOC
Pu-238	0.000	—	0.000	—
Pu-239	0.955	0.570	0.955	0.626
Pu-240	0.040	0.167	0.040	0.151
Pu-241	0.005	0.217	0.005	0.181
Pu-242	0.000	0.042	0.000	0.038

Table 5. Approximate plutonium rod mass loadings for $\text{PuO}_2(\text{ThO}_2)$ and $\text{PuO}_2(\text{UO}_2)$ fuel compositions containing weapons-grade plutonium, natural thorium, and depleted uranium.

Isotope	$\text{PuO}_2(\text{ThO}_2)$ (g/rod)		$\text{PuO}_2(\text{UO}_2)$ (g/rod)	
	BOC	EOC	BOC	EOC
Pu-238	0.0	—	0.0	—
Pu-239	81.9	22.4	74.4	33.4
Pu-240	3.4	6.5	3.1	8.0
Pu-241	0.4	8.0	0.4	9.8
Pu-242	0.0	1.5	0.0	2.0
Total	85.7	38.4	77.9	53.2

The BOC rod mass loadings are based on a unit cell k -infinity of 1.40 at 300 K. The $\text{PuO}_2(\text{ThO}_2)$ fuel burnup is 47.3 g/rod plutonium and the $\text{PuO}_2(\text{UO}_2)$ fuel burnup is 24.7 g/rod plutonium for 33 GWD/MT. The plutonium rod mass of the $\text{PuO}_2(\text{ThO}_2)$ fuel composition decreases at a slightly faster rate than the $\text{PuO}_2(\text{UO}_2)$ fuel, because ^{238}U breeds ^{239}Pu . The EOC total plutonium rod masses for these two fuel compositions are both larger than the 13–20 g/rod plutonium remaining in a UO_2 fuel rod.

Despite the improved plutonium mass loadings, temperature coefficients, and delayed neutron fraction, thorium as an additive may not be desirable from the standpoint that ^{232}Th will breed fissile ^{233}U , a potential nuclear weapons material. It is expected that significant quantities of ^{233}U would be produced with the anticipated ThO_2 loadings, particularly in the case of a pure $\text{PuO}_2(\text{ThO}_2)$ fuel composition.

3.1.3.5 Gadolinium Plus Thorium Additive [$\text{PuO}_2(\text{ThO}_2)(\text{Gd}_2\text{O}_3)$]. The addition of gadolinia (Gd_2O_3) to a $\text{PuO}_2(\text{ThO}_2)$ fuel composition allows very high plutonium mass loadings relative to the $\text{PuO}_2(\text{ZrO}_2)$ fuel composition. Figure 8 shows the rod mass loading relationship between plutonium and gadolinia for a $\text{PuO}_2(\text{ThO}_2)(\text{Gd}_2\text{O}_3)$ fuel composition and Table 3 provides the mass loadings, volume fractions, and corresponding

burnup times. The addition of 1.0 g/rod Gd_2O_3 to a $\text{PuO}_2(\text{ThO}_2)$ fuel composition allows the plutonium rod mass to be increased from 85.5 to 204.6 g/rod. Similarly, a 10.0 g/rod Gd_2O_3 loading allows the plutonium rod mass to increase from 85.5 to approximately 480.0 g/rod.

The prompt fuel temperature coefficient for the 1.0 g/rod Gd_2O_3 mass loading in a $\text{PuO}_2(\text{ThO}_2)$ fuel composition is strongly negative as shown in Figure 2 and tabulated in Table 1. Presumably, the prompt fuel temperature coefficient will become less negative with increasing Gd_2O_3 content due to the reduction in ^{232}Th and the increase in ^{239}Pu as indicated in Figure 2.

The isothermal temperature coefficient for the 1.0 g/rod Gd_2O_3 mass loading in a $\text{PuO}_2(\text{ThO}_2)$ fuel composition is strongly negative as shown in Figure 7. In general, addition of Gd_2O_3 to a $\text{PuO}_2(\text{ThO}_2)$ fuel composition causes the isothermal temperature coefficient to become less negative.

These high ^{239}Pu fuel rod loadings may be useful depending on plutonium disposition goals. For example, heavily loaded fuel rods would reduce the total number of fuel rods/assemblies that would need to be fabricated and at the same time produce a faster drawdown on the 50 MT plutonium stockpile. In addition, longer fuel cycles (greater than 3 years) could also be supported as proposed in some plutonium burner concepts. If the goal were to induce fission product radioactivity in the plutonium stockpile for self-protection, relatively short burnups (approximately 1 year or less) using heavily loaded plutonium fuel rods could be an efficient method. It should be noted that heavily loaded plutonium fuel rods can also be achieved with the burnable poison fuel compositions that do not contain thorium.

3.1.3.6 Gadolinium Additive [$\text{PuO}_2(\text{ZrO}_2)(\text{Gd}_2\text{O}_3)$]. The burnable poison, gadolinia (Gd_2O_3), can be added to a $\text{PuO}_2(\text{ZrO}_2)$ fuel composition in very small mass quantities (<1.0 g/rod) to provide a significant amount of holddown reactivity and allow for greater plutonium mass loadings. Figure 9 shows the rod

Figure 8. Plutonium and gadolinia (Gd_2O_3) rod mass relationship for a $\text{PuO}_2(\text{ThO}_2)(\text{Gd}_2\text{O}_3)$ fuel composition.

Figure 9. Plutonium and gadolinia (Gd_2O_3) rod mass relationship for a $\text{PuO}_2(\text{ZrO}_2)(\text{Gd}_2\text{O}_3)$ fuel composition.

mass loading relationship between plutonium and gadolinia for a $\text{PuO}_2(\text{ZrO}_2)(\text{Gd}_2\text{O}_3)$ fuel composition and Table 3 provides the mass loadings, volume fractions, and corresponding burnup times.

The addition of relatively small rod masses of gadolinia to the $\text{PuO}_2(\text{ZrO}_2)$ fuel composition permits large increases in plutonium rod mass loading. For example, 0.34 and 1.23 g of gadolinia per fuel rod can balance the reactivity of 39.0 and 97.4 g of plutonium per rod, and consequently, the plutonium fuel rods/assemblies could burn for approximately 1.7 to 4.2 years, respectively, in a 3,000 MW(t) PWR with an average rod power of 58.88 kW (Table 3).

Natural gadolinia contains seven isotopes: ^{152}Gd (0.2%), ^{154}Gd (2.2%), ^{155}Gd (14.8%), ^{156}Gd (20.5%), ^{157}Gd (15.7%), ^{158}Gd (24.8%), ^{160}Gd (21.8%). The gadolinium isotope, ^{157}Gd , has the largest thermal neutron cross section at 254,000 barns and provides the bulk of the hold-down reactivity. Gadolinia could also be added in larger quantities than required at BOC conditions in order to maintain sufficient hold-down concentrations throughout the fuel cycle.

The prompt fuel temperature coefficient is negative for the case of 1.23 g/rod Gd_2O_3 and 97.4 g/rod plutonium. The prompt coefficient ranges from -0.390 to -0.259 pcm/K over the temperature range of 600–2400 K. Again, Gd_2O_3 could be added in greater quantities than required at BOC conditions, in order to further improve the prompt temperature coefficient.

The isothermal temperature coefficients at BOC for four different Gd_2O_3 and plutonium rod mass loadings are shown in Figure 10. The isothermal temperature coefficients are strongly positive, but become less positive with increasing Gd_2O_3 and plutonium loading. An increase in only the Gd_2O_3 rod mass loading (holding the plutonium rod mass constant) tends to make the isothermal temperature coefficients more positive, because the gadolinium is holding down considerable reactivity that is unleashed when the

spectral thermal peak is shifted upward in energy with increased moderator temperature. This effect is most pronounced for poisons like gadolinium and europium that possess, relative to ^{239}Pu , very large thermal absorption cross sections with steep $1/v$ tail gradients.

3.1.3.7 Erbium Additive [$\text{PuO}_2(\text{ZrO}_2)(\text{Er}_2\text{O}_3)$]. The primary reason for consideration of erbia as a burnable poison is that it should provide most of the same favorable neutronic characteristics of gadolinia and at the same time improve upon the isothermal temperature coefficient. The ^{167}Er isotope has two low energy thermal absorption resonances (0.460 and 0.584 eV) that overlap the ^{239}Pu thermal fission/capture resonance at 0.3 eV. The reactivity increase associated with a moderator temperature rise and the corresponding spectral shift of thermal neutrons into the 0.3 eV ^{239}Pu fission resonance should be mitigated to some extent by the ^{167}Er capture.

The addition of erbia to the $\text{PuO}_2(\text{ZrO}_2)$ fuel composition, rather than gadolinia, requires greater mass loadings to achieve comparable plutonium rod mass loadings. For example, in order to achieve a 39.0 or a 97.4 g/rod plutonium mass loading requires an erbia loading of 22.5 or 43.3 g/rod, respectively, relative to the 0.34 and 1.23 g/rod gadolinia (Table 3). Figure 11 shows the plutonium and Er_2O_3 mass loading relationship for a fuel rod. Plutonium rod mass loadings of 39.0 and 97.4 g/rod will allow the fuel rods/assemblies to burn for approximately 1.7 to 4.2 years, respectively, in a 3,000 MW(t) PWR with an average rod power of 58.88 kW (Table 3).

Erbium has six naturally occurring isotopes: ^{162}Er (0.14%), ^{164}Er (1.61%), ^{166}Er (33.6%), ^{167}Er (22.95%), ^{168}Er (26.8%), and ^{170}Er (14.9%). All six isotopes have good resonance absorption properties that should contribute significantly to the prompt fuel temperature coefficient. However, only two isotopes, ^{166}Er and ^{167}Er , are included in the prompt temperature coefficient calculation because of the lack of readily available cross-section libraries for the other four isotopes.

Figure 10. Isothermal temperature coefficient comparison for a $\text{PuO}_2(\text{ZrO}_2)(\text{Gd}_2\text{O}_3)$ fuel relative to the $\text{PuO}_2(\text{ZrO}_2)$ fuel composition.

Figure 11. Plutonium and erbia (Er_2O_3) rod mass loading relationship for a $\text{PuO}_2(\text{ZrO}_2)(\text{Er}_2\text{O}_3)$ fuel composition.

The prompt coefficient calculated for the fuel composition with 43.3 g/rod Er_2O_3 and 97.4 g/rod plutonium has a very favorable negative coefficient, -0.749 to -0.372 pcm/K, over the entire temperature range of 600–2400 K (Table 1 and Figure 2). The prompt coefficient would be even more negative if resonance absorption for all six erbium isotopes had been included in the calculation. These four erbium isotopes are also expected to provide additional holddown reactivity that would in turn allow for increased plutonium rod mass loadings.

The isothermal temperature coefficient curves for a $\text{PuO}_2(\text{ZrO}_2)(\text{Er}_2\text{O}_3)$ fuel composition at two different Er_2O_3 mass loadings are shown on Figure 12. The curves for both Er_2O_3 mass loadings are strongly negative over the PWR operational moderator temperature range (550–600 K).

Adding more Er_2O_3 (holding plutonium mass constant) could improve the prompt and possibly the isothermal temperature coefficients even further. Erbium has a relatively flat thermal absorption cross section in the thermal neutron energy range and any spectral shifting of neutrons upward in energy would have only a minimal reactivity increase due to the $1/v$ tail effect and a significant reactivity decrease due to the additional erbia absorption in the low-lying capture resonance. This is in contrast to gadolinia and europia.

The burnup rate of erbium over an LWR fuel cycle is expected to be somewhat less than that of europium, because the thermal neutron absorption cross sections for erbium are smaller than europium and the erbium mass loadings per rod are 10 times larger than europium at BOC. Depletion of ^{167}Er will also be partially offset by transmutation of ^{166}Er . It is expected that the prompt fuel and isothermal temperature coefficients will remain negative over a 3-year fuel cycle because of the expected relatively slow depletion rate of

^{167}Er , the buildup of ^{240}Pu and other fission products, and the depletion of ^{239}Pu .

3.1.3.8 Europium Additive [$\text{PuO}_2(\text{ZrO}_2)(\text{Eu}_2\text{O}_3)$]. The burnable poison europium has spectral neutronic characteristics similar to those of erbium. The isotope, ^{151}Eu , has two thermal absorption resonances at 0.321 and 0.461 eV that should mitigate ^{239}Pu reactivity increases due to moderator thermal spectral shifts.

The addition of europia to a $\text{PuO}_2(\text{ZrO}_2)$ fuel composition, rather than erbia, requires less europia (factor of 10 reduction) to achieve comparable plutonium rod mass loadings. For example, in order to achieve a 39.0 and a 97.4 g/rod plutonium mass loading, only 2.0 and 4.43 g/rod of europia are required relative to the 22.5 and 43.3 g/rod erbia (Table 3). Figure 13 shows the plutonium and Eu_2O_3 mass loading relationship for a fuel rod. Plutonium rod mass loadings of 39.0 and 97.4 g/rod will allow the plutonium fuel rods/assemblies to burn for approximately 1.7 to 4.2 years, respectively, in a 3,000 MW(t) PWR with an average rod power of 58.88 kW (Table 3).

Europium has two naturally occurring isotopes: ^{151}Eu (47.8%) and ^{153}Eu (52.2%). Both isotopes have good resonance absorption properties that contribute significantly to both the prompt fuel and isothermal temperature coefficients. However, resonance parameter data for ^{153}Eu are not readily available in the current neutron cross-section libraries and, therefore, could not be included in the calculation.

The prompt fuel temperature coefficient calculated for the fuel composition with 4.43 g/rod Eu_2O_3 and 97.4 g/rod plutonium has a favorable negative coefficient, -0.426 to -0.242 pcm/K, over the temperature range of 600–2400 K (Table 1 and Figure 2). The prompt coefficient is expected to be even more negative with the inclusion of ^{153}Eu resonance absorption.

Figure 12. Isothermal temperature coefficient comparison for a $\text{PuO}_2(\text{ZrO}_2)(\text{Er}_2\text{O}_3)$ fuel relative to the $\text{PuO}_2(\text{ZrO}_2)$ fuel composition.

Figure 13. Plutonium and europia (Eu_2O_3) rod mass loading relationship for a $\text{PuO}_2(\text{ZrO}_2)(\text{Eu}_2\text{O}_3)$ fuel composition.

The BOC isothermal temperature coefficient curves for a $\text{PuO}_2(\text{ZrO}_2)(\text{Eu}_2\text{O}_3)$ fuel composition at two different Eu_2O_3 mass loadings corresponding to 39.0 and 97.4 g/rod plutonium are shown on Figure 14. The temperature coefficients for both Eu_2O_3 mass loadings are strongly negative over the PWR operational temperature range (550–600 K). For the lower Eu_2O_3 mass loading case (39.0 g/rod plutonium), the coefficient is positive over part of the temperature range (300–450 K).

The positive isothermal temperature coefficient over the low part of the temperature range may not be a problem. Considerable isothermal heating of the core will result from the primary cooling pumps. The pumps would be capable of bringing the isothermal temperature up to hot standby at ~555 K and at these elevated temperatures the isothermal temperature coefficient would no longer be a concern. For cooldown

accident scenarios, the spectral shift has a mitigating effect on the reactivity transient.

The BOC isothermal temperature coefficients are also expected to be more negative than the calculated values, because thermal resonance data for ^{153}Eu were not readily available in the current cross section libraries and, therefore, could not be included in the calculation. ^{153}Eu also has an ideal low energy thermal resonance at 0.457 eV that would enhance the ^{151}Eu spectral shift reactivity holddown. In addition, an optimally moderated fuel assembly could probably be designed to further improve the isothermal temperature coefficient.

The addition of more europia (holding plutonium mass constant) will improve the prompt, but not the isothermal temperature coefficients. Europium has a relatively steep $1/v$ thermal absorption cross-section tail and a thermal neutron spectral shift will result in a reactivity increase.

Figure 14. Isothermal temperature coefficient comparison for a $\text{PuO}_2(\text{ZrO}_2)(\text{Eu}_2\text{O}_3)$ fuel relative to the $\text{PuO}_2(\text{ZrO}_2)$ fuel composition.

Of the three plutonium oxide fuel compositions with burnable poisons, only the $\text{PuO}_2(\text{ZrO}_2)(\text{Eu}_2\text{O}_3)$ fuel composition was depleted to estimate plutonium and europium isotopic composition and rod mass loadings during a 3-year fuel cycle. The chosen $\text{PuO}_2(\text{ZrO}_2)(\text{Eu}_2\text{O}_3)$ fuel composition had an initial BOC mass loading of 97.4 g/rod plutonium and 4.43 g/rod Eu_2O_3 . A single fuel rod was burned at an average power level of 58.88 kW/rod based on a 3,000 MW(t) reactor with 193 17×17 PWR fuel assemblies with 264 rods per assembly. The reactivity of the rod was reduced to zero at approximately 900 full power days corresponding to a burnup of 544 GWD/MT.

The plutonium and europium rod masses as a function of burnup time are shown on Figures 15 and 16, respectively. The total plutonium at the end of a 3-year burnup (75% CF) is approximately 47.0 g/rod (>50% FIMA). The amount of plutonium remaining per rod is more than that compared to the $\text{PuO}_2(\text{ThO}_2)$ fuel composition, but less than that compared to the $\text{PuO}_2(\text{UO}_2)$ fuel composition (Table 5). The ^{151}Eu isotope exhibits a high burnup rate [i.e., after a 1-year burnup (75% CF), the ^{151}Eu rod mass is reduced by approximately 92% (0.154 g/rod ^{151}Eu remaining)]. The ^{151}Eu transmutes via ^{152}Eu to ^{153}Eu . The ^{153}Eu concentration remains relatively constant over the first 2 years and then burns out slowly over the last year.

The high burnup of ^{151}Eu leads to concerns about the isothermal temperature coefficient over the fuel cycle. However, like gadolinium, europium has a large thermal cross section that would provide significant thermal self-shielding. The combined fuel rod self-shielding of both the europium and the ^{239}Pu will reduce the europium burnup rate and produce a radial spatial distribution in the rod during depletion. This spatial depletion is not accounted for in the ORIGEN2

depletion calculations and, therefore, leads to an overprediction of the europium burnup rate.

