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Control of civilian plutonium inventories using burning in a non-fertile fuel

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Abstract

The increasing inventories of plutonium generated by commercial nuclear power production represent a potential source for proliferation of nuclear weapons. To address this threat we propose separating the plutonium from the other constituents of commercial reactor spent fuel and burning it in a non-fertile fuel based on a zirconium dioxide matrix. The separation can be performed by the Purex process currently in use, but we recommend development of a more compact separation technology that would produce less secondary waste than currently used technology and would allow for more stringent accounting of plutonium inventories. The non-fertile fuel is designed for use in conventional light water power reactors and does not require development of new reactor technology.

1. Introduction

Nuclear energy has been used to generate electricity commercially since the early 1960s. Development of nuclear power stations was carried out rapidly in North America, with 72 licensed reactors generating 12% of the electricity produced in the US in 1979 [1]. Nuclear power growth in the US slowed during the 1970s and 1980s because of a number of factors including increased cost of reactor construction and operation, public concerns over reactor safety, and uncertainties about the methods available to dispose of spent nuclear reactor fuel. In Europe, development of nuclear power followed a path similar to that in the US, but resulted in a much larger fraction of the electrical energy generation by nuclear power in some countries [2].

Countries in Latin America, Asia and along the Pacific Rim started development of nuclear power later, but will become increasingly important users over the coming years. Spent fuel discharges in Asia, Africa, and Latin America are expected to increase from 2% to 7% of world-wide discharges from the 1980s to the 2000s, while those from the Pacific Rim (Japan, Taiwan, and South Korea) are expected to increase from 11% to 15% of total discharges [3]. Most of these countries are rapidly developing their industrial base and are in need of large growth in their electric power production capability to supply industrial needs as well as to improve the standard of living of their populations. If future world-wide energy growth is to occur without significant increases in release of greenhouse gases and atmospheric pollutants, nuclear power must play an important role in many of these developing countries.

Nuclear power generation is presently dominated by the use of light water reactors (LWR), with annual spent fuel discharges of about 5000 t, which is about 50% of total spent fuel discharges from all reactor types [3]. The Canadian-designed heavy-water-moderated reactors (CANDU) account for about 20% of spent fuel discharges worldwide, but produce only about 10% as much energy as the LWRs. Other reactor types, which use different fuel forms, account for about 30% of worldwide fuel discharges [3]. These proportions are expected to remain relatively stable over the next 15 years.

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The spent nuclear fuel contains non-fissile ^{238}U, residual ^{235}U, fission products produced when energy was released by splitting ^{235}U into two fission product species (plus some neutrons), and higher atomic number actinides formed by capture of neutrons by ^{238}U and subsequently formed products of neutron capture and radioactive decay. It is through this neutron capture process that plutonium is formed in the reactor fuel. Some of the ^{239}Pu formed in the fuel subsequently fissions inside the reactor and adds to the energy produced by the fuel. At the end of burning of normal LWR fuel, the spent fuel contains about 0.5% ^{239}Pu and about 1% total plutonium [4]. At discharge, CANDU reactor spent fuels have produced considerably less energy per unit mass of fuel and contain much less total plutonium. The CANDU fuel, however, contains a higher proportion of its plutonium as fissile ^{239}Pu because of its lower burnup.

Total plutonium discharged from commercial reactors world-wide is expected to rise from approximately 650 t at the end of 1990 to almost 1400 t by the end of 2000 [3]. This plutonium is and will be held in two main forms: (a) intact spent fuel destined for direct geologic disposal and (b) plutonium separated from spent fuel by reprocessing of the fuel. The amount of plutonium separated from spent fuel by reprocessing is expected to reach approximately 300 t by the end of 2000; this should be compared with the total of weapon-grade plutonium in the world, which is estimated to be about 260 t [3]. In addition to planning for disposition of weapon-grade plutonium, we must plan for the control and disposition of plutonium arising from commercial power generation.