Despite the high ^{151}Eu burnup rate, the isothermal temperature coefficient will acquire negative feedback contributions from the buildup of ^{240}Pu , ^{153}Eu , and other fission product resonance absorbers over the depletion cycle.

The plutonium isotopic content by weight percent at four points in the burnup cycle is given in Table 6 for the $\text{PuO}_2(\text{ZrO}_2)(\text{Eu}_2\text{O}_3)$ fuel composition with the initial BOC mass loading of 97.4 g/rod plutonium and 4.43 g/rod Eu_2O_3 . The 1-, 2-, and 3-year time points correspond to full power days adjusted for a 75% CF.

Table 6. Approximate plutonium isotopics as a function of yearly burnup time for a $\text{PuO}_2(\text{ZrO}_2)(\text{Eu}_2\text{O}_3)$ fuel composition containing weapons-grade plutonium.

Isotope	Pu Isotopics			
	BOC	1 yr	2 yr	3 yr
Pu-239	0.955	0.850	0.728	0.596
Pu-240	0.040	0.104	0.144	0.157
Pu-241	0.005	0.044	0.116	0.210
Pu-242	0.000	0.002	0.012	0.037

The BOC plutonium isotopic weight percentages are those assumed in this study for weapons-grade plutonium. The BOC rod mass loadings are based on a PWR unit cell k-infinity of 1.40 at 300 K. The 3-year plutonium isotopic composition for the $\text{PuO}_2(\text{ZrO}_2)(\text{Eu}_2\text{O}_3)$ fuel composition is very similar to those of the $\text{PuO}_2(\text{ThO}_2)$ and $\text{PuO}_2(\text{UO}_2)$ fuel compositions (Table 4).

Further studies are required to calculate the temperature coefficients at EOC and other points in the fuel cycle for the $\text{PuO}_2(\text{ZrO}_2)(\text{Eu}_2\text{O}_3)$ fuel composition.

Figure 15. Plutonium isotopic rod mass content as a function of burnup time for a $\text{PuO}_2(\text{ZrO}_2)(\text{Eu}_2\text{O}_3)$ fuel composition.

Figure 16. Europium isotopic rod mass content as a function of burnup time for a $\text{PuO}_2(\text{ZrO}_2)(\text{Eu}_2\text{O}_3)$ fuel composition.

3.1.4 Conclusions. The following conclusions are based on the neutronic fuel performance analyses of the plutonium oxide fuel compositions:

- A weapons-grade $\text{PuO}_2(\text{ZrO}_2)$ fuel composition without a poison additive is not a viable composition for a conventional or advanced LWR because the plutonium mass loading per rod is too low (premature burnup even for a 1-year burnup at power); the prompt fuel Doppler temperature coefficient is small and positive over a portion of the operational temperature range; the isothermal temperature coefficients are strongly positive over the entire operational temperature range at BOC; and a fuel rod and assembly would be overmoderated and require fuel assembly redesign. The $\text{PuO}_2(\text{ZrO}_2)$ fuel composition requires a poison additive to improve its performance characteristics.
- Enrichment of weapons-grade plutonium with ^{240}Pu (blending reprocessed spent fuel) in a $\text{PuO}_2(\text{ZrO}_2)$ fuel results in only a slight improvement in performance characteristics for moderate enrichments up to 18% ^{240}Pu and, therefore, is not an attractive LWR fuel form. High ^{240}Pu enrichments will require reprocessing and tend to breed fissile ^{241}Pu , thereby, extending burnup times and reducing the rate of plutonium consumption.
- The addition of ThO_2 to a weapons-grade $\text{PuO}_2(\text{ZrO}_2)$ fuel composition has potential as a new and viable LWR fuel form. A pure $\text{PuO}_2(\text{ThO}_2)$ fuel has a strong negative prompt fuel Doppler temperature coefficient, a strong negative isothermal temperature coefficient, and allows a heavy plutonium mass loading per fuel rod resulting in long burnup times. However, ^{232}Th does breed ^{233}U , a potential nuclear weapon material.
- The addition of Gd_2O_3 to a pure $\text{PuO}_2(\text{ThO}_2)$ fuel composition allows for heavy plutonium mass loadings per rod. The advantages to fabricating such fuel rods would be a reduction in the total number of fuel rods or assemblies required to use 50 MT plutonium, faster drawdown of the 50 MT stockpile, and when burned in an LWR, the 50 MT plutonium could become "self-protecting" with fission product radioactivity more efficiently and perhaps quicker than other disposition options. High plutonium mass loadings can also be achieved with the burnable poison fuel compositions (gadolinium, erbium, and europium) that do not contain thorium.
- A $\text{PuO}_2(\text{ZrO}_2)(\text{Gd}_2\text{O}_3)$ fuel composition exhibits several attractive fuel performance characteristics, namely, large holddown reactivity for small gadolinia mass loadings, a negative prompt temperature coefficient, and sufficient plutonium mass loadings for long burnup times. This fuel composition does exhibit a positive isothermal temperature coefficient at BOC, but given an optimal gadolinia mass loading and with minor fuel assembly redesign (optimal moderation configuration), the positive isothermal temperature coefficient could be minimized.
- A $\text{PuO}_2(\text{ZrO}_2)(\text{Er}_2\text{O}_3)$ fuel composition has potential as a new and viable LWR fuel form. The addition of erbia can provide for sufficient holddown reactivity to achieve acceptable weapons-grade plutonium mass loadings and burnup times necessary for an LWR fuel cycle. In addition, this fuel composition exhibits a negative prompt fuel Doppler temperature coefficient and a strong negative isothermal temperature coefficient.
- A $\text{PuO}_2(\text{ZrO}_2)(\text{Eu}_2\text{O}_3)$ fuel composition has potential as a new and viable LWR fuel form with similar fuel performance characteristics to the $\text{PuO}_2(\text{ZrO}_2)(\text{Er}_2\text{O}_3)$ fuel composition. Europium isotopes may also have potential as a gamma-emitting seed material for self-protection enhancement of spent or irradiated fuel.
- Plutonium oxide, zirconium oxide, and burnable poison oxides are expected to be

fully compatible and relatively easy to fabricate with current LWR fuel fabrication technology.

- A plutonium oxide fuel composition with a significant volume fraction of zirconium oxide will require partial substitution of the zirconium oxide (approximately 5–10 wt%) with CaO in order to thermally stabilize the single-phase crystalline structure during fuel temperature transients, particularly at low temperatures. All oxide fuel compositions evaluated in this study composed of $\text{PuO}_2(\text{ZrO}_2)$ would have to be changed to $\text{PuO}_2(\text{ZrO}_2)(\text{CaO})$. Substitution of zirconium with calcium is expected to result in only minor neutronic differences.
- Optimal moderation of standard PWR fuel rods/assemblies with low plutonium mass loadings (short burnup cycles) would require complete redesign. Possible redesign options include:
 - Cladding thickness increase
 - Lattice pitch decrease
 - Fuel rod diameter increase
 - Parasitic cladding material.

Innovative options include spray coating the fuel pellets or the cladding with resonance absorption materials, or the possible use of a resonance absorption material such as tungsten-rhenium for the cladding. Temperature coefficient behavior could also be improved with these options.

3.1.5 Future Work

A considerable amount of neutronic analysis work is still required to fully explore the feasibility of using a weapons-grade plutonium oxide fuel form in a conventional or advanced LWR. This future work includes:

- Unit cell calculations
 - Neutronic performance of a $\text{PuO}_2(\text{ZrO}_2)(\text{CaO})$ fuel form with burnable poisons.
 - Neutronic performance of a $\text{PuO}_2(\text{ZrO}_2)(\text{CaO})$ fuel form with fission product additives.
 - Neutronic performance of a $\text{PuO}_2(\text{ZrO}_2)(\text{CaO})$ fuel form with weapon impurities.
 - Optimal moderation studies and reevaluation of the neutronic performance characteristics for selected fuel compositions and loadings with emphasis on minimization of fuel assembly redesign. Innovative options, such as spray coating and use of unique cladding resonance absorption materials, could also be included.
 - Performance of isotopic depletion calculations for select fuel compositions and fuel cycle lengths. Calculation of temperature coefficients at different points in the fuel cycle.
 - Development of unit cell models with appropriate transport and depletion neutronic computer codes to evaluate the spatial and time dependence of the plutonium and poison depletion in a fuel rod.
 - The effect of soluble ^{10}B poison in the coolant on the fuel composition performance characteristics (e.g., isothermal temperature coefficient).

- Fuel assembly calculations
 - Development of fuel assembly models to evaluate neutronic performance characteristics.
 - Evaluation of the potentially viable plutonium oxide fuel compositions with burnable poisons.
 - Evaluation of the use of both PuO_2 and UO_2 fuel rods in a fuel assembly.
 - Evaluation of the use of heterogeneous poison rods (e.g., Er_2O_3) dispersed in the lattice.
 - Evaluation of the assembly power distributions for the different options as a function of burnup.
 - Evaluation of assembly redesign for the inclusion of additional control rods.
- Core calculations
 - Development of two- and three-dimensional core sector models to evaluate neutronic performance characteristics, such as temperature coefficients, control rod worths, and power distributions at different points in the operating cycle.
 - Neutronic evaluation to determine number and position of PuO_2 and UO_2 fuel assemblies.
 - Establishment of thermal leakage effects on core performance characteristics.
 - Calculation of the effective delayed neutron fraction.
 - Performance of kinetic evaluations to determine reactor core dynamic response for different PuO_2 core loadings.
- Development of fuel management schemes to maximize burnup in PuO_2 assemblies.
- General tasks
 - Processing of ENDF-6 data to obtain necessary isotope neutron cross-section libraries.
 - Development of neutron cross-section data for isotopes not available in the ENDF-6 data.
 - Other potential plutonium fuel forms and cladding materials that could be considered for LWRs might include:

Fuel forms

PuC
 PuC_xO_y (TRISO)
 $\text{PuC}(\text{ZrC})$
 PuZr
 Pu-stainless steel
 Pu-nitrides

Cladding materials

Stainless steel
 Tungsten-rhenium.

3.2 Fabrication Technology

3.2.1 Introduction. Processes exist for fabricating UO_2 and MOX fuels (mixed oxides of uranium and plutonium), and extensive fabrication of these fuels has been performed. To fabricate the fuel compositions used in the neutronic analysis described in Section 3.1, these fabrication processes would have to be revised. The use of only ZrO_2 as a diluent for PuO_2 creates a potential homogeneity problem. ZrO_2 has a monoclinic crystal structure below approximately 1100°C and a tetragonal structure above 1100°C . The solid solubility of the face centered PuO_2 in ZrO_2 will be limited because of the difference in crystal structures. However, based on a pseudo-ternary fuel containing urania, the addition of about 15 mol% calcium oxide to zirconia stabilizes a single-phase, face-centered cubic

crystallographic structure that would permit greater solid solubility of the PuO_2 with the calcia stabilized zirconium dioxide. The ternary fuel was developed for the Power Burst Facility at the INEL. Variations of this fuel have been used for plate-type fuel elements and duplex fuel elements for the LWR breeder reactor. The application of UO_2 and MOX fuel fabrication techniques are evaluated in this section.

3.2.2 Fuel Fabrication Technology Overview. The major proportion of the world's operating power reactors are water cooled and use uranium dioxide (UO_2) fuel clad in zirconium alloy. Usually, the starting material is U_3O_8 for the natural uranium fuel types and UF_6 for the enriched uranium fuel types. For mixed oxide fuels, the starting material may be either UO_2 and PuO_2 , which is now the most common route, or coprecipitated mixed oxides currently being developed as an alternate.⁵

Fuel fabrication involves mechanical mixing of plutonium and uranium oxide powders, followed by milling, granulation, pelletizing, and sintering.⁶ When the average crystallite size is large,

wet-stirred ball milling can produce granular powder more suitable for dry pressing.

Figure 17 shows a typical fuel assembly manufacturing flow sheet for fabricating nuclear fuel for commercial use. In all plants, the flow sheet can be quite similar, although special requirements may exist for various fuel types.⁵

The significant steps in manufacturing involve powder preparation, pelletizing, and sintering processes. It must, however, be mentioned that in the Commonwealth of Independent States (CIS) an extrusion process has been applied for many years. The main manufacturing steps for producing the cladding tubing are quite similar for the zircaloy and Zr-Nb. The manufacturing of fuel rods, starting with pellets and ending with the welding of end caps, although quite similar in all plants, incorporates proprietary manufacturing techniques that vary from one plant to another.

The present design for fast breeder reactor fuel rods usually includes MOX fuel pellets clad into stainless steel tubes, together with UO_2 axial blanket and stainless steel hexagonal wrappers.⁷ For LWRs, zircaloy cladding replaces the stainless steel cladding.

Figure 17. Typical fuel assembly manufacturing flow sheet.

3.2.3 Powder Preparation Techniques.

This section provides discussion of the techniques for powder preparation, fuel pellet fabrication, and the parameters that can influence the associated physical properties. These processes are discussed with respect to their applicability to the fabrication of pseudo-ternary fuels of PuO_2 with CaO and ZrO_2 .

There are three techniques that can be used to prepare powders. The techniques are (1) the coconversion process, (2) the integrated dry route process (mechanical blending), and (3) the coprecipitation process. Process selection depends on the chemical form of the starting materials and the degree of homogeneity required. MOX fuel requires near homogenous blending for good neutronic characteristics and fuel performance.

Where fuel reprocessing is allowed, such as in the United Kingdom, Germany, France, and Belgium, the fuel solubility by nitric acid is required.

Storage of recycled plutonium as PuO_2 powder offers significant savings in active volume (and hence cost) when compared to storage and transport of MOX fuels. PuO_2 powder provides greater flexibility in choosing MOX fuel compositions. The integrated dry route process has been used in the United Kingdom since 1976.⁸

The coprecipitation process is favored on technical grounds if the starting material is a plutonium nitrate solution; however, economics would have to be considered in the process selection.

The integrated dry route and the coprecipitation processes are used at the Siemens Hanau fuel fabrication plant at Hanau, Germany.⁹ Until 1980, Siemens/Kraftwerk Union used the integrated dry route process and then switched to the coprecipitation process in 1981 to enhance the PuO_2 dissolution by nitric acid.¹⁰ Belgium fabricates MOX fuel by mechanical blending but uses a special process to obtain very fine UO_2 and PuO_2 powders, which when mixed and blended result in a dissolvable fuel form.

3.2.3.1 Coconversion Process (Thermal Microwave Denitration Process).

The process converts mixed-nitrate solutions of uranium, plutonium, or thorium into their oxides. The process uses microwaves as the source of heat for denitration and offers several advantages:

- Unlike other processes, no additional chemicals are used—only heat is used to convert the solution into an oxide powder
- No waste products are formed—water and nitrous oxide vapors generated during denitration can be converted back to nitric acid and recycled back to the reprocessing plant
- Microwave heating is remote, so there is no need to replace heating elements like in resistance heating
- It can be used to overcome problems encountered in powders with low thermal conductivities when a heat source, like a resistance heating element, becomes separated from a region where heat is required.

Figure 18 shows a typical process flow diagram of the process.¹¹ A constant volume of Pu-U nitrate-mixed solution is fed into the denitration vessel and denitrated by microwave heating into $\text{PuO}_2\text{-UO}_3$ powder, which is converted to $\text{PuO}_2\text{-UO}_2$ powder by a calcination-reduction process. The microwave heating converts the plutonium nitrate solutions into MOX powder ($\text{Pu:U} = 1:1$).¹¹

For the preparation of ZrO_2 and CaO powders, a process similar to that for the MOX powders can be used in which a solution of zirconium and calcium nitrates, along with plutonium nitrate solution, is fed into the denitration vessel and denitrated by microwave heating into $\text{ZrO}_2\text{-CaO-PuO}_2$ powder. If the solubility in the nitrate solutions is not exceeded, the resulting powder will be a solid solution.

3.2.3.2 Integrated Dry Route Process.

Figure 19 schematically shows a typical integrated dry route process for UF_6 to UO_2 conversion.¹²

In a similar fashion to the preparation of UO_2 powders, plutonium oxide is formed from plutonium nitrate by precipitation as the oxalate, which is a more crystalline precipitate than the hydroxide and offers easier handling under remote plant conditions.⁸ The crystalline structure is maintained during calcination to the oxide.

For the ZrO_2 - PuO_2 based fuels, the integrated dry route process would require the fabrication or procurement of the individual powders, PuO_2 , ZrO_2 , and CaO . These powders would have to be mechanically mixed and blended but would not necessarily be in a solid solution.

For mechanically blended powders, the degree of homogeneity achieved in the sintered pellet is dependent on the efficiency of the milling/blending stage. Interdiffusion rates of UO_2 and PuO_2 at normal sintering temperatures (1600 to 1650°C) are too slow to allow correction of inhomogeneity caused by inadequate mechanical blending. There is no reason to expect that adequate diffusion of the zirconium, plutonium, or

calcium ions would occur during sintering to form a solid solution of ZrO_2 , CaO , and PuO_2 .

3.2.3.3 Coprecipitation Process. This process employs plutonium hydroxide and ammonium diuranate. Figure 20 shows a flow diagram of the process. Powder produced by the technique is extremely active and pellets produced from it normally sinter to densities above 96% of theoretical.

For the ZrO_2 - PuO_2 based fuels, a similar approach for the MOX fuels may be tried. Ammonium hydroxide is added to the nitrate solution of plutonium, zirconium, and calcium to precipitate plutonium hydroxide, calcium hydroxide, and zirconium hydroxide, although the latter may show more characteristics of a hydrated oxide. The object of this precipitation is to form a solution of the hydroxides. If these hydroxides are not completely soluble in each other, there will be a homogeneity problem. The hydroxides also may be a gelatinous form, which creates handling problems. Other precipitates may be tried, for example, the oxalates. For

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Figure 20. Typical flow diagram for plutonium hydroxide ammonium diuranate coprecipitation process.

plutonium, the oxalate would be a better defined crystal structure than the plutonium hydroxide. This process would require substantial development.

3.2.4 Fuel Pellet Fabrication. This section briefly describes the factors that can influence the characteristics of pellets and that should be considered in meeting the specifications of the pellets. It also describes the characteristics of pellets that depend on the powder produced by typical powder-making processes described in the previous subsection.

In principle, there are four approaches that can be used to meet pellet specifications ⁷:

1. Control of specific area of the powder
2. Control of green (unsintered pellet) density by vibration or compacting pressure
3. Mixing of different amounts of U_3O_8 powder and, in some processes, pore former to the virgin UO_2 powder

4. Control of sintering temperature, time, and atmosphere.

Inherent properties of powders have the largest influence on density and porosity characteristics of the pellets. Variation of pellet prepressing conditions and sintering temperatures and times change pellet density. Use of binders and additives of various types influence pellet porosity.⁵

In practice, sintered density is modified by adjusting UO_2 , pore former, and U_3O_8 proportions whereas powder properties, pressing conditions, and sintering conditions are kept constant. Centerless grinding is used to achieve final outside dimensions of the fuel pellets.

Figure 21 shows a typical flow sheet for industrial manufacturing of pellets.⁵ The processes shown include two concepts based on how powders were prepared—wet conversion and dry conversion.

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Figure 21. Typical flow diagram for industrial manufacturing process for pellets.

A mechanical pulverizing method such as ball milling can be used to pulverize powders in mixed-oxide fuel fabrication. It is low cost, uses simple equipment, and creates less fluctuation in plutonium content.¹³ Figure 22 shows the effect of ball milling to the properties of blended powder and sintered pellet. Typically ball milling for 4-6 hours is sufficient to produce a powder that can be further processed into a homogeneous and high-density plutonium pellet.

3.2.5 Evaluation of Physical Characteristics. This section describes the general physical characteristics (density, microstructure) of powder/pellets and the factors that influence the characteristics.

Crystalline size can significantly influence the sintered pellet density. As the crystalline size increases, the relative softness of the granules produced by wet grinding increases and the rate of sintering on a microscopic scale decreases. Thus, larger crystalline powders can be used to produce green pellets. This powder sinters more slowly, which develops a high density microstructure with uniform porosity. On the other hand, if the crystallite size is too small, high-density regions can occur within the green pellet. These regions, in turn, can densify rapidly, pull away from surrounding matrix, and produce void.¹⁴

For thorium-uranium powders, bulk microwave denitration followed by heat treatment and stirred-ball milling is a viable method for fabrication of high density pellets. Pellets with geometric densities of over 96% of theoretical can be produced. In powders produced by this process, the specific surface area is related to crystalline size, not particle size, as it often is in other particulate systems.¹⁴

3.2.6 Discussion. The fuel combinations discussed in Section 3.1 were primarily based on plutonia diluted with zirconia. Different poisons such as gadolinia, erbia, or europia were added to limit the reactivity of plutonium. These fuel mixtures are substantially different than the fuel com-

positions used in the standard fabrication processes.

The use of only ZrO_2 as a diluent for PuO_2 creates a potential homogeneity problem. ZrO_2 has two crystal forms, a monoclinic crystal structure at low temperature and a tetragonal structure at high temperature. The solid solubility of the face-centered PuO_2 in ZrO_2 will be limited because of the difference in crystal structures. However, based on a pseudo-ternary fuel containing uranium, the addition of about 15 mol% calcium oxide to zirconium stabilizes a single-phase, face-centered cubic crystallographic structure that would permit greater solid solubility of the PuO_2 with the calcia-stabilized zirconium dioxide. A ternary fuel was developed for the Power Burst Facility at the INEL based on UO_2 . Variations of this fuel have been used for plate-type fuel elements and duplex fuel elements for the LWR breeder reactor.

The extrapolation of the $\text{UO}_2\text{-ZrO}_2\text{-CaO}$ phase diagram to the $\text{PuO}_2\text{-ZrO}_2\text{-CaO}$ phase diagram is not warranted because of the difference in plutonium and uranium chemistries. The Pu-O phase diagram does not exhibit any hyperstoichiometric phases (oxygen/plutonium ratios greater than 2). The uranium-oxygen system exhibits a number of compounds with oxygen/uranium ratios greater than 2.00. Phase equilibria with plutonium, zirconium, and calcium oxides would have to be established, as well as basic thermal and mechanical properties of these fuels.

The coconversion process appears to be the most direct process for converting nitrate solution of plutonium zirconium and calcium into a homogeneous mixture of the oxides. This process also appears to be energy intensive as compared with the integrated dry route process or the coprecipitation process. If fuel reprocessing is required and as a consequence a solid solution is required, the coprecipitation process is the best choice because the integrated dry route process may not result in a solid solution fuel. This process would have to be modified for the additions of zirconia and calcia to the fuel.

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Figure 22. Effect of ball milling for mixing of PuO_2 and UO_2 powders.

3.2.7 Conclusions. Fuel fabrication of MOX fuels are well established processes that are applicable to fabrication of a zirconium-plutonium oxide fuel. A crucial decision in the selection of an appropriate fabrication process is whether reprocessing plutonium fuels will be required to achieve the desired burnup because reprocessing requires a nitric acid dissolvable fuel, which in turn requires the fuel to be a solid solution of plutonium with the matrix.

The coconversion process for the powder fabrication appears appropriate, whether or not fuel reprocessing is required. This process is likely to yield a solid solution of the $\text{ZrO}_2\text{-PuO}_2$ fuels when CaO is added as a stabilizer. Development will be minimal in adapting this process to weapons-grade plutonium dispositioning. However, this process appears not to be currently used as much as the integrated dry route process (mechanical blending) and the coprecipitation process probably because of the intensive energy requirements. The disadvantages may be higher energy requirements than the other two powder

processes and the handling of the waste streams. For no further reprocessing, the integrated dry route process and the coprecipitation process are also applicable, but the coprecipitation process will require development for the ternary fuels. If reprocessing is required, the integrated dry route is not applicable because it is not likely to yield a solid solution.

3.2.8 Future Work. Further work that will be required includes:

- Development of phase equilibria for the ternary fuel plutonium oxide, zirconium oxide, and calcium oxide
- Development of a coprecipitation fuel fabrication process for the ternary fuel
- Examination of the feasibility of reprocessing the ternary fuel and if reprocessing is required, development of a fuel reprocessing methodology

- Economic study to select coprecipitation or coconversion process
- Evaluation of potential facilities for fabricating ternary fuels in the United States.

3.3 Performance and Compatibility

3.3.1 Introduction. The oxide fuels, consisting of mixtures of uranium and plutonium oxides, thorium and plutonium oxides, or other mixed oxides of plutonium with other metal oxides, offer generally high melting points for large safety margins and compatibility with most cladding materials such as stainless steel and zirconium alloys. However, despite these advantages, these fuels have relatively low thermal conductivity, which drives fuel temperatures higher and results in a large amount of stored energy in the fuels. The thermal conductivity, in a large part, determines the fuel performance of MOX fuel.

3.3.2 Fuel Thermal Conductivity and Temperatures. The thermal conductivity of $\text{UO}_2\text{-PuO}_2$ fuels, as an example, is shown in Figure 23 for 20% PuO_2 MOX fuel. Thermal conductivity decreases with increasing temperature as a result of the effect of temperature on lattice vibrations and reduction in the mean free path of the phonons. Near 1873 K, the thermal conductivity begins to increase as a result of the electronic contribution to the thermal conductivity. The addition of PuO_2 slightly decreases the thermal conductivity compared with that for UO_2 . The thermal conductivity of PuO_2 is much lower than that of UO_2 . For comparison, the thermal conductivity of monoclinic/tetragonal ZrO_2 is plotted in this figure. However, the addition of CaO to stabilize the face-centered cubic structure increases the thermal conductivity of this structure compared with that of ZrO_2 for temperatures greater than 1500 K. For normal operating temperatures of fuel of less than 1900 to 2100 K, the thermal conductivity of the CaO -stabilized ZrO_2 is not much higher than that of UO_2 . Therefore, addition of PuO_2 is expected to slightly lower the

thermal conductivity below that of UO_2 . A lower thermal conductivity would result in only marginally higher fuel temperatures relative to a UO_2 fuel.

The temperature distribution in a PWR pellet was estimated at 525 W/cm (16 kW/ft) and 394 W/cm (12 kW/ft). These temperature estimates are based on a PWR fuel rod with a 0.804 cm OD fuel pellet. Because of the low thermal conductivity, the fuel temperatures attained are high (Figure 24). These calculations indicate centerline temperatures near 2200°C at a lineal power level of 525 W/cm (16 kW/ft) and near 1680°C at a lineal power level of 394 W/cm (12 kW/ft). The fuel surface temperatures are 643°C at 525 W/cm and 560°C at 394 W/cm. The temperature gradient is very high near the surface of the pellet.

The fuel cycle economics of fast reactors requires the fuel to be capable of sustaining long residence times (up to 5 years) in the reactor.⁸ The objective can be achieved in two ways: first, by developing fuel that is able to operate to high values of burnup and neutron damage dose, and second, by designing a core of high fuel inventory and low mass rating (in watts per gram) so that burnup is accumulated relatively slowly. If the power rating is reduced, the fuel operates at a lower temperature. Low-temperature operation leads to high fission gas retention, which in turn may result in reduced fuel life because of swelling and mechanical interaction between fuel and clad. Swelling and mechanical interaction can be overcome by adopting a larger fuel rod diameter, which increases the linear power rating and hence the fuel temperature.

A limit on the linear power rating of fast reactor fuel rods arises from two important considerations. The fuel centerline temperature must not reach the melting point, which causes fuel slumping and redistribution to produce potential "hot spots" within the fuel column. In addition, the fuel surface temperature adjacent to the clad must not reach a level where clad mechanical properties are impaired and clad corrosion rates are enhanced.

Figure 23. Comparison of thermal conductivities for $\text{UO}_2(\text{PuO}_2)$, $\text{CaO}(\text{ZrO}_2)$, and ZrO_2 .

Figure 24. UO_2 fuel temperature distribution at different power levels.

While economics would dictate that fuel rods have the highest possible fissile density, voidage is necessary within the fuel column to accommodate swelling due to fission products so that the problem of fuel/clad mechanical interaction will be avoided. The optimum smeared fuel density is in the range of 80 to 85% of theoretical density (TD). An annular pellet of high matrix density (>95% TD) provides good fuel column stability under reactor transient conditions and reaches a lower fuel temperature for a given linear rating than a solid fuel pellet.

The temperature distribution in the fuel is an essential parameter in determining the fractional fission gas release because the temperature gradient determines the diffusion of the fission gases to the grain boundaries with subsequent formation of release channels.¹⁰ Fission gas release is plotted as a function of power in Figure 25. The fuel rods used for Figure 25 all had comparable irradiation conditions and a suitable power history neglecting burnup-dependent releases. Remarkably, UO₂ rods of comparable design (with respect to fuel cladding gap, rod free vol-

ume, prepressurization, etc.) fit well into this picture. MOX fuel shows increasing porosity above a local burnup of 70,000 MW/MTHM because of the agglomeration of fission gas.

The stoichiometry of the fuel has important implications for irradiation performance that affects fuel component transport mechanisms, the chemical state of fission products, clad corrosion rates, and thermal conductivity. For example, the thermal conductivity is lower for hypostoichiometric fuels (e.g., O/M ratio of 1.94) than for a stoichiometric fuel.

Based on all failure causes and all types of MOX fuels fabricated by Belgonucleaire, the overall failure rate is currently 8×10^{-5} (99.992% integrity).¹⁵ Discarding the failures unrelated to the fuel rod design or fabrication such as crud buildup from inadequate water chemistry and cladding fretting from debris carried by the coolant, the overall failure rate is 1.5×10^{-5} (99.9985% integrity). The other types of defects are welding defects in the end plugs and cladding hydriding.

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Figure 25. Fission gas release in MOX fuels as a function of average rod power.

3.3.3 Conclusion. The low thermal conductivity of oxide fuels leads to high fuel temperatures and large temperature gradients that cause fuel restructuring at high temperatures. The restructuring in the oxide pellet is the primary mechanism for gaseous fission product release in oxide fuels. This fission gas release drives the requirement for the initial porosity in the fuel, the size of the plenum at the top end of the fuel rods, and the amount of prepressurization to mitigate cladding collapse during irradiation. Lowering the temperature of the fuels will circumvent fission gas release, but with oxide fuels, it requires substantially lowering the power levels. However, lower fuel temperatures result in retained fission products, which leads to higher fuel swelling. Density and oxygen/metal ratios are part of the fuel rod design to control fuel performance.

3.3.4 Future Work. In order to develop an appropriate fuel design based on the ternary oxide fuels, the following recommendations are proposed:

- Determine the thermal conductivity and heat capacity of ternary fuels as a function of composition (plutonium composition and stoichiometry) and temperature
- Determine the fission product release and fuel swelling as a function of temperature and burnup
- Determine the mechanical properties such as creep as a function of temperature and burnup
- Develop a materials properties database for the ternary fuels.

4. ALUMINUM-PLUTONIUM METALLIC FUELS

4.1 Neutronic Analyses

4.1.1 Introduction. This section describes the neutronic performance characteristics of aluminum-plutonium fuel compositions containing weapons-grade plutonium for use in a low-pressure, low-temperature LWR. The aluminum-plutonium neutronic analyses are very similar to the plutonium oxide neutronic analyses in Section 3.1 (i.e., the methodology, assumptions, computer codes, and unit cell geometry are the same in both analyses).

Weapons-grade, aluminum-plutonium fuel compositions considered in the neutronic analyses include aluminum-plutonium with the burnable poison additives: gadolinium, erbium, and europium. Specific fuel compositions analyzed include the following:

- $\text{PuAl}_4(\text{Al})$
- $\text{PuAl}_4(\text{Al})(\text{Gd})$
- $\text{PuAl}_4(\text{Al})(\text{Er})$
- $\text{PuAl}_4(\text{Al})(\text{Eu})$.

In addition, a plutonium-zirconium with zirconium hydride fuel composition [$\text{PuZr}(\text{ZrH}_{1.6})$] was analyzed and the results are included in this section.

As directed by CISAC, aluminum-plutonium fuel compositions containing uranium are not considered. The primary intent and goal of this study is to investigate pure plutonium fuels that do not breed ^{239}Pu (via ^{238}U) and whose usage would expedite the consumption of the nuclear weapons plutonium stockpile.

The neutronic analyses are preliminary investigations and cursory in nature, but do provide general insights into important reactor physics parameters and trends that can be expected for the plutonium fuel compositions. Based on the neutronic analyses here, the aluminum-plutonium

fuel composition with the greatest potential for use in a low-pressure, low-temperature LWR is the aluminum-plutonium with an erbium or europium additive.

4.1.2 Unit Cell Model Description. Neutronic calculations are based on a two-dimensional infinite array of lattice cells or unit cells with dimensions based on a typical commercial PWR lattice. The unit cell geometry, dimensions, and materials are the same as depicted on Figure 1 with the following exceptions: (a) the fuel is aluminum-plutonium [$\text{PuAl}_4(\text{Al})$] and (b) the cladding is aluminum metal.

The PWR lattice was chosen as the reference lattice for the aluminum-plutonium neutronic calculations for ease of calculation and comparison with the plutonium oxide fuel composition results.

A plate type fuel assembly rather than a cylindrical fuel rod assembly is also an option for the aluminum-plutonium fueled lattice. The neutronic analysis of a plate-type fuel assembly is also performed.

4.1.3 Discussion. This section presents analytical neutronic fuel performance results for the aluminum-plutonium fuel compositions previously listed. In general, the aluminum-plutonium results and trends are similar to the plutonium oxide results in Section 3.1. This is expected because the only significant changes between the two cases are the replacement of zirconium and oxygen with aluminum in the fuel, zircaloy clad with aluminum clad, and lower reactor moderator and fuel temperatures.

The prompt coefficients calculated for the different fuel compositions are derived from k -infinity values calculated at discrete fuel temperatures over the temperature range of 300–500 K with a fixed moderator temperature of 300 K. This operational fuel temperature range is arbitrarily chosen with the following reactor design features in mind: (a) low pressure, (b) low temperature, and (c) high coolant flow rates.

Noncommercial reactors of this type typically operate with fuel temperatures over the temperature range of 300–500 K under normal conditions.

The isothermal temperature coefficient is a measure of the combined thermal reactivity feedback response to uniform heating of both the light water moderator and the fuel. The isothermal temperature coefficient results include reactivity feedback mechanisms from Doppler broadened resonances (prompt feedback) and moderator thermal neutron spectral shifts. The effects of fuel thermal expansion and moderator density changes on the isothermal temperature are not considered in the analysis, because these effects are expected to be relatively small for the operating temperatures of interest. The isothermal temperature coefficient is expected to become more negative with moderator temperature increase and density reduction.

For a low-pressure, low-temperature reactor, the moderator/coolant temperature could typically be between 300–400 K. For calculational purposes, the moderator temperature is arbitrarily chosen to be 300 K with a constant mass density of 1.0 g/cc. Isothermal temperature coefficients are then calculated over the temperature range of 300–500 K.

The three burnable poisons (gadolinium, erbium, and europium) considered were chosen for the same neutronic reasons as discussed in Section 3.1.2.

4.1.4 Neutronic Results. The neutronic performance results for the aluminum-plutonium fuel form with burnable poisons are presented in this section. Results include weapons-grade plutonium rod mass loadings, estimated burnup times, prompt fuel temperature coefficients, and isothermal temperature coefficients. Rod mass loadings are based on a standard PWR UO_2 lattice.

4.1.4.1 Uranium Oxide (UO_2) Reference Case. The PWR unit cell with a UO_2 fuel rod (3.2 wt% ^{235}U) at room temperature (300 K) was

chosen as the reference case. The unit cell k -infinity value is calculated to be approximately 1.40 at BOC conditions and 300 K and is used as a basis for the determination of fuel rod mass loadings of plutonium and burnable poisons.

4.1.4.2 Plutonium Mass Loading [$\text{PuAl}_4(\text{Al})$]. A $\text{PuAl}_4(\text{Al})$ fuel composition with no burnable poisons contains only a small amount of weapons-grade plutonium in each fuel rod (i.e., approximately 8.85 g/rod for a PWR unit cell corresponding to a k -infinity value of 1.40 at 300 K). This ^{239}Pu loading represents a 14% increase in loading over the 7.8 g/rod predicted for the plutonium oxide, $\text{PuO}_2(\text{ZrO}_2)$ fuel rod (Table 7). The slight increase in mass loading is attributed primarily to the higher thermal absorption cross section of aluminum relative to zirconium and oxygen.