Reprocessing plants presently in use are based on the Purex extraction process developed in the US in the late 1940s and early 1950s. This process involves an organic liquid extraction from a nitric acid solution of dissolved spent fuel and generates considerable volumes of secondary low and intermediate level radioactive wastes. In addition, plutonium contained in waste solutions or held on cladding from which the fuel was dissolved can amount to 0.5 to 1.5% of the plutonium in the spent fuel. If a country wanted to divert plutonium for clandestine use, the analytical uncertainties associated with the undissolved fuel on the cladding and the trace plutonium in the waste streams are sufficient to hide the diversion despite strict application of international safeguards measures.

The energy content in plutonium is a potential asset given a cost-effective reprocessing cycle and adequate safeguards control. We propose a fuel cycle that would separate plutonium from spent fuel using electrochemical means and then use the plutonium in a fuel based on zirconium dioxide. This fuel would be burned in standard light water reactors and then disposed of in the same manner now intended for uranium dioxide-based fuels. The reduction in the volume of spent fuel requiring deep geologic disposal would help offset the cost of plutonium separation and fuel fabrication.

2. Electrometallurgical processing

We propose electrometallurgical (EM) processing as an alternative to the separation of Pu from spent fuel by the Purex process. The reason for this is that the EM process requires a much smaller plant size than Purex, generates much less secondary waste, and allows for greater accuracy in the accounting of plutonium and transuranic element inventories.

The EM process was originally developed to facilitate rapid recycling of fuel from the Integral Fast Reactor (IFR) [5,6]. The IFR is a metal-fueled, sodium-cooled, reactor that has an integral EM process facility that allows very short-term fuel recycling. The heart of the EM process is an electrorefiner [7] that operates with a molten salt electrolyte to separate uranium from fission product and transuranium (TRU) elements. The metal fuel is chopped and placed in the anode compartment of the electrorefiner, and a potential is applied between the anode compartment and a steel cathode. Pure uranium is deposited on the cathode, while the fuel dissolves at the anode. The chemically active fission products, such as cesium, strontium, iodine, etc., uranium, and the TRU elements dissolve into the molten salt, and the noble metal fission products remain in the anode compartment. The TRU elements accumulate in the molten salt and are recovered periodically using a liquid cadmium cathode. While the TRU elements will not deposit as solid metals on a steel cathode, the cadmium reduces their chemical activity sufficiently that they will deposit in the cadmium as, for example, $PuCd_6$. All of the TRU elements behave similarly in this system, so no TRU separations occur and, in fact, are not possible. The rare earth elements are partitioned between the molten salt and the cadmium cathode.

Two types of radioactive waste are produced by the EM process: a metal waste form [8] that includes the noble metal fission products dissolved in a metal matrix made from the fuel cladding, and a ceramic waste form [9] that includes electrorefiner salt with its fission product content absorbed in zeolite and hot-pressed together with a glass frit. Early testing of these waste forms indicate that their performance should be acceptable for disposal in a geologic repository for high-level radioactive waste.

While the EM process was originally designed for processing metallic fuels, a modification of the process was developed during the early 1990s [10] to extract TRU elements from light water reactor (LWR) spent fuel for use as fuel for the IFR. For this purpose, the EM process was modified by adding a head-end reduction step to convert the oxide spent fuel to metals that could be introduced directly into the electrorefiner. The process flow sheet is shown in Fig. 1 and the mass balance for each of the process steps is included in Table 1.

In a large-throughput plant, the LWR spent fuel assemblies would be introduced into an inert-gas-filled, shielded cell and chopped or shredded into small pieces of 1 to 2

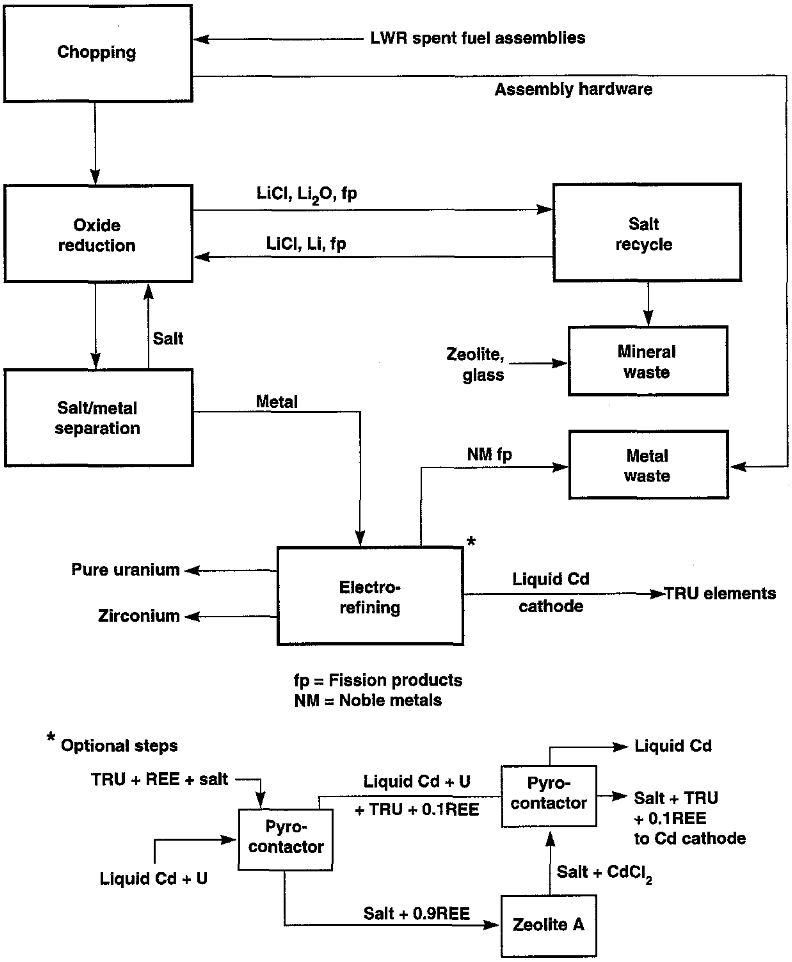

Fig. 1. Electrometallurgical treatment process for light water reactor fuel with zirconium recovery for use as fuel matrix.

cm characteristic dimensions. During the chopping operation, the fission gases in the plenum of the rod, including xenon and krypton, would be released to the shielded cell atmosphere. Cryogenic distillation could be used to separate and collect the xenon and krypton for storage until the krypton has decayed sufficiently for release. The chopped fuel would be placed in baskets that carry the fuel, cladding, and assembly hardware through the process.

In the reduction step, the fuel baskets are immersed in liquid LiCl at 650°C and lithium metal is added. Most of the spent fuel oxides are converted to metals. Important exceptions include the alkalis and alkaline earths, which are converted to chlorides and dissolve in the salt. Some of the rare earth fission products remain as oxides, which are insoluble in the salt and remain in the fuel basket, while others form complex oxides with lithium that are soluble in the LiCl. Other fission products, including iodine, selenium, and tellurium, form compounds with lithium that are soluble in the LiCl. The actinide elements and noble metal fission products are converted to metals and remain in the fuel basket. Extensive experiments have shown [11] that complete reduction of the actinide elements is achieved and they are not dispersed in the salt phase.

The lithium that reduces the fuel to metal becomes Li_2O that dissolves in the LiCl. The solubility of Li_2O in LiCl is limited to about 3.3%; therefore, the salt must be processed to remove the Li_2O before further reductions can be done. The Li_2O is decomposed electrochemically using an inert anode at which oxygen gas is evolved. Lithium metal is produced at the cathode for recycle to the next reduction cycle. The soluble fission products accumulate in the LiCl, so a small waste stream is withdrawn to control the steady-state level of these fission products during processing.