Despite the relatively low 8.85 g/rod plutonium loading, an aluminum-plutonium fuel rod could burn for up to 1 year, assuming a 1,000 MW(t) reactor and an average rod power of 58.88 kW (Table 7).

As in the case of the plutonium oxide $\text{PuO}_2(\text{ZrO}_2)$ fuel composition with only 7.8 g/rod plutonium in a PWR lattice, this aluminum-plutonium fuel composition with a 8.85 g/rod plutonium loading in a PWR lattice is also overmoderated. The lattice design would have to be modified [i.e., decrease pitch, increase clad thickness, increase fuel rod thickness, or use of a parasitic clad or fuel matrix (e.g., stainless steel) and/or the plutonium rod mass loading increased to achieve an optimal moderation configuration].

The prompt temperature coefficients for a weapons-grade $\text{PuAl}_4(\text{Al})$ fuel are relatively small, but negative, -0.62 to -0.48 pcm/K over the fuel temperature range of 300–500 K. Table 8 gives the tabulated prompt fuel temperature coefficient values. The small negative coefficient for the $\text{PuAl}_4(\text{Al})$ fuel is an improvement over the corresponding oxide case, and it will become more negative with burnup (i.e., buildup of ^{240}Pu and other fission product resonance absorbers.)

The isothermal temperature coefficient for a $\text{PuAl}_4(\text{Al})$ fuel form is strongly positive, +3.8 to +7.0 pcm/K as shown in Figure 26. The positive coefficient is very similar to the oxide fuel behavior. As in the oxide case, the isothermal temperature coefficient can also be improved through redesign of the lattice geometry, increased plutonium mass loading, or use of a burnable poison or parasitic absorbing cladding or fuel matrix.

4.1.4.3 Pu-240 Enrichment [$\text{PuAl}_4(\text{Al})$].

An increase in the ^{240}Pu isotopic content (^{240}Pu enrichment via reprocessing) of an aluminum-plutonium fuel composition is expected to produce similar results to the oxide case (i.e., slight increase in plutonium rod mass loading, improved negative prompt temperature coefficient, and less positive isothermal temperature coefficient.) No specific calculations have been performed to date for an aluminum-plutonium fuel composition with increased ^{240}Pu enrichments.

4.1.4.4 Gadolinium Additive [$\text{PuAl}_4(\text{Al})(\text{Gd})$]. The burnable poison, gadolinium, can be added to a $\text{PuAl}_4(\text{Al})$ fuel composition in very

small mass quantities (≤ 1.0 g/rod) to provide a significant amount of holddown reactivity and allow for greater plutonium mass loadings. For example, a 0.51 and a 1.0 g/rod gadolinium mass loading can balance the reactivity of 58.0 and 92.5 g/rod plutonium, respectively (Table 7). Figure 27 shows the plutonium and gadolinium mass loading relationship for a fuel rod.

For plutonium rod loadings of 58.0 and 92.5 g/rod, an aluminum-plutonium fuel rod could burn for up to 7.5 and 12.0 years, respectively, assuming a 1,000 MW(t) reactor and an average rod power of 58.88 kW (Table 7).

The prompt and isothermal temperature coefficients have not yet been calculated for the $\text{PuAl}_4(\text{Al})(\text{Gd})$ fuel compositions. However, the prompt coefficients are expected to be slightly more negative than the corresponding oxide case, $\text{PuO}_2(\text{ZrO}_2)(\text{Gd}_2\text{O}_3)$. Similarly, the isothermal temperature coefficients are expected to be positive, with the same coefficient behavior at the low end of the temperature range (300–350 K), i.e., slightly more positive because of the more thermalized spectrum in the aluminum-plutonium case.

Table 7. Summary of rod mass loadings and estimated plutonium burnup times.

Fuel composition	PuAl_4 VF (x)	Al (matrix) VF (z)	Xx (metal) VF (w)	Pu (g/rod)	Al (total) (g/rod)	Xx (g/rod)	Burnup time (yr)
$\text{PuAl}_4(\text{Al})$	0.0110	0.9890	0.00000	8.85	519	0	1.2
$\text{PuAl}_4(\text{Al})(\text{Gd})$	0.0721	0.9276	0.00033	58.01	509	0.51	7.6
	0.1150	0.8844	0.00065	92.52	502	1.00	12.1
$\text{PuAl}_4(\text{Al})(\text{Er})$	0.1250	0.8518	0.02320	100.57	489	40.97	13.1
$\text{PuAl}_4(\text{Al})(\text{Eu})$	0.05906	0.9389	0.00200	47.52	510	2.021	6.2
	0.1268	0.8692	0.00400	102.01	498	4.042	13.3

K-infinity = 1.40

Reactor @ 1,000 MW(t)

Single rod volume = 192.69 cm³

Fuel rod length = 12.0 ft

Fuel rod radius = 0.4095 cm

Average fuel rod power = 19.62 kW/rod

VF = volume fraction of the fuel

x = volume fraction of PuAl_4 in the fuel

z = volume fraction of aluminum in the fuel

w = volume fraction of burnable poison in the fuel

Xx = burnable poison (Gd, Er, Eu)

Table 8. Prompt fuel Doppler temperature coefficient comparison for the different fuel compositions.

Fuel composition	Mod. temp. (K)	Fuel temp. (K)	K-infinity	Temp. (K)	Temp. coeff. (pcm/K)
PuAl₄(Al) (x = 0.011, z = 0.989)	300	300	1.4084620	325	-0.0620
	300	350	1.4084005	375	-0.0564
	300	400	1.4083445	425	-0.0523
	300	450	1.4082926	475	-0.0485
	300	500	1.4082445		
PuAl₄(Al)(Gd) (x = 0.115, z = 0.8844, w = 0.00065)	300	300	—	325	—
	300	350	—	375	—
	300	400	—	425	—
	300	450	—	475	—
	300	500	—		—
PuAl₄(Al)(Er) (x = 0.125, z = 0.8518, w = 0.0232)	300	300	1.4010352	325	-1.1900
	300	350	1.3998682	375	-0.9597
	300	400	1.3989285	425	-0.8930
	300	450	1.3980552	475	-0.8383
	300	500	1.3972364		
PuAl₄(Al)(Eu) (x = 0.1268, z = 0.8692, w = 0.004)	300	300	1.4556148	325	-0.5921
	300	350	1.4549878	375	-0.5462
	300	400	1.4544099	425	-0.5102
	300	450	1.4538705	475	-0.4798
	300	500	1.4533636		

x = fuel volume fraction of PuAl₄

z = fuel volume fraction of Al (matrix)

w = fuel volume fraction of burnable poison

Figure 26. Isothermal temperature coefficient for a PWR unit cell with a $\text{PuAl}_4(\text{Al})$ fuel composition.

Figure 27. Plutonium and natural gadolinium rod mass loading relationship for a $\text{PuAl}_4(\text{Al})(\text{Gd})$ fuel composition.

4.1.4.5 Erbium Additive [PuAl₄(Al)(Er)].

The addition of the burnable poison erbium (Er) to an aluminum-plutonium fuel composition improves all of the evaluated fuel neutronic characteristics. The PuAl₄(Al)(Er) fuel composition allows for a range of plutonium mass loadings to achieve a desired fuel cycle length and exhibits negative prompt fuel and isothermal temperature coefficients at BOC conditions. The PuAl₄(Al)(Er) fuel composition has very good potential for use in a low temperature reactor application.

A plutonium mass loading of 100.57 g/rod can be achieved with 40.97 g/rod erbium (Table 7). Figure 28 shows the mass loading relationship for weapons-grade plutonium and erbium in an aluminum matrix.

For a plutonium rod mass loading of 100.57 g/rod, an aluminum-plutonium fuel rod could burn for up to 13.1 years, assuming a 1,000 MW(t) reactor and an average rod power of 58.88 kW (Table 7). A more reasonable fuel cycle length, such as 3–5 years, would require less plutonium and erbium per fuel rod [i.e., between 23.0 and 38.4 g/rod plutonium and an erbium mass loading of only 6.3 and 13.2 g/rod (interpolated from Figure 28)].

The prompt fuel coefficients calculated for the PuAl₄(Al)(Er) fuel composition with 100.57 g/rod plutonium and 40.97 g/rod erbium are negative, -1.19 to -0.838 pcm/K, over the temperature range of 300–600 K (Table 8). The prompt temperature coefficient results are based only on the two erbium isotopes ¹⁶⁶Er and ¹⁶⁷Er. The prompt temperature coefficient would be even more negative if cross-section data were on hand for the other erbium isotopes (¹⁶²Er, ¹⁶⁴Er, ¹⁶⁸Er, ¹⁷⁰Er). Inclusion of these erbium isotope cross sections in the calculations would provide additional holddown reactivity for further increased plutonium mass loadings.

The isothermal temperature coefficients for a PuAl₄(Al)(Er) fuel composition are strongly negative for the 100.57 g/rod plutonium and

40.97 g/rod erbium mass loading. Figure 29 shows the negative isothermal temperature coefficient behavior over the temperature range of 300–500 K.

The addition of extra erbium (holding plutonium mass constant), should it be needed at some point in the burnup cycle due to depletion, could improve the prompt and possibly the isothermal temperature coefficients even further. Erbium has a relatively flat absorption cross section in the thermal neutron energy range and any spectral shift of thermal neutrons upward in energy would have only a minimal reactivity increase due to the 1/v tail effect and a significant reactivity decrease due to the additional erbium absorption in the two thermal capture resonances. This is in contrast to gadolinium and europium.

Fuel cycle dependent plutonium and burnable poison isotopics have not yet been calculated; however, the depletion of ¹⁶⁷Er will be partially offset by the transmutation of ¹⁶⁶Er into ¹⁶⁷Er.

4.1.4.6 Europium Additive [PuAl₄(Al)(Eu)]. The addition of europium (Eu) to an aluminum-plutonium fuel composition produces favorable neutronic properties similar to erbium, although the isothermal temperature coefficients are slightly positive for the PWR lattice geometry and specific compositions analyzed. The PuAl₄(Al)(Eu) fuel composition isothermal temperature coefficients are, however, considerably less positive than those of a PuAl₄(Al) fuel composition with no burnable poison.

The PuAl₄(Al)(Eu) fuel composition allows for a range of plutonium mass loadings to achieve a desired fuel cycle length and exhibits a negative prompt fuel temperature coefficient behavior at BOC conditions. In addition, the europium mass required to achieve comparable plutonium mass loadings is 10 times less than erbium. A plutonium mass loading of 47.5 and 102.0 g/rod plutonium can be achieved with 2.0 and 4.0 g/rod Eu (Table 7). Figure 30 shows the plutonium and europium mass loading relationship for a PuAl₄(Al)(Eu) fuel composition.

Figure 28. Plutonium and natural erbium rod mass loading relationship for a $\text{PuAl}_4(\text{Al})(\text{Er})$ fuel composition.

Figure 29. Isothermal temperature coefficient for a $\text{PuAl}_4(\text{Al})(\text{Er})$ fuel composition in a standard PWR fuel rod.

Figure 30. Plutonium and natural europium rod mass loading relationship for a $\text{PuAl}_4(\text{Al})(\text{Eu})$ fuel composition.

For a plutonium rod mass loading of 47.5 and 102.0 g/rod, an aluminum-plutonium fuel rod could burn for up to 6.2 and 13.3 years, respectively, assuming a 1,000 MW(t) reactor and an average rod power of 58.88 kW (Table 7). A more reasonable fuel rod loading for a 3-year fuel cycle would require 25.0 g/rod plutonium and 3.1 g/rod europium.

The prompt fuel temperature coefficient calculated for the fuel composition with a 102.0 g/rod plutonium and 4.0 g/rod europium loading is negative, but one-half the magnitude of a corresponding $\text{PuAl}_4(\text{Al})(\text{Er})$ fuel composition with comparable plutonium mass loading. The prompt temperature coefficient ranges between -0.592 and -0.480 pcm/K over the temperature range of 300–500 K (Table 8). The prompt coefficient is expected to be more negative when ^{153}Eu is included in the calculation. Due to the lack of processed resonance parameter data in the available neutron cross section sets, ^{153}Eu could not be included in the calculation.

The BOC isothermal temperature coefficient for a $\text{PuAl}_4(\text{Al})(\text{Eu})$ fuel composition is slightly positive, +1.5 to +0.25 pcm/K, over the temperature range of 300–500 K for the 102.0 g/rod plutonium and 4.0 g/rod europium mass loading case. The isothermal temperature coefficient behavior is shown on Figure 31.

Although the BOC isothermal temperature coefficient for a $\text{PuAl}_4(\text{Al})(\text{Eu})$ fuel composition is shown to be slightly positive in the PWR lattice, the lattice is almost certainly overmoderated. Redesign of the lattice to achieve an optimal moderation configuration will improve the isothermal temperature coefficient. In the companion plutonium disposition study, entitled *A New Reactor Concept Without Uranium or Thorium for Burning Weapons-Grade Plutonium* (Volume 3), the isothermal temperature coefficient is calculated to be negative for a slightly undermoderated lattice. Therefore, redesign of the PWR lattice will allow the $\text{PuAl}_4(\text{Al})(\text{Eu})$ fuel composition to exhibit a negative isothermal temperature coefficient behavior.

Figure 31. Isothermal temperature coefficient for a $\text{PuAl}_4(\text{Al})(\text{Eu})$ fuel composition in a standard PWR fuel rod.

The isothermal temperature coefficient is also expected to be more negative with the inclusion of ^{153}Eu in the calculation and thereby take advantage of its spectral absorption properties. ^{153}Eu also has an ideal low energy thermal resonance at 0.457 eV that would enhance the ^{151}Eu spectral shift reactivity holddown. In addition, the calculated isothermal temperature coefficients should be more negative with burnup and the buildup of ^{240}Pu and other fission products.

Doubling the europium concentration in the fuel and keeping the plutonium mass loading constant does not result in a negative isothermal temperature coefficient, but instead has just the opposite effect (i.e., a factor of four increase in the positive direction.) The reason for this is the increased europium loading is now holding down more reactivity. As the thermal peak shifts upward in energy, fewer thermal neutrons are absorbed in the relatively steep ^{151}Eu $1/v$ absorption tail at low energy resulting in increased reactivity. The same would be true of gadolinium in a $\text{PuAl}_4(\text{Al})(\text{Gd})$ fuel composition.

4.1.5 Aluminum-Plutonium Plate Fuel. As an option for a plutonium fuel assembly redesign, to obtain an optimally moderated fuel assembly and improve the isothermal temperature coefficient, the cylindrical fuel rod could be replaced with a plate type fuel assembly. The plate type fuel assembly option could also provide additional structural strength, heat transfer area, and utilize an established fabrication technology. A preliminary evaluation for this type option was performed for a Materials Test Reactor (MTR) assembly design at the INEL.

A fully explicit, heterogeneous MCNP model of MTR fuel plate assembly was constructed for the preliminary neutronic mass loading and moderation determination. The MTR fuel plate assembly is shown on Figure 32. For this study, the fuel plate meat was represented with weapons-grade plutonium. The MCNP calculated k -infinity value for a fuel plate loading of 5.9 g plutonium was 1.34. Reactor-grade plutonium was used in the Phoenix fuel test experiments.

Figure 32. Cross-sectional view of a typical MTR fuel assembly with dimensions.

Calculations also showed that the MTR fuel assembly with 5.9 g/plate weapons-grade plutonium is overmoderated. Decreasing the already narrow water gap between plates (0.119 in.) could be prohibitive from a fabrication and thermal-hydraulic safety standpoint. Therefore, the solution in this case is to increase the parasitic absorption of the fuel assembly in order to increase the plutonium mass loading and, thereby, improve the moderation condition. Parasitic absorption can be increased by adding a burnable poison to the aluminum-plutonium fuel meat or by substituting aluminum for a material with a larger neutron absorption cross section, such as stainless steel. For the latter case, the side plates and cladding could be stainless steel and the fuel meat a stainless steel cermet. The stainless steel cermet fabrication technology using uranium is developed.

4.1.6 Plutonium-Zirconium (Zirconium Hydride) Fuel Compositlons. A plutonium-zirconium fuel form containing weapons-grade

plutonium is also considered. The PWR unit cell geometry as shown in Figure 1 is used in the analysis with the substitution of plutonium-zirconium hydride fuel composition for the oxide fuel form and a zirconium cladding instead of a zircaloy cladding.

The $\text{PuZr}(\text{ZrH}_{1.6})$ fuel composition was selected as a potential fuel form because of the unique thermal neutron scattering properties of the bound hydrogen atoms in the ZrH matrix. The bound hydrogen atoms exhibit thermal neutron upscattering phenomena with increasing fuel temperature, resulting in a prompt spectral hardening response. However, as the calculational results will show, prompt thermal upscatter is not necessarily a desirable feature for a weapons-grade plutonium fuel form. Thermal neutron upscattering into the ^{239}Pu 0.3 eV fission resonance will produce a prompt reactivity increase and lead to a very undesirable positive prompt fuel (Doppler) temperature coefficient.

Figure 33 shows the increase in k-infinity with increasing fuel temperature for the plutonium-zirconium fuel composition with two different volume fractions (VF) of zirconium hydride, namely,

- PuZr(ZrH_{1.6}) (10% VF ZrH_{1.6})
- PuZr(ZrH_{1.6}) (>99.99% VF ZrH_{1.6}).

The fuel composition with >99.99% volume fraction of ZrH_{1.6} has, as expected, a more pronounced increase in k-infinity with increased temperature relative to the fuel composition with a 10% volume fraction of ZrH_{1.6} (Figure 33). The prompt temperature coefficient ranges between approximately +5.0 and +7.0 pcm/K over the fuel temperature range of 500–900 K with a constant light water moderator temperature of 400 K.

Although the PuZr(ZrH_{1.6}) fuel form containing weapons-grade plutonium exhibits the unde-

sirable positive prompt fuel temperature coefficient, the addition of erbium or europium with their unique thermal spectral absorption properties may provide a solution. However, without further study, it is not clear whether the ZrH thermal upscattering will enhance the fuel composition absorption properties and produce a negative reactivity feedback or whether the poison additive is needed simply to cancel the upscattering reactivity increase. In the latter case, it may be appropriate to simply remove the hydride from the fuel form and resort to a plutonium-zirconium (PuZr) fuel form containing weapons-grade plutonium with a burnable poison, erbium or europium. The PuZr and PuAl fuel forms are expected to have similar neutronic characteristics.

If reprocessing were required, both the PuZr(ZrH_{1.6}) and PuZr fuel forms could be reprocessed and recycled in the Integral Fast Reactor system.

Figure 33. K-infinity as a function of fuel temperature for a PuZr(ZrH_{1.6}) fuel composition in a standard PWR fuel rod.

4.1.7 Conclusions. The following conclusions are based on the neutronic fuel performance analyses of the aluminum-plutonium metallic fuel compositions:

- A $\text{PuAl}_4(\text{Al})$ fuel composition containing weapons-grade plutonium in a PWR unit cell geometry is very reactive and will allow a plutonium loading of only 8.85 g/rod. The $\text{PuAl}_4(\text{Al})$ fuel composition has a relatively small negative prompt fuel temperature coefficient, a strongly positive isothermal temperature coefficient, and, relative to the oxide fuel forms, a good thermal conductivity. To be a viable fuel form in most practical reactor concepts, the $\text{PuAl}_4(\text{Al})$ fuel composition would require a burnable poison additive to improve its fuel performance characteristics (e.g., erbium or europium).
- The $\text{PuAl}_4(\text{Al})(\text{Er})$ and $\text{PuAl}_4(\text{Al})(\text{Eu})$ fuel compositions containing weapons-grade plutonium both have potential as a new and viable fuel form for use in a low-temperature reactor application. The addition of erbium or europium burnable poisons to the $\text{PuAl}_4(\text{Al})$ fuel composition allows for increased plutonium mass loadings (i.e., longer burnup or cycle times) and exhibits negative prompt fuel temperature coefficients and negative isothermal temperature coefficients. In the case of the $\text{PuAl}_4(\text{Al})(\text{Eu})$ fuel composition, the isothermal temperature coefficient can be made more negative with an optimally moderated lattice.
- The plutonium mass loading in an aluminum-plutonium fuel composition will determine the fabrication method for manufacturing the fuel rods or plates. The plutonium mass loading, in turn, will be based on the reactor fuel cycle length.
- The $\text{PuZr}(\text{ZrH}_{1.6})$ fuel form exhibits an undesirable positive prompt fuel Doppler temperature coefficient and at present does not appear to be a front-runner, fuel-form candidate for weapons-grade plutonium

fuels. A PuZr fuel form would have similar neutronic characteristics to the aluminum-plutonium fuels analyzed in this study and could be reprocessed and recycled in the Integral Fast Reactor system.

4.1.8 Future Work. Future neutronic work for the aluminum-plutonium fuel forms would involve very similar tasks to those outlined in the future work section for the plutonium oxide fuels in Section 3.1.5.

4.2. Fuel Element Fabrication

4.2.1 Introduction. The fabrication of aluminum-plutonium fuels for a plutonium recycling program was developed approximately 30 years ago. These fuels were manufactured into both plate-type and metal-clad fuel rods for application in a low-temperature reactor. The fabrication of the aluminum-plutonium alloys is discussed first, followed by a discussion of the fuel forms. The latter is divided into low-enriched plutonium fuels and high-enriched plutonium fuels.

4.2.2 Aluminum-Plutonium Metal Alloy Fabrication. Al-Pu fuels have been irradiated in the Plutonium Recycle Test Reactor (PRTR) as part of a Plutonium Utilization Program, which was to provide base technology for the use of plutonium fuel in commercial power reactors.¹⁶ Approximately 360 experimental fuel elements were irradiated in the PRTR using a basic 19-rod cluster fuel element design incorporating UO_2 , Al-Pu, and $\text{UO}_2\text{-PuO}_2$ fuels. The PRTR was originally loaded with 75 Al-Pu elements in 1962. The spike enrichment elements used during initial operation of the PRTR contained nonsegmented, hot extruded Al-2.0 wt% Ni-1.8 wt% 1.8 to 3.35 wt% plutonium alloy cores inserted into zircaloy tubes. These Al-Pu elements were irradiated at maximum rod powers of 15 kW/ft to burnups of 83% FIMA (0.74×10^{20} fissions/cm³).

Similar fuel was fabricated for the Experimental Boiling Water Reactor (EBWR) at Argonne National Laboratory.¹⁷ The objective of the EBWR demonstration was to show that plutonium fuels could perform satisfactorily in power

reactors (boiling water reactors) and to provide useful engineering and physics data. Ten special rods were fabricated from Al-Pu alloy with 3.35 wt% plutonium and 2 wt% nickel in an aluminum matrix. Five rods contained 8 wt% Pu-240 and the other five contained 26 wt% Pu-240.

A fabrication process was developed, and 144 coextruded fuel elements were prepared for the Trans Plutonium Program¹⁸ at the Savannah River Laboratory. The rods were 0.94 in. in diameter and 60 in. in length. The cladding was aluminum (X-800 alloy) and was 0.04–0.120 in. thick. The fuel cores were aluminum with 7.35 wt% plutonium. The fuel elements were coextruded in an extrusion press, which was mounted in a plutonium-contaminated glove box.

The manufacture of 2S aluminum clad, aluminum-10 wt% plutonium alloy and aluminum-5 wt% plutonium alloy cored plates was developed for Argonne National Laboratory–University of California irradiation tests in the MTR.¹⁹ These elements were fabricated into napkin “rings.” Forty-four of these contained 5 wt% plutonium alloy cores and 47 contained 10 wt% plutonium alloy cores.

Using Al-Pu fuel,^{20–23} the Phoenix Fuel Program at Pacific Northwest Laboratories had as its primary objective the exploration and evaluation of the longer lifetime inherent in the use of the isotope ²⁴⁰Pu as a burnable poison in nuclear reactor cores. The unusual property of ²⁴⁰Pu as a burnable poison is that it converts to the fissile isotope ²⁴¹Pu upon absorbing a neutron; this is known as the Phoenix effect. The Phoenix fuel element was similar in design to the standard MTR fuel element in that all external dimensions were the same for both. The basic element of the Phoenix fuel subassembly was a flat plate with nominal dimensions of 0.080 in. thick by 2.648 in. wide by 25.125 in. long. The plate consisted of three layers: an aluminum layer 0.020 in. thick, a fuel sheet composed of a aluminum-21 wt%-plutonium alloy 0.040 in. thick, and another 0.020 in. thick aluminum layer. The fuel was placed between the two flat sheets of aluminum, heated, and rolled into one sheet with positive bonding between the layers. Because the fuel section was

not as long or wide as the two aluminum sheets, the fuel was encased entirely by the aluminum in the rolling process.

Aluminum-clad Al-20 wt% ²³³U and Al-23 wt% plutonium plate fuel subassemblies have been fabricated for the Purnima III critical facility and the Kamini research reactor.²⁴ This fabrication is similar to the fuel fabrication for the Phoenix fuel and ANL plate fuel tested in the MTR. The fabrication flow sheet consists of preparing the master alloy using aluminum and uranium or plutonium metals as feed materials, remelting and casting the fuel alloy ingots, rolling, picture framing and sandwiching the fuel alloy between aluminum sheets, roll bonding, locating the fuel alloy core outline by x-ray radiography, and trimming and machining to final dimensions.

In discussing the fabrication of the Al-Pu alloys, examination of the Al-Pu phase diagram is useful in understanding the fabrication issues (Figure 34).²⁵ For the alloys previously used, the plutonium concentration varied from 1.8 to 3.35 wt% (0.21 to 0.39 at%) plutonium or about 21 wt% (2.9 at%) plutonium. These alloys bracket the eutectic composition, taken to be 2.0 at% (15.64 wt%). However, there is some disagreement as to the exact composition and temperature of this invariant point. Values of 1.66 at% at 642°C and 640°C, and 2.00 at% at 635°C have been reported. The value of 2.0 at% at 640°C is assumed for this discussion.

The alloys containing 1.8 to 3.35 wt% plutonium are hypoeutectic alloys that would consist of face-centered cubic aluminum with 0.27 wt% (0.03 at%) plutonium dissolved in the aluminum and PuAl₄, which is an orthorhombic structure of a brittle intermetallic phase of plutonium and aluminum. Assuming a 3.35 wt% alloy at room temperature, this alloy would consist of two phases, 95.1 vol% aluminum and 4.9 vol% AlPu₄. All of the AlPu₄ and 18 vol% of the aluminum is contained in the 21.8 vol% eutectic structure. The remaining matrix is 78.2 vol% aluminum (proeutectic aluminum). Some ductility of these alloys is expected because of the large amount of aluminum in the matrix, which should allow rolling or extrusion of these alloys.

Figure 34. Aluminum-plutonium phase diagram.

The other alloy (21 wt% plutonium) is a hyper-eutectic alloy. This alloy contains 30.5 vol% PuAl₄ and 69.5 vol% aluminum at room temperature. All of the aluminum and 65 vol% of the PuAl₄ is in the eutectic structure. The remaining 35 vol% PuAl₄ will be deposited in the grain boundaries (proeutectic PuAl₄). Because most intermetallic compounds are brittle and because of the large amount of PuAl₄ in the grain boundaries, deformation of this alloy by rolling or extrusion will be difficult.

Small amounts of nickel have been added to the Pu-Al alloys to improve their corrosion resistance in water. Zirconium or titanium also has been added to improve the ductility of these alloys. Additions of these elements are expected to affect the microstructure, but ternary phase diagrams are not available.

4.2.3 Preparation of Aluminum-Plutonium Alloys. The preparation of plutonium/aluminum alloys by the direct reduction of PuF₄ and PuO₂ with liquid aluminum has been used in addition to the direct addition of plutonium or plutonium-

aluminum master alloys to liquid aluminum. However, the addition of plutonium or a plutonium compound suffers from the disadvantage that when plutonium is added to a light metal such as aluminum, the plutonium may separate before alloying due to the low melting point (660°C), low density (2.7 g/cc) of aluminum, and the high density of plutonium (15.9 g/cc).

In the final stages of development of the plutonium/aluminum alloys, the plutonium yield for the conversion of oxide to the metal ranged between 95% and 99%. Therefore, a small amount of oxide will have to be recycled into the production process.

The processes for the preparation of aluminum-plutonium alloys described above meet the permissible releases and personnel exposure allowed approximately 30 years ago. Current safety and environmental regulations, which are much more restrictive than those of the 1960s, will require substantial changes to minimize personnel exposure and minimize the waste

streams. A detailed discussion of this process is included in Section A-1 of Appendix A.

4.2.4 Fabrication of Aluminum-Plutonium Fuel Forms. Different Al-Pu fuel forms have been developed for plate and cylindrical fuel elements. These vary from extruded rods in zircaloy tubes to aluminum clad extruded fuel rods for low-mass loaded plutonium fuels (plutonium contents less than the eutectic composition) to various forms of plate fuel for high-mass loaded plutonium fuels (plutonium contents greater than the eutectic composition). The fabrication of these various fuel forms is outlined in Section A-2 of Appendix A.

The low-mass loaded, cylindrical fuel elements were fabricated about 40 years ago, essentially on a laboratory scale. Plutonium handling and fabricating was done under hoods or in unconfined areas with limited use of glove boxes. Although the practices were acceptable and complied with the existing safety and environmental regulations, those practices would not meet current safety and environmental regulations. The fabrication processes would have to be upgraded or developed to conform with existing regulations and scaled up to full-production levels.

The fabrication of plate fuel by the picture-frame process is a well established process. It is used in the United States to fabricate plate fuel loaded with uranium for experimental reactors such as the Advanced Test Reactor (ATR) at the INEL and the TRIGA reactors at various universities. Plate fuel loaded with plutonium has been fabricated in India with less restrictive regulations than in the United States. The fabrication of plate fuel loaded with plutonium would have to be upgraded to conform with current regulations and minimize the waste streams.

4.2.5 Conclusions. Al-Pu alloys can be prepared by either melting metallic plutonium in molten aluminum or by the reduction of plutonium fluorides and plutonium oxides by molten aluminum in a cryolyte flux. Reductions between 95–99% have been reported. Segregation was a major problem for the 1960's technology in the

casting of aluminum-plutonium alloys. Although the ductility of low-concentration plutonium alloys may not be a problem, zirconium and titanium additions have enhanced the ductility of the high-mass loaded plutonium in aluminum-plutonium alloys. Small additions of zirconium do not appreciably effect the eutectic temperature with aluminum. Melting facilities would have to be improved over what was used 30 years ago to comply with current safety and environmental regulations. Vacuum arc melting using current technology should overcome any segregation problem and allows larger quantities of fuel to be melted.

Several forms of the metallic aluminum-plutonium alloys have been fabricated over the years that include zircaloy-encapsulated aluminum-plutonium rods, aluminum-clad wires, cylindrical-shaped aluminum-clad plate fuels, and aluminum-clad plate fuels fabricated by the frame technique. The trend is aluminum-clad plate fuel fabricated by the picture-frame technique. This process is currently being used for uranium-based fuels in the United States and plutonium fuels in India. The fabrication process will need to be more automated than previously used because of ALARA requirements and the minimization of mixed wastes (mixture of hazardous chemicals and radioactive materials).

4.2.6 Future Work. The following tasks are recommended:

- Develop a fabrication process for zircaloy-clad metallic aluminum-plutonium rods using current technology
- Examine the feasibility for reprocessing the aluminum-plutonium fuels, and if reprocessing is required, develop the reprocessing methodology
- Evaluate potential facilities for fabricating both zircaloy-clad rod fuels and aluminum-clad plate-type fuels
- Determine the fission product release and swelling of the metallic fuels

- Develop a materials properties database for the aluminum-plutonium fuels to identify the deficiencies in the material properties and propose a plan to resolve the deficiencies
- Evaluate the solubility of the poison additives (e.g., erbium) to the aluminum-plutonium fuel.

4.3 Performance and Compatibility

4.3.1 Introduction. This section discusses the corrosion behavior of the aluminum-plutonium alloys. Another important aspect of the performance issues is fission product release and fuel swelling. Because of limited time and scarce data, these issues were not addressed.

Aluminum-plutonium alloys with high corrosion resistance at high temperature, 350°C (660°F), were required for the enrichment of the PRTR fuel. The reactor was designed to operate with cooling water outlet temperature at 277°C (530°F). The alloys when used as core materials can withstand PRTR operating conditions in the event of a major cladding failure. Corrosion studies on aluminum-uranium alloys²⁶ and aluminum-plutonium alloys²⁷ had revealed rapid corrosion rates. Corrosion studies on eutectic aluminum-silicon-uranium alloys and eutectic aluminum-silicon-plutonium alloys revealed that these alloys have higher corrosion resistance. However, the use of the eutectic alloys can produce a considerable amount of foaming during chemical separation because of the high silicon content (13 wt%) in the solution. Alloys (with less than 13 wt% of silicon) were required, which could have minimum processing difficulties and at the same time possess high corrosion resistance. Corrosion studies on aluminum-nickel and aluminum-nickel-uranium alloys have revealed that the addition of nickel in the alloys can improve their corrosion resistance. These studies led to an investigation of corrosion resistance for

two types of aluminum base alloys: aluminum-silicon-plutonium and aluminum-nickel-plutonium. The aluminum-silicon-plutonium alloys used silicon less than 13 wt% (an Al-Si eutectic composition is 13 wt% silicon). The nickel-aluminum-plutonium alloys selected for study used varying amounts of nickel.

The corrosion behavior of aluminum-based aluminum-plutonium alloys having silicon, nickel, and titanium as additional alloying elements is reviewed. The effects of cooling rates of alloy casting on their corrosion behavior is presented.

4.3.2 Chemistry of Alloys and Their Corrosion Behavior. Tables 9, 10, and 11 show the nominal composition of four kinds of alloy systems.²⁸ Table 9 shows the composition of Al-Si-Pu alloys, Table 10 that of Al-Ni-Pu alloys, and Table 11 that of Al-Ni-Ti-Pu and Al-Si-Ti-Pu alloys. Each of the alloys contained 2 wt% plutonium. These alloys used commercial grade aluminum, 99.45% aluminum minimum.

Cast eutectic Al-Si alloys (silicon 13 wt%) with plutonium content up to 15 wt% have exhibited good corrosion resistance with a cast structure. Because of difficulties with chemical processing of Al-Si alloy with eutectic composition, it was desired to develop corrosion resistance of Al-Si-Pu alloys with less than 13 wt% silicon. Table 9 shows the typical compositions of Al-Pu alloys, which have less than 13 wt% silicon. Addition of 12 wt% silicon to Al-Pu alloys with plutonium up to 15 wt% resulted in good corrosion resistance and made them less sensitive to working.

Table 9. Compositions (wt%) of Al-Si-Pu alloys.

Alloy	Si	Pu	Al
1	11.0	2.0	Balance
2	5.0	2.0	Balance
3	1.0	2.0	Balance

Table 10. Compositions (wt%) of Al-Ni-Pu alloys.

Alloy	Ni	Pu	Al
4	1.0	2.0	Balance
5	3.0	2.0	Balance

Table 11. Compositions (wt%) of Al-Ni-Pu-Ti and Al-Ni-Si-Pu alloys.

Alloy	Ni	Si	Ti	Pu	Al
6	1.0	1.0	—	2.0	Balance
7	2.0	—	0.1	1.8	Balance
8	3.5	—	0.1	2.0	Balance

Table 10 shows compositions of typical Al-Ni-Pu alloys. Nickel used as an alloying element is beneficial for corrosion resistance. Although an increase in nickel content can increase the corrosion resistance of the alloy, limited amounts are used because of the high absorption cross section of nickel. These alloys also exhibited good corrosion resistance.

Table 11 shows the compositions of typical quaternary alloys. In a study of Al-Si-Pu alloys, it was observed that this alloy became corrosion resistant as a result of formation of Pu-Si intermetallic compound. Based on the observation of corrosion resistance behavior of the alloys in the presence of an intermetallic compound, silicon was used in a quaternary Al-Ni-Si-Pu alloy (Alloy No. 6 in Table 11). Plutonium in Alloy No. 6 is believed to be a Pu-Si intermetallic compound. Nickel and the Pu-Si intermetallic compound contributed to higher corrosion resistance of the quaternary alloy (Alloy No. 6). The Al-Ni-Si-Pu quaternary alloy, which has both nickel and silicon as alloying elements, exhibited higher corrosion resistance than Al-Si-Pu (Table 9).