The fuel baskets are removed from the LiCl and transferred into the electrorefiner, where they become anode baskets by application of a potential between the baskets and a steel cathode. The electrorefiner operates at 500°C, and the electrolyte is the LiCl–KCl eutectic composition with 1 to 2 mol% UCl_3 added as the ionic transport

Table 1
Simplified mass balance for EM process applied to LWR spent fuel based on one tonne initial heavy metal. All units are kg

Substance	Oxide reduction				Electrorefining		
	fuel feed	from salt recycle	to salt electrolysis	to electrorefining	to U product	to TRU product	to metal waste
Uranium	955	0.091	0.095	955	947.91	2.82	4.27
Plutonium	8.47	8.10E – 04	8.50E – 0.4	8.47		8.47	
Americium	0.87	8.30E – 05	8.70E – 05	0.87		0.87	
Neptunium	0.54	5.20E – 05	5.40E – 05	0.54		0.54	
Curium	0.05	4.80E – 06	5.00E – 06	0.05		0.05	
Noble metals [a]	12.29			12.29			12.29
Rare earths	10.36		7.77	2.59		2.59	
FPa	5.63	489	494				
FPb	0.79		0.79				
Oxygen	133.84						
Li_2O		12.98	259.6				
Lithium		121.46	7.01				
Cladding [b]	267.06			267.06			267.06

	Salt electrolysis		
	from reduction	to recycle	to ceramic waste
Uranium	0.095	0.091	3.83E – 03
Plutonium	8.50E – 04	8.10E – 04	3.40E – 05
Americium	8.70E – 05	8.30E – 05	3.50E – 06
Neptunium	5.40E – 05	5.20E – 05	2.20E – 06
Curium	5.00E – 06	4.80E – 06	2.00E – 07
Rare earths	7.77		7.77
FPa	494	489	5.63
FPb	0.79		0.79
Li_2O	259.6	12.98	0.13
Lithium	7.01	121.46	0.064
Zeolite			857.5
Glass			535.9

FPa = fission products that form compounds with Li and dissolve in LiCl + the LiCl. FPb = fission products that form compounds with lithium and decompose at the oxygen anode during electrolysis.

[a] Noble metals = fission products more noble than U.

[b] Approximately 250 kg Zr could be separated by separate electrorefining.

medium. When metal fuels are electrorefined, the chemically active fission products, such as cesium, strontium, and the rare earths, dissolve into the electrolyte at this step; however, in the case of processing LWR oxide fuels, these fission products are removed to the salt phase during the oxide reduction step. The fraction of rare earth elements that partitioned to the metal phase as oxides during the lithium reduction step will react with the UCl_3 to form rare earth chlorides and UO_2. This small quantity of UO_2 will remain in the anode basket along with the noble metal fission products to become part of the metal waste stream.

As the uranium and TRU elements are dissolved at anodic potential, pure uranium is deposited at the cathode. The TRU element tri-chlorides are thermodynamically more stable than UCl_3 and, therefore, metallic TRU elements cannot deposit with the uranium. The TRU tri-chlorides remain in solution in the electrolyte salt. When sufficient TRU has collected in the electrolyte so that the TRU/U ratio is greater than two, the TRU can be removed from the electrolyte using a liquid cadmium cathode. Deposition of TRU metals in the liquid cadmium cathode is possible because the TRU elements form intermetallic compounds, such as $PuCd_6$, while uranium does not form the intermetallic compound above 472°C. Therefore, uranium has an activity of unity in the cathode, while the TRU elements have activities in the cadmium of about 10^{-3} to 10^{-4}, thus favoring deposition of the TRU metals as intermetallic compounds. The TRU metals are recovered by distilling the cadmium for recycle and melting the TRU product to produce a metal ingot.

The presence of some rare earth elements (REE) in the TRU product was seen as an advantage in the IFR flow sheet because it reduced the possibility that material would be attractive for weapons use. With the non-fertile fuel discussed below, the REE content reduces the reactivity of the fuel after too short a burning time and reduces strongly the burnup of the fuel. The REE content of the TRU product can be reduced to about 2 wt% from the 17 wt%

shown in Table 1 by using a high-temperature centrifugal contactor (pyrocontactor) step. This involves a counter flow of molten salt with TRU + REE in one direction and liquid Cd with some U in the other direction through a series of centrifugal contactors. The