4.3.3 Discussion. Figure 35 shows corrosion rates of typical Al-Pu alloys tested at 350°C (660°F) in deionized water.²⁸ It also shows the effect of pH on corrosion rates. An increase in pH of the solution increased the corrosion rate. A decrease in the formation of a corrosion resistance film at higher pH as compared with that at lower pH is believed to be the cause for the difference in corrosion rates. This figure shows

that alloy No. 8 (Table 11) has minimum corrosion rates compared to other alloys under identical test conditions. This alloy and other alloys (No. 5 in Table 10 and No. 6 in Table 11) that exhibited good corrosion resistance had fine grain size and fine and uniform distribution of second-phase particles.

Figure 36 shows a typical microstructure of an alloy that exhibited good corrosion resistance with a cast structure.²⁸ The alloys with small grain size (Figure 36a) and with fine and uniformly distributed second-phase particles and intermetallic compounds (Figure 36b) passed the corrosion tests. The alloys that remained intact after 24 hours at 350°C (660° F) in the autoclave were assumed to be corrosion resistant. Alloys with coarse grain size (Figure 36c) and with nonuniformly distributed second-phase particles (Figure 36d) failed the corrosion tests.

It appears that grain size and distribution of second-phase particles contribute significantly to the corrosion behavior of the alloys. The alloys that have smaller grain size and more uniformly distributed finer second-phase particles have higher corrosion resistance. This kind of structure results when an alloy experiences fast cooling rates during casting. A mold at lower temperature provides higher cooling rates than a mold at higher temperature. For example, alloys cast in an unheated mold had higher cooling rates, which produced smaller grain size and fine and uniformly distributed second-phase particles, whereas the alloys that were cast into a mold at higher temperatures (for example, 300°C) produced coarse grains and nonuniform distribution of second-phase particles. Casting of alloys into low temperature molds can provide more sites for the nucleation of grains and second-phase particles. Thus, casting of alloys into unheated molds is expected to promote finer grain size and more uniform second-phase particle distribution during subsequent mechanical processing such as extrusion of the alloy.

The review has also revealed that the maximum melting temperature and extrusion temperature of the casting had no effect on the corrosion resistance within the investigated range.

4.3.4 Conclusions. This review presents corrosion resistance of aluminum-plutonium, aluminum-silicon-plutonium, and aluminum-nickel-silicon-plutonium alloys at high temperature. Based on the limited data available, the major conclusions are:

- Alloys with small grain size and fine second-phase particles distributed uniformly can provide higher corrosion resistance
- Alloys cooled at faster rates during casting promote formation of structures beneficial for higher corrosion resistance

- Aluminum-nickel-silicon-plutonium alloys can provide higher corrosion resistance than aluminum-silicon-plutonium alloys.

4.3.5 Future Work. In order to develop an appropriate fuel design based on the ternary oxide fuels, the following recommendations are proposed:

- Determine the corrosion rates for longer durations, range of flow rates, and under irradiation
- Determine the fission product release and swelling as a function of temperature and burnup
- Develop a database of material properties for the aluminum-plutonium fuels.

Figure 35. Corrosion resistance of typical aluminum-plutonium alloys in static deionized water at 350°C (660°F).

LF93 0037

Figure a.

Grain size extruded rod that
passed corrosion test
100X.

Figure b.

Second phase particles –
extruded rod that passed corrosion test
100X.

Figure c.

Grain size extruded rod that
failed corrosion test
100X.

Figure d.

Second phase particles –
extruded rod that failed corrosion test
100X.

Neg. 2548, 2626, 3037 and 3036 PMO

Figure 36. Typical microstructures of aluminum-silicon-nickel-plutonium alloys.

5. CARBIDE FUELS

5.1 Fabrication Technology

5.1.1 Introduction. The fabrication of mixed uranium-plutonium carbide fuels analogous to the mixed oxide fuels of uranium and plutonium (MOX fuels) is discussed, as well as potential fuels of plutonium carbide with other metal carbides such as niobium and zirconium carbide. These fuels are considered for plutonium burning because of their higher thermal conductivity and lower operating temperatures than that of the oxide fuels (Figure 37). The carbide fuels also have a higher density, which allows an increase in fissile density. Because of the limited experience with PuC fuels, fabrication details for PuC fuels are not available, but are formulated from those of UC fuels based on the similarity in their chemistries.

Two fuel forms are considered for the carbide fuels. The first is a pellet form contained in a metal tube that may be a refractory metal such as niobium, molybdenum, tantalum, tungsten, or a iron-based alloy such as stainless steel. The other

fuel form is plutonium carbide particles dispersed in a graphite matrix, similar to the fuels used in high-temperature gas reactors, except that plutonium carbide or mixed carbide (containing plutonium) kernels are used instead of uranium carbides. The fabrication of metal-cladded carbide fuels and particle-dispersed fuels is discussed in the next two subsections.

5.1.2 Metal-Cladded Plutonium Carbide Fuel Rods. An example of a plutonium carbide fuel element is one consisting of a stack of plutonium carbide pellets stacked inside a stainless steel (Type 347) or a refractory metal (tungsten, molybdenum, niobium, or tantalum) tube cladding. The metal cladding may be as small as 5 mm OD with a 0.25 mm wall thickness. The pellet OD is slightly smaller than the cladding inside diameter to allow radial clearance. The fuel rods could equally be larger, but the actual size would depend on neutronic and thermal/hydraulic analyses. It is not expected that the size of the pellets or the cladding would effect the fabrication process.

LF93 0038

Figure 37. Thermal conductivity of uranium (5 wt% plutonium) oxide and carbide.

The fabrication of a metal-cladded carbide fuel rod consists of fabricating the metal tubes and the carbide pellets. An end plug is welded to the tube at one end, the appropriate number of carbide pellets are loaded to achieve the required stack length, and the fuel rod is pressurized with an inert gas such as helium and the remaining end plug is welded, sealing the fuel rod. The fabrication of four candidate cladding materials (molybdenum, tungsten, niobium, and tantalum) is discussed next, followed by fabrication of the PuC pellets.

The first step in the production of molybdenum and tungsten powders is the reduction of the oxides to form metal powders.²⁹ Both metal powders are produced by hydrogen reduction of oxides at elevated temperatures. Molybdenum is usually reduced from MoO₃ or from ammonium dimolybdate, which forms MoO₃ when heated for the first stage of reduction to MoO₂. Tungsten powder is reduced from ammonium paratungstate, which is also heated in air or hydrogen to form WO₃, which is reduced to WO₂ in hydrogen. MoO₂ and WO₂ are reduced to metal powders using hydrogen reduction at higher temperatures than are used for the formation of the dioxides. The molybdenum powders can be used to fabricate alloys using vacuum arc casting or electron-beam melting. Electron beam melting units can be used to produce molybdenum or tungsten alloy ingots, but the electrodes must first be prepared using powder-metallurgy techniques.

Commercial vacuum arc casting molybdenum alloys are currently processed initially by extrusion because earlier forging alternatives resulted in lower yields due to oxidation and cracking. Molybdenum tubing can be drawn to tubes with outside diameters ranging from 32 to 0.05 mm with corresponding wall thicknesses ranging from 2.5 to 0.05 mm. Tungsten tubes are not drawn but are formed by chemical vapor deposition.

The production of niobium and tantalum alloy mill products is accomplished following the process flow diagram depicted in Figure 38.³⁰

Melting niobium and tantalum alloy ingots is accomplished by a combination of electron beam melting for purification and consumable electrode vacuum arc melting for final alloy addition and composition control. After one or more electron beam melts, the as-melted ingot is analyzed for impurities and alloy composition. Necessary alloy additions are gas tungsten arc welded into the electron beam melted ingot to form the electrode for the first of two consumable vacuum arc melts to ensure a homogeneous final ingot composition. Generally, ingot size is not limited by melting capacity, but by primary working equipment capability. Arc melting of niobium and tantalum is accomplished at <1 micrometer (1×10^{-3} torr).

Primary breakdown of the ingot microstructure is accomplished either by direct forging or extrusion. Niobium-based alloys can be worked by forging or extrusion in the temperature range 800 to 1000°C, but the tantalum-based alloys are normally heated to 1300°C for forging or extrusion. To prevent interaction of the billet with the heating medium, billets are protected by an evacuated mild steel hermetically sealed or purged cladding. Also hafnium silicide, molybdenum, or tungsten coating can be applied to protect the billet during heating for forging or extrusion. Before proceeding to secondary working operations, billet conditioning to remove contaminated materials or defects is accomplished by mechanical and chemical means.

Secondary working operations are generally carried out from room temperature to 260°C. Working can be accomplished readily in this temperature range with minimal concern for oxidation of the billets. Both the niobium-based and tantalum-based alloys can be readily worked at room temperature.

LF93 0039

Figure 38. Process flow diagram for niobium and tantalum alloys.

The fabrication of stainless steel tubing is not as difficult as the fabrication of refractory metal tubes. The last melting stage of stainless steel is done in an electric furnace that may use vacuum arc melting to degas and reduce inclusion content. The stainless steel is fabricated into tubes by extrusion. Tubing has been made from hypodermic needle sizes to as large as 20-in.-diameter pipes used in nuclear power plants.

The fabrication of the plutonium carbide pellets is very similar to the fabrication of UO_2 or MOX pellets described elsewhere. The essential difference is the conversion of plutonium oxide into plutonium carbide. This process generally occurs with the plutonium oxide powders. Graphite is mixed with plutonium oxide in the correct proportions to form PuC. The resulting mixture is heated to carbothermally convert the PuO_2 to PuC with the liberation of CO or CO_2 . Pellets are formed from the PuC powder with processes similar to those for fabricating MOX fuel pellets.

5.1.3 Particle-Dispersed Graphite Fuels.

The fabrication of the PuC particle-dispersed fuels in graphite parallels that for UC_x particle dispersed fuels (Figure 39). Details of the process may vary. These fuels have been fabricated on a laboratory scale, and process scale up to a production mode would have to be demonstrated.

The first part of this process would be to fabricate PuC particles or microspheres on the order of 0.1 to 0.2 mm diameter and coat these particles with two layers of graphite of different densities. The inner layer is a porous graphite layer to trap the fission products released from the fuel. The outer layer of graphite is a seal coating. The latter coating is overlaid with a carbide coating (zirconium or niobium carbide), which then forms a BISO particle, or in place of this carbide coating, silicon carbide and another layer of dense graphite is applied to form a TRISO particle. The purpose of all these coatings is to retain the fission products that are generated. The second part is to extrude these particles in a graphite matrix without fracturing the particles.

LF93 0040

Figure 39. Plutonium carbide BISO fuel particle.

A gelation process has been used to fabricate UC_x , UCO , and ThO_2 microspheres. The gelation processes can be further subdivided into internal gelation and external gelation processes. The internal gel precipitation process starts with the dissolution of plutonium oxide powder in nitric acid to form an acid-deficient plutonium nitrate solution. This solution is then mixed with a carbon source (carbon black) and urea. The mixture is chilled, then hexamethylenetetramine is added. The ionic charge in the liquid droplet is neutralized throughout the droplet with ammonia, which is contained in the hexamethylenetetramine. The droplet is stable only below approximately 280 K. Increasing the temperature of the droplet in a bath of trichloroethylene, silicon oil, hexane, or other heated liquid releases the ammonia in the droplet, causing gelation.

Internal gel precipitation has disadvantages centered around forming and maintaining the broth in a refrigerated condition and handling the toxic organic liquids (trichloroethylene). The broth is unstable when formed and will eventually gel even with refrigeration. Therefore, the broth

must be used soon after formation to prevent gelling in the liquid lines.

For the external gelation process, a process similar to that for the internal gelation process is used. The fuel is precipitated from a nitric acid solution in the form of a very stable sol that consists of a fine dispersion of the oxide in an aqueous solution. This sol is mixed with graphite and is allowed to settle in an ammonium hydroxide medium, which extracts the water from the gel as it settles. A spherical particle is formed from minimization of the surface energy. The particles are then heated, as in case of the PuC pellet fabrication, to carbothermically convert the oxide to carbide.

The gelation process generates large quantities of contaminated effluent, and the particles that do not meet specification cannot be immediately introduced into the process stream without reprocessing. Any mixed carbides containing plutonium fabricated with this technique will need development to form homogeneous gels.

In order to overcome some of these difficulties, another process was being developed that is based upon freeze drying (cryochemical process) to form the spherical particles (Figure 40). A slurry of the oxide mixed with graphite is sprayed into a cryogenic fluid and frozen. The particles are removed and placed into a freeze dryer in which the water is removed under vacuum leaving the particle frozen from the heat of sublimation of the water. Rejected particles can be easily reintroduced to the slurry and recycled. The waste effluent streams may be much less than those from the gelation process. This process still needs some optimization for the fabrication of uranium carbide fuels or mixed carbide fuels with uranium; not withstanding developing a new fabrication process for the plutonium carbide-based fuels. After the freeze-drying process, the particles are fired at high temperatures to carbothermically convert the oxide to a carbide.

Coating processes are based on chemical vapor deposition techniques. The pyrocarbon coating processes use a mixture of an inert carrier gas and an organic compound at high temperatures.

The coat of low density pyrocarbon layer adjacent to the fuel kernel provides void volume for the collection of fission products and for dimensional changes of the kernel during irradiation.³¹ This coating is applied by cracking acetylene in argon in a fluidized bed between 1420 and 1670 K. The coating porosity, which is critical, is controlled by temperature, coating rate, bed surface area, particle size, and coating gas composition. An inner, high-density, isotropic pyrolytic carbon layer is added over the buffer layer. This layer seals the porous graphite layer and protects the fuel kernel from hydrogen chloride attack during deposition of the silicon or zirconium carbide layer. For deposition of this layer propylene is endothermically pyrolyzed above 1570 K. Acetylene can also be used to deposit this coating. The

LF93 0029

Figure 40. Cryochemical fuel fabrication process outline for making ZrC-coated UC_2 microspheres.

isotropy and the degree of sphericity are enhanced by high temperatures and deposition rates, but the required high density is obtained by reducing the reaction temperature.

The carbide coating, which is SiC for a TRISO particle and ZrC or NbC for a BISO particle, is the primary load-bearing member and fission product diffusion barrier in the fuel particle. This carbide coating requires high strength to resist the stresses imposed by the internal gas pressure from fission gas generated during irradiation. This coating process uses a halide such as ZrCl_4 or NbCl_5 ³² for these carbides or methyltrichlorosilane for the SiC and hydrogen mixture to reduce the halide to a carbide with the release of hydrogen chloride as an effluent. The decomposition takes place around 1200 to 1400°C with the addition of methane as a source of carbon for ZrC or NbC and between 1400 and 1800°C for SiC.³³ NbC and ZrC have been deposited at higher temperatures (1800 to 2000°C) using the diffusion of carbon in the substrate as a source of carbon. Although high deposition rates could be obtained at the higher temperature, the coating quality may suffer from entrapment of chloride in the coating and the environmental release of toxic hydrogen chloride effluent. Improved coatings are obtained from the slower deposition rates at the lower temperatures.

An alternative process for depositing carbide coatings is an organometallic-coating process. This process uses a metal-organic compound that contains the carbon and hydrogen, and thus simplifies the control of the reactants. This process is a low-temperature process occurring between 200 and 400°C.

With an organometallic complex it is possible to assemble the desired components of a composite material into a single precursor enhancing process control $\text{Zr}(\text{CH}_2\text{C}(\text{CH}_3)_3)_4$ for ZrC, $\text{Nb}(\text{C}_6\text{H}_5\text{CH}_3)_2$ for NbC, thereby providing a low-temperature route (ergo low energy) to complex composite materials. While organometallics do decompose at temperatures lower than many conventional metal-halide precursors, the use of robust organometallics in high-temperature pro-

cesses could lead to better high-quality, high-temperature materials.

The organometallic precursor contains only the metal, carbon, and hydrogen and are therefore "tailored" for the production of metal carbide films (the thermodynamic end product). Many examples of these MR_n complexes have been reported for zirconium, hafnium, niobium, and tantalum where R is an alkyl ligand, carbocyclic ligand (e.g., benzene or cyclopentadiene), or some combination thereof, and most can be prepared (10–100 g quantities), in high yield, "one-pot" syntheses starting from the binary metal halide and readily available alkali metal reagents using standard (at least for the organometallic chemist) techniques.

The organometallic candidates decompose at low temperatures, and generally yield amorphous material that require high-temperature firing (>800°C) in order to form crystalline metal carbide. The amorphous carbide offers the potential to seal the cracks and open porosity that should remain sealed after the material has crystallized upon heating over 800°C. All of the metal carbide materials prepared by bulk pyrolysis contain some amount (2–9%) of amorphous carbon.

The fuel particles are mixed with a mixture of graphite powder, carbon black, and a binder. The graphite powder is coal or oil pitch. There can be substantial variation in the properties of the graphite powder arising from the source of the pitch, the manufacturer, and the coking process. Carbon black is produced from the incomplete combustion of a hydrocarbon such as methane or ethane. A number of different polymers have been used for binders. For elements manufactured in the 1960s for nuclear propulsion, a binder was based on partially polymerized furfuryl alcohol.³⁴ This polymer is diluted with additional furfuryl alcohol. Four percent maleic acid anhydride is added to the binder as a catalyst to increase its thermosetting property. A different binder consisting of octadecanol and polystyrene is used for HTGR fuel elements.

The binder, fuel particles, and graphite powders are mixed together in a blender for about

25 minutes. The blended mixture is further blended by extruding the mixture to distribute the binder onto the particles. The "green" extruded elements are heated at 250°C to cure the binder and complete the thermosetting process and then baked at 450°C to remove the volatiles. The elements are heated for 4 hours to graphitize the binder.

5.1.4 Conclusions. Fuels based on plutonium carbide or metal carbides mixed with plutonium carbide offer an advantage to lower the fuel temperature for a given power level. Two fuel forms may be used, one where carbide pellets are contained in a metal jacket and the other of particles dispersed in a graphite matrix. From a fabrication point of view, both forms can be fabricated based on uranium technology, but process development will be required.

5.1.5 Future Work. Several tasks would have to be performed to develop the carbide fuels. These tasks would depend on the fuel form selected for plutonium burning. However, certain tasks would be generic to either fuel form. The generic tasks are as follows:

- Determine the phase equilibria in the plutonium-zirconium-carbon system
- Determine the thermal conductivity and heat capacity as a function of composition, burnup, and temperature
- Determine the fission product release and fuel swelling as a function of temperature and burnup
- Determine the diffusion rates of significant fission products in the fuel and develop fission product release and swelling models
- Develop a materials properties' database to identify any deficiencies and develop a plan for resolving those deficiencies
- Develop carbide fabrication technology for either pellet or particle fuels
- Evaluate potential facilities for fabricating carbide fuels
- Develop organometallic coating process for high-temperature, face-centered cubic carbides.

6. CONCLUSIONS

This study focused on three fuel forms (oxides, metallics, and carbides) to contain weapons-grade plutonium metal for disposition in thermal nuclear reactors. The plutonium oxide fuel form is for use in a conventional or advanced LWR; the aluminum-plutonium fuel form is for a low-temperature LWR; and the plutonium carbide fuel form is for a high-temperature graphite reactor (HTGR) or possibly an LWR.

In all fuel forms, the highly reactive weapons-grade plutonium must be balanced with a thermal resonance absorber [i.e., a fertile heavy metal material (depleted uranium or thorium) or a burnable poison (e.g., gadolinium, erbium, europium)]. The requirements of this study focus on the neutronics of burnable poisons and neglect the use of uranium that would tend to breed more fissile material (potential nuclear weapons material).

In the oxide fuel form, plutonium oxide would be uniformly mixed with zirconium/calcium oxide and a burnable poison or thorium oxide. The calcium oxide provides thermal stability and greatly improves the thermal conductivity (comparable to UO_2) of the zirconium oxide. Plutonium oxide fuel compositions containing ZrO_2 will also contain CaO (Zr and Ca are neutronically similar) and form a ternary fuel composition $\text{PuO}_2(\text{ZrO}_2)(\text{CaO})$ with an additional burnable poison oxide.

The neutronic performance results for the plutonium oxide fuel compositions analyzed show the $\text{PuO}_2(\text{ZrO}_2)(\text{ThO}_2)$, $\text{PuO}_2(\text{ZrO}_2)(\text{Er}_2\text{O}_3)$, and $\text{PuO}_2(\text{ZrO}_2)(\text{Eu}_2\text{O}_3)$ to be potential fuels for use in an LWR. The fuel composition with thorium may not be desirable from the standpoint that it breeds fissile ^{233}U .

There are at least three fabrication processes that can be adapted to fabricate $\text{PuO}_2(\text{ZrO}_2)(\text{CaO})$ powders, namely, coconversion, integrated dry route, and coprecipitation. Of the three processes, adaptation of the coconversion process appears to have the least developmental risk, primarily

because microwaves are used to directly denitrate heavy metal nitrate solutions into an oxide powder, thereby eliminating the need for chemical additives and the production of waste products. The integrated dry route would have the highest developmental risk and the coprecipitation process would be of an intermediate risk. If it were desired to reprocess the spent plutonium oxide fuel, the integrated dry route process would have to be eliminated because dissolution in nitric acid (solid solution) is the only means available for dissolving plutonium oxide.

The ternary oxide fuel forms with the burnable poison oxide additives are expected to be compatible. In addition, the oxide fuel forms are expected to be compatible with most potential cladding alloys such as zirconium-based alloys or the stainless steels. The low thermal conductivity of oxide fuels leads to high fuel temperatures and large temperature gradients that cause fuel restructuring at high temperatures. The restructuring in the oxide pellet is the primary mechanism for gaseous fission product release in oxide fuels. This fission gas release drives the requirement for the initial porosity in the fuel, the size of the plenum at the top end of the fuel rods, and the amount of prepressurization to mitigate cladding collapse during irradiation.

The aluminum-plutonium-based metallic fuels have much higher thermal conductivity relative to the oxide fuels, which results in lower fuel temperatures. Alloying agents, such as titanium, zirconium, and nickel, can be added to the aluminum-plutonium alloy to reduce the corrosion of the fuel while in contact with water.

The fabrication processes for the aluminum-plutonium fuels have been well developed in the past. However, substantial effort would have to be expended to recapture some of the plutonium-specific technology from 30 years ago and modify current aluminum-uranium fabrication technology facilities to handle weapons-grade plutonium.

For aluminum-plutonium fuels with relatively high plutonium content (greater than 15 wt%), the

plate fuel form is recommended because of the brittle nature of the fuel. Plutonium-bearing fuel rods could be fabricated for smaller amounts of plutonium (5–10 wt%) in metal clad fuel rods.

The neutronic performance results for the aluminum-plutonium fuel compositions analyzed show the $\text{PuAl}_4(\text{Al})$ with erbium (Er) fuel composition to be a viable fuel candidate for use in a noncommercial, low temperature thermal reactor.

An advanced fuel form based on the metal-clad carbide fuels could be used in a water reactor environment. The carbides have substantially higher thermal conductivities compared with the oxides that would result in lower fuel temperatures. However, fuel development would be required. An alternative is the use of carbide fuels in a high-temperature, gas-cooled graphite reactor. A number of processes exist for fabricating carbide microspheres, but all would require substantial development.

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Appendix A

Preparation and Fabrication of Aluminum-Plutonium Alloys

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Preparation and Fabrication of Aluminum-Plutonium Alloys

A-1. PREPARATION OF ALUMINUM-PLUTONIUM ALLOYS

For the Plutonium Recycle Test Reactor (PRTR) program,¹ 1,400 g of plutonium was dissolved in 10,000 g of aluminum at 950°C in 10 minutes. Visible normal (centerline) segregation occurred in the hypoeutectic Al-Pu alloys cast above 800°C. The lower casting limit was set at 725°C to produce good surfaces, reduce air entrapment, and eliminate possible segregation in the crucible.

Two air melting induction furnaces were used for melting aluminum plutonium alloys. The furnaces are enclosed in a hood, which had three work areas—an upper charging floor, a low level used for handling molds and castings, and three separate areas used for alloy preparation.

The crucibles used were 6-in. ID and had a capacity of 25 lbs of aluminum. The power required to melt the 25 lbs of alloy was generated by a 50 kW 3,000 Hz motor generator set. The melting crucibles were made from clay-graphite or graphite.

Particular emphasis in the development of casting techniques was placed on eliminating or reducing machining operations to save time and reduce scrap generation and recovery problems. Aluminum/plutonium billets, which required no surface machining, were produced for coextruded cladding.

The reduction of PuO₂ with aluminum directly to an aluminum 1.8 wt% plutonium alloy was investigated during the PRTR program.¹ A cryolyte flux is used to dissolve the aluminum oxide generated during the reduction. This reduction eliminates the need for forming, analyzing, and diluting a master alloy. It is particularly valuable in cases where small quantities of oxide are available, only small quantities of alloy are desired, or a high weight percent plutonium-aluminum alloy is desired.

Experimental fuel rods for the Canadian Heavy Water Reactor at Chalk River have been prepared using reduction processes for both PuAl₄ and PuO₂.^{2,3} The plutonium yield for this process averaged 95% in alloying 231 g of aluminum. Alloys for a second fuel rod were prepared by the aluminum reduction of pressed PuO₂.

In a typical experiment, a charge of 217 mg of plutonium as plutonium dioxide, 1 g cryolyte, and a 1.5 g aluminum ingot were heated in a graphite crucible in air for 20 minutes at 1200°C. The resulting alloy button contained 208 mg of plutonium, a 96% yield. Plutonium dioxide is reduced readily by an excess of liquid aluminum at 1200°C in the presence of liquid cryolyte, forming plutonium-aluminum alloys with a plutonium yield above 99%. Because little reaction occurred, however, even after 3 hours at 1000°C, later experiments were carried out in a vacuum furnace. Alloys containing 2.5 wt% plutonium were produced by heating plutonium dioxide and aluminum for 3 hours at 1100°C. The unreacted plutonium dioxide was present in pockets that were separated from the alloy by a barrier layer of aluminum oxide.

Alloys containing up to 25 wt% plutonium were prepared by the reaction of aluminum with plutonium dioxide—cryolyte mixtures in air. Uranium yields vary from 93 to 98% and the plutonium yields are higher than those of the uranium. The solubility of PuO₂ in cryolyte was 0.01%.

Plutonium trifluoride is reduced more rapidly at 900°C than at 1125°C, with liquid aluminum owing to the evolution of gaseous aluminum monofluoride at the lower temperatures.³ The preparation of other binary plutonium alloys by the reduction of plutonium fluorides or dioxide with beryllium, gallium, magnesium, silicon, thorium, and uranium has also been studied. The reduction of a plutonium compound offers

particular advantages when applied to the preparation of plutonium alloys, namely:

- Elimination of the expensive steps of producing and manipulating the chemically reactive plutonium metal
- An inert gas atmosphere within the glove box system may not be required.

However, the reduction of a plutonium compound suffers from the disadvantage that when plutonium metal is added to a light metal such as beryllium, the plutonium may separate before

alloying due to the low melting point 640°C and high density 15.9 to 19.8 g/cc.

In the final stages of development, the plutonium yield for the conversion of nitrate solution to the oxide and then to alloy ingot averaged 98%.

The processes for the preparation of aluminum-plutonium alloys meet the permissible releases and personnel exposure allowed approximately 30 years ago. Current safety and environmental regulations will likely require substantial changes to minimize personnel exposure and limit the plutonium releases.

A-2. FABRICATION OF LOW-PLUTONIUM CONTENT ALUMINUM-PLUTONIUM ALLOY FORMS

A number of different Al-Pu fuel forms have been developed containing small amounts of plutonium. These vary from extruded rods loaded into zircaloy tubes and aluminum clad extruded fuel rods to various forms of plate fuel. The fabrication of these various fuel forms is outlined below. These fuel forms are applicable to the hypoeutectic alloys (Pu < 15.6 wt%).

A-2.1 Zircaloy-Clad Al-Pu Fuel Rods

The first fuel elements for the PRTR were clad with zircaloy seamless tubes.^{4,5} These fuel elements were clusters of 19 eight-foot-long, 0.565-in.-diameter fuel rods that contain either uranium dioxide (UO₂) or Al-1.8 wt% plutonium. The fuel rods are 88 in. long, 0.565 in. in diameter, and encased in a zircaloy jacket approximately 0.035 in. thick. Inter-rod spacing is achieved by spiral wire wrapping. They have been tested to 80% burnup. For PRTR, the process for producing spike fuel elements for the test reactor calls for casting Al-1.8 wt% plutonium billets, extruding billets into rods, and inserting the rods in zircaloy tubing. It was desirable to cast billets to exact size in diameter and length to eliminate machining, which is time consuming and generates a large amount of scrap.

Billets had to be free from segregation, gas entrapment, or other casting defects that would give rise to troubles during extrusion. The diameter of the billet was determined by the size of the extrusion container and controlled by the diameter of the mold. Molds were machined from solid graphite to a wall thickness of 0.75 in. and a base thickness of 4 in.

A billet length of 9-1/2 in. is required for two 88-in. fuel rods to be obtained from each extrusion. The fuel rods containing the Al-1.8 wt% pin alloy were assembled by inserting extruded alloy rods into zircaloy sheath tubes. The first core loading consisted of 1.8 wt% plutonium in an alu-

minum alloy. The rods were capped and welded. For the initial PRTR loading, the majority of the Al-Pu alloy elements were clad with zircaloy-4.

Extrusion ratios of 27 to 1 at 500°C at 81,500 psi were employed. Diametrical variation of fuel cores is held to about 0.0015 in. A slip fit clearance of 0.005 in. between fuel core and cladding was found to be satisfactory. Overall yields using this process amounted to as much as 85%.

The zircaloy tubes are made from double vacuum melted ingots.⁶ The ingots are surface conditioned to remove casting defects and are then forged and machined to extrusion billet dimensions. The billets are sheathed in Cu-3Si, copper, or 1005 plain carbon steel and copper prior to extrusion. These metal sheaths act as a lubricant and also protect the tube against oxygen and nitrogen contamination during extrusion. Billets are extruded at approximately 845°C. The protective sheaths are removed from the extruded tubes by pickling in nitric acid. After dejacketing, the tubes are either tube reduced or drawn to the desired size. Intermediate vacuum anneals are usually required and annealing is done at approximately 790°C.

Zirconium has the potential of interacting with the aluminum forming lower melting eutectics, which could lead to premature liquefaction of the core in the event of an abnormal transient.

A-2.2 Aluminum-Clad Split Cylinders

Another unique fuel form was developed for Argonne National Laboratory in the form of split cylinders, 1-1/4 in. OD and 2 in. long containing 5 or 10 wt% plutonium. Total wall thickness was 0.060 in.⁴ The aluminum-plutonium cores were 0.020 in. thick, clad on both sides by 0.02 in. of bonded-on 2S aluminum and edge sealed by a 2S aluminum frame. Sixteen locating bosses were welded to the specimens.

The specimens were prepared by roll cladding the aluminum-plutonium alloy cores with 2S alu-

minum using the picture-frame/cover-plate technique. These compacts were made up of a four-cavity frame, holding four cores, and two cover plates.

The sequence of operations for preparing the specimens was worked out using an Al-10 wt% uranium core alloy instead of the plutonium alloys. The fabrication process is outlined in Table A-1.

While the cladding was done in an open rolling mill without contamination of the equipment, this was thought to be undesirable and if further work is to be done on similar pieces, full hooding and ventilation of the rolling mill and heating furnaces should be investigated. In a large-scale operation, it would probably be necessary to provide separate hoods and rolling mills for fabrication of the

Table A-1. Fabrication process for split cylinders.

Step	Description
Fabrication of picture frames, covers, and tubes	Twelve-gauge 2S aluminum sheet was rolled to 0.075 in. thickness for the picture frames. Four core cavities were blanked from these plates.
Casting and prefabrication of the cores	The castings were made individually in 6-g melts. They were vacuum melted and solidified in magnesium oxide crucibles forming buttons approximately 3/4 in. diameter by 3.8 in. thick. These were cleaned and hammered down to 1/4 in. thick in a service hood attached to the furnace hood. After flattening, the castings were placed in plastic boxes and transferred to a hood-enclosed 2-1/2 in. by 4 in. bullion mill and rolled at room temperature to 0.180 in. thickness. They were then vacuum annealed at 450°C and furnace cooled. After annealing, the plates were rolled to 0.085 in. and re-annealed. The plates were badly warped after rolling. They were straightened and sized by cross rolling at 45 in. to the axis of the original rolling direction.
Assembling and welding the compacts	The cores were blanked from the rolled plates using the same die as was used to make the cavities in the picture frames in a 10-ton, hand-operated Carver laboratory press. The operation was carried out in an open-front hood.
	Welding was done in a hood similar to the one used in blanking and assembling the cores. An ac arc welder with a high-frequency arc starter was used. The sandwiches were protected by clamping between 2-7/8 in. × 6 in. × 1/2 in. copper plates, which acted as a heat reservoir and prevented overheating and oxidation of the specimen in the bonding area.

bare plutonium alloy and for the clad alloy specimens so that external contamination of the clad specimens would not take place by transfer from the mill rolls. Hoods and ventilation should probably be provided for the platen shears, form roller, stud welder, and identification notches.

The roll cladding operation was carried out during a period of rain and extremely high humidity. This was an objectionable atmosphere for the work and may have induced blistering. A controlled humidity atmosphere would be desirable for such work.

A-2.3 Aluminum Cladded Rods

A fabrication process was developed, and 144 coextruded fuel rods were prepared for the Trans Plutonium Program⁷ at the Savannah River Laboratory. The rods were 0.94 in. in diameter and

60 in. in length. The cladding was aluminum (X-800 alloy) and was 0.04–0.120 in. thick. The fuel cores were Al-7.35 wt% plutonium. The fuel elements were coextruded in an extrusion press, which was mounted in a plutonium contaminated glove box.

The melt temperature of the Al-7.75 wt% plutonium was 775°C and billet cores were individually cast by pouring the melt into a one-piece, hot (about 300°C) graphite mold. Eight to fourteen billet cores were made per melt. A hot top was provided on the mold to feed the solidification shrinkage and removed by cut-off saw. All coextrusion billet parts were degreased with trichloroethylene, etched in sodium hydroxide, and etched in nitric-hydrofluoric acid. Outgassing tubes were connected and outgassed at 500°C.

The surface condition of the extrusion was improved by minimizing the amount of lubricant (oil graphite dispersions used on the extrusion die), but this led to considerable galling and necessitated cleaning of the die in a caustic solution after one to three extrusions. The benefits of improved surface conditions compared with frequent cleaning need to be weighed for future development.

A 280-ton coextrusion press was used to extrude the fuel and cladding. Al 1100 cladded Al-U alloy billet cores were extruded and machined and placed in aluminum cladding as cursory extrusion experiments. The 1245 Al was alloyed with plutonium at 850°C to 950°C in an air melting induction furnace. Both induction and manual stirring was used.

The coextruded billet is 2-1/2 in. OD and 12 in. long in which the leading edge is dished and the trailing edge is ball shaped. The final diameter of the rods was 0.94 in. OD and the length was 60 in. The flow process is shown below:

- Al 1245 alloy plutonium
 - Master alloy
 - Remelt, dilute to Al-7.35% plutonium alloy

- Cast fuel core
- Sample
- Radiograph
- Remove hot top machine core
- Degrease and etch
- Al X-800 alloy
 - Machining cladding components
 - Degrease and etch
- Assemble
 - Coextrusion billet
 - Weld
 - Outgas
 - Extrude
 - Decontaminate
 - Straighten
 - Radiograph
 - Machine ends
 - Final radiographs
 - Ultrasonic bond test
 - Degrease and etch
 - Inspect and measure
 - Ship.

A-2.4 Fabrication of High-Plutonium Content Al-Pu Alloy Forms

A-2.4.1 Aluminum-Cladded Wire Fuel. A wire fuel form consisting of Al-Pu fuel had been fabricated for Savannah River.⁸ Sixty alloy pins

clad in aluminum were prepared. The specifications follow:

- Overall OD of pin: 0.0625 +0.000, -0.002 in.
- Overall length of pin: 0.500 +0.000, -0.005 in.
- Cladding thickness: 0.005 to 0.015 in.
- Cladding material: 1100 or 6063 aluminum
- Core dimensions: To depend on cladding dimensions
- Core alloy concentration: To be varied based on actual core dimensions, but to range between 7 and 19 wt% plutonium in Pu-Al alloy.

The function of the cladding was to prevent plutonium contamination; hence, there was no need to bond the cladding and the core.

The cladding components were fabricated from 1100 Al wire 1/16 in. in diameter. Cans were cut to 0.532-in. lengths and a 0.035-in. diameter hole was drilled 0.517 in. deep, with a flat bottom #65 drill, leaving a 0.015-in. thick bottom cap. End cap material was fabricated from the same material by a series of passes through draw plates to 0.035-in. diameter. Cleaning of the cladding components was accomplished by rinsing in trichloroethylene and drying in a vacuum oven for 2 hours at 150°C.

The core material was cast as cylinders 0.375 in. in diameter, approximately 2 in. long in a heated graphite mold. The alloy composition was 15.75 wt% plutonium.

Billets 1/4 in. long were cut from the cylinders. These were extruded through an 87-to-1 reduction in area to final size of 0.032 in.

The extrusion was of the vertical forward type through a flat face shear die with a 0.035-in. diameter die opening. A 20-ton hydraulic press, ordinarily used for oxide compacting, was used

for the extrusion. Temperature measured at the top of the extrusion container was 450°C for the first extrusion and 500°C for the final two extrusions. Extrusion pressure ranged between 150,000 psi and 220,000 psi on the 0.370-in. diameter stem. Approximately 24 in. of wire was obtained from each extrusion. The wire was inserted into a Lucite fixture and cut to 0.470-in. length, the ends faced with a file; and after final gauging for length and diameter, the cores were weighed. Each core was cleaned in ethyl alcohol and wiped dry. Measurable contamination was generally less than 1,000 disintegrations per minute.

Sealing of the final end was done by fusion welding using alternating current with the tungsten inert gas process.

The completed pins were checked for smearable contamination and monitored in a standard chamber counter for alpha radiation.

The average plutonium analysis was given as 15.75 wt% plutonium. This was an average of six samples of the extruded wire. The maximum analysis was 16.05 wt% plutonium and the minimum 15.5 wt% plutonium.

The extrusion conditions were quite critical due to the 87-to-1 reduction and the relatively low ductility of the alloy. Six extrusions were attempted and only three were successful within the limits of the press. The reason for this appeared to be die and billet container finish rather than temperature. A stem fracture occurred on the sixth and final attempt to extrude. Some galling was observed on the extruded surface of the alloy. The extrusion process would need to be redesigned.

The most critical part of the fabrication process was the welding of the unsealed end of the pin. This was due to the difficulty in controlling depth of penetration in order to keep from alloying the weld metal with the core material. The original specifications called for an overall length of 0.500 in., leaving a maximum of 0.015-in.-thick end cap. However, when the first 10 closures were attempted and only one did not have a

contaminated weld zone, the length specifications were relaxed to 0.500–0.005 in. With this new length, the overall welding reject rate was still 65%. It was found that the distance the pin protruded from the chill block was very important in controlling depth of penetration.

A-2.4.2 Aluminum-Cladded Plate Fuel. The Phoenix Fuel Program conducted by Pacific Northwest Laboratory had as its primary objective the exploration and evaluation of the longer lifetime potential inherent in the use of the isotope ^{240}Pu as a burnable poison in nuclear reactor cores.^{6, 9–11} The homogeneity specification established for the Phoenix fuel plate requires the plutonium content of the core to vary no more than 10%.

The first cores fabricated for roll plate assemblies were resistance melted in air and cast into graphite molds. The first cores were cast to width and thickness and machined to length. Plates fabricated from these cores met homogeneity limits, but contained micro-discontinuities caused by either porosity or inclusions. All other fabricated cores have been induction melted, cast to billets in graphite molds, and the billets extruded to core shape. The extrusions are cut to length to provide a finished core. Plate assemblies rolled with these cores are generally free from voids and discontinuities and well within homogeneity limits. In addition to providing excellent core characteristics, the extrusion process provides high yields with 97% of the original melt cast and 80% of the extrusion usable. Using this fabrication process, it is estimated that the total plutonium content of individual fuel plates will vary 4% and fuel elements less than 2%.

A-2.4.3 Taper Control. The peaking problems associated with the Phoenix fuel require the use of a tapered core on the bottom end of the fuel plate. Four types of end configurations were rolled at 6-to-1 reductions, using uranium-aluminum alloy cores as a stand-in for the plutonium-aluminum core and 1100 cladding. From the results of this test, the elliptical end shape was selected as best, and four plutonium aluminum

plates were fabricated. The Pu-Al core plates exhibited marked differences from the U-Al cores, indicating the U-Al alloy is a poor stand-in for Pu-Al alloy. These first Pu-Al fuels exhibited dog-earing at corners, triangular voids at core ends, and dog-boning and clad thinning at core ends. Additional development plates were fabricated using 1100 clad plates with 1100 inserts at the core ends, 1100 clad plates with 6061 inserts at the core ends, and 6061 clad plates. Dog-earing was eliminated on all plates by chamfering the edges of the cores. The 1100 alloy clad plates with 1100 inserts still exhibited extreme dog-boning. The 1100 alloy clad plates with 6061 inserts reduced dog-boning, but did not eliminate it. The 6061 alloy clad plates exhibited no dog-boning and had tapers close to those desired. An additional problem involving inserts was the length of insert required. It was necessary to enclose the entire end of the core to reduce dog-boning, and this resulted in a vertical bond line extending from the core to the fuel plate edge that does not receive full reduction pressure during rolling. This bond interface often does not bond, providing an unacceptable water path to the core. It is possible that additional core shaping could make 1100 clad acceptable or that inserts could be redesigned to gain bond line reduction, but 6061 was selected as the preferred clad and no further 1100 clad development was undertaken.

A-2.4.4 Cladding Selection. The choice of cladding depended on corrosion conditions, strength requirements, and fabricability. Two choices examined in detail were 6061 and 1100 alloys. 1100 alloy is the standard MTR cladding and 6061 the standard High Flux Integral Reactor (HFIR) and Advanced Test Reactor (ATR) cladding. 6061 alloy aluminum was selected as the preferred Phoenix fuel cladding for the following reasons:

- 6061 alloy eliminates dog-boning and allows the fabrication of a fuel plate with a tapered core
- If it is necessary to increase heat flux beyond existing MTR standards, the 6061 alloy is preferable based on a greater vol-

ume of favorable in-reactor and ex-reactor data

- The 6061 alloy is stronger than 1100 providing greater resistance to fuel deformation
- The 6061 alloy has more potential for advanced applications
- The 6061 clad fuels are less susceptible to scratches and other surface defects.

A-2.4.5 Bonding and Destructive Testing.

The Phoenix fuel plate requires a metallurgical bond on the clad-to-core and clad-to-frame interfaces. The quality of the metallurgical bond obtained with rolled plate fuels depends upon the total reduction ratio used, reduction per rolling pass, rolling temperature, cleanliness of components, and material at interface. Test coupons were rolled at temperatures of 500, 530, and 560°C and reduction ratios from 6:1 to 12:1 to determine desirable fabrication conditions. The test coupons consisted of three 6061 plates with a layer of 1100 aluminum inserted at one interface. The results of the rolling tests as determined by metallography indicated that reductions of 10 to 1 are required to completely break up bond line oxide layers. The higher temperatures appear only slightly better bonded, and the use of a 1100 alloy interface greatly enhances bonding. No grain growth across the bond line occurs on the hot rolled plate, but on good bonds the oxide layer is well broken up providing metal-to-metal contact and there are no voids. Grain growth across the bond line will occur if the plates are cold rolled and annealed as is required on HFIR and ATR fuels. Because all initial Phoenix plates were hot rolled only at reductions of 6:1, grains did not grow across the bond line and the oxide layer was clearly visible. However, void-free bonds meeting standard MTR requirements were obtained at the 6-1 reduction.

A convenient method of using 1100 alloy aluminum at the interface is to use 6061 Al clad with 1100 aluminum as plate assembly components. This technique is used on HFIR and ATR fuels and permits the fabrication benefits of a 1100 to 1100 bond to be used on 6061 clad fuels. As a

result of this test work and HFIR and ATR experiences, the 6061 Al clad material was selected as the preferred cladding material and 12:1 selected as the reduction ratio for future development plates.

Destructive testing is used to qualify fabrication processes and as a process control on representative samples. Phoenix destructive test samples are checked for clad and core thickness, end taper shape, bond integrity, and plutonium content. A 2% sample rate was used during Phoenix plate manufacturing as an in-process control.

A-2.4.6 Nondestructive Testing. All Phoenix development plates were nondestructively tested to evaluate the plates and testing method. The nondestructive tests used were ultrasonic scanning for voids, unbonds, and discontinuities; radiographs for core shape; densitometer scans of radiographs for density homogeneity; gamma counting for homogeneity; dye penetrant for nonbonds; and blister tests.

X-ray radiographs were used to locate cores and evaluate core shape, as well as to provide radiographs for densitometer evaluation of plate density. The radiograph method of locating cores is adequate, but not as handy as the fluoroscope systems normally used for plate manufacture. A densitometer with a 1/6-in.-diameter aperture was used to measure film density. The plate center was used as one standard and the frame as another; the variation in density across the plate was plotted. The system provided a good measure of density variances and an excellent plot of core end tapers. Gamma counting was also used as a homogeneity measurement technique on some development plates. The system worked well, and is considered more accurate than the film density system on a point basis. However, the radiograph film density method meets process requirements and was selected as the primary homogeneity measurement tool due to availability of equipment, the resulting visual record of entire plate, and rapid measurement of core taper.

Zy-glow liquid dye penetrant tests were used to evaluate suspected nonbonds on plate edges. The

test is good when used to locate suspect defects, but does not provide a measurement of depth of defects. All actual defects found with this technique were also located with ultrasonic techniques.

All test plates were blister tested by heating to rolling temperature for 1 hour after the completion of hot rolling. After cooling, the plates were examined for blisters and any plates having blisters in the finished plate area were considered rejects.

The standard nondestructive tests selected were the blister test, through transmission ultrasonic tests, and the x-ray radiograph with film densitometer test.

A-2.4.7 Purnima III and Kamini Fuel Plate Fabrication. Aluminum-clad Al-20 wt% ^{233}U and Al-23 wt% plutonium plate fuel subassemblies have been fabricated for the Purnima III crit-

ical facility and the Kamini research reactor.¹² The process flow sheet for the fabrication of Al-U and Al-Pu fuel plates and subassemblies is shown in Figure A-1. The main steps are as follows:

1. Preparing Al-40 U and Al-40 plutonium master alloys using aluminum and uranium or plutonium metals as starting materials
2. Remelting master alloy, dilution by adding aluminum, and casting Al-20 U and Al-23 Pu fuel alloy ingots
3. Hot rolling of fuel alloy ingots
4. Fuel alloy core preparation, picture framing, and sandwiching in aluminum plates
5. Roll bonding
6. Locating fuel alloy core by x-ray radiography

Figure A-1. Process flow sheet for the fabrication of Al- ^{233}U and Al-Pu fuel plates and subassemblies.

7. Decontamination
8. Trimming
9. Straightening and machining to final dimensions
10. Roll swaging of eight fuel plates in the grooved spacer strips
11. Encasing in aluminum cover box and riveting the coolant entry channel and gripping handle of the subassembly.

A-2.4.8 Alloy Preparation. The essential features of binary Al-U and Al-Pu alloys in aluminum-rich compositions are analogous and are summarized in Table A-2.

The increasing divergence between the solidus and the liquids of the hypereutectic Al-U and Al-Pu alloys imparts a pronounced tendency to macrosegregate, especially during slow cooling of the ingots, and leads to the formation of coarse columnar grains of UAl_4 or $PuAl_4$ by peritectic reaction. The UAl_4 and $PuAl_4$ phases are brittle and are responsible for severe cracking of the ingots during rolling. This problem is avoided by addition of small (1 to 2 wt%) amounts of zirconium during preparation of the master alloy.

The starting materials used for alloy preparation were nuclear-grade aluminum pieces, uranium or plutonium metal buttons, and zirconium sponge. The aluminum, plutonium or uranium, and zirconium were loaded in the ratio of 58:40:2 by weight in a yttria-coated graphite crucible. The crucible was heated to 1523 K under a vacuum of 10 Pa in a vacuum induction furnace (5 kHz) housed inside a glove box, inductively stirred for 20 minutes, and poured into an alumina-coated graphite mold having four bores. The recovery was 95 to 98 wt% of the initial charge.

The master alloy was diluted to the required composition by adding nuclear-grade aluminum and remelting the charge in a yttria-coated graphite crucible using the same induction furnace. The fuel alloy ingots were cast in split-type, alumina-coated graphite or surface-oxidized aluminum

molds with twin cavities. The graphite mold often led to a deep shrinkage cavity that adversely affected the recovery of the alloy. This problem was avoided with aluminum molds.

A-2.4.9 Rolling of the Fuel Alloy. The Al-U-Zr and Al-Pu-Zr slabs were soaked at 800 K for 30 minutes in a resistance heating furnace attached to a glove box housing a two-high reversible rolling mill. The rolls were preheated to 523 to 573 K to avoid chilling of the ingots during hot rolling. Silicon oil was very effective in preventing the alloys from sticking to the roll during the hot rolling. The ingots were reduced to 4 mm in four stages with intermittent soaking at 800 K for 30 minutes. The hot-rolled strips were finally cold rolled to a thickness of 3.2 mm and subjected to x-ray radiography to evaluate their macrohomogeneity.

A-2.4.10 Picture Framing of Fuel Alloy Core and Roll Bonding. The Al-U and Al-Pu fuel alloy core pieces, aluminum frame, and aluminum cover plates were degreased in trichloroethylene (TCE), followed by chemical treatment in a NaOH bath, neutralization in dilute nitric acid, washing in demineralized water, and drying. Next, the fuel core was fitted into the aluminum picture frame and sandwiched between the aluminum cover plates by tack welding.

The aluminum-clad fuel sandwiches (6.5 mm thick) were soaked at 700 K for 45 minutes and hot rolled in a two-high reversible rolling mill to 2-mm-thick fuel plates in three successive passes without intermittent heating. The rolls were heated to 573 to 623 K, and silicon oil was used as lubricant. The first pass established intimate contact between the mating surfaces of the plates of the fuel sandwich. The two subsequent passes caused bonding of the mating surfaces by plastic deformation.

A-2.4.11 Annealing and Blister Testing of Roll-Bonded Fuel Plate. The roll-bonded fuel plates were annealed at 673 to 773 K for 30 minutes. The annealing treatment revealed non-bonded areas by forming blisters due to the expansion of entrapped gases in these locations.

Table A-2. Relevant features of Al-U and Al-Pu systems.

Features	Al-U	Al-Pu
Congruen. melting phase	UAl ₂	PuAl ₂
Peak temperature of the liquids and the melting point of congruent melting phase (K)	1895	1813
Peritectic reaction temperatures (K) and phases		
L(Al-64U)+UAl ₂ UAl ₃	1625	—
L(Al-70 Pu) + PuAl ₂ PuAl ₃	1675	—
L(Al-15.5 U) + UAl ₃ UAl ₄	1005	—
L(Al-33.2 Pu) + PuAl ₃ PuAl ₄	1188	—
Lowest temperature of the liquidus (K)	919	925
Eutectic composition	13 wt% U	12.6 wt% Pu
Range of solidification (X)		
Al-40 U	800	—
Al-40 Pu	—	650
Al-20 U	470	—
Al-23 Pu	—	430
Nucleating phase at the start of solidification		
Al-40 U	UAl ₃	—
Al-40 Pu	—	PuAl ₃
Al-20 U	UAl ₃	—
Al-23 Pu	—	PuAl ₄
Solid solubility in aluminum (wt%)		
At peak solvus temperature	0.06	0.05
At 623 K	0.04	0.025

A-2.4.12 Decontamination of Aluminum-Clad Fuel Plates. The fuel plates were degreased in TCE and subjected to chemical treatment to remove smearable and nonmearable alpha-particle (from plutonium or ²³³U) contamination and to control the thickness of the fuel plates within the specified limit.

The fuel plates were dipped in NaOH (100 g/l) bath for a few minutes to remove the contaminated aluminum layers and treated with 30% HNO₃ + 2% HF solution for 30 seconds to dissolve any uranium- or plutonium-bearing particles on the surface of the clad. Finally, the fuel

plates were washed with demineralized water, cleaned with methanol, and dried.

A-2.4.13 Core Location by X-ray Radiography and Trimming. The roll-bonded fuel plates were subjected to x-ray radiography to reveal the outline of the fuel alloy core for shearing to final size in the subsequent step. From the radiograph, the necessary aluminum margin was marked, and the outline was transferred onto tracing paper. The paper template was accurately positioned over the fuel plate and trimmed with a hand shear.

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The surface waviness and undulations of the rollbonded fuel plates were straightened by placing them between a pair of electrically heated (520 K) brass plates and applying a pressure of 25 to 30 MPa with a hydraulic jack.

A-2.4.14 Roll Swaging of Fuel Plate. A novel swaging tool was developed to lock the fuel plates into the grooves of the spacers of the sub-assemblies. This tool consists of a pair of self-locating profiled rolls fitted into the contoured recesses of a 5-mm-thick steel plate. A blind slit along the centerline of this plate holds a wedge-like arrangement. The distance between the swaging rolls is changed by adjusting this wedge to achieve the required depth of penetration during the swaging action. The profile of the rim of the rolls and the contour in the recesses of the steel plate are designed for (a) precise self-location of the rolls, (b) movement and rotation of the wheels

for swaging action, and (c) ease of withdrawal after swaging.

The eight fuel plates to be assembled are first positioned in the three pairs of the grooved spacer strips and then transferred onto a fixture mounted on the tool carriage of a bench lathe while the swaging tool is fixed to its tail stock. The swaging action is initiated when the tool is introduced into one of the gaps between the fuel plates in a controlled fashion. The sharp rim of the swaging rolls digs into the wider grooves of the spacer strips. Thus, the ridges of the grooves flow plastically onto the fuel plates and lock them in position. The swaged joint is further strengthened by repeating this action in succession. After completing the swaging operation in the first two pairs of spacer strips with respect to all eight fuel plates, the fixture is disengaged and the ends are reversed to approach the last unswaged pair of spacer strips.

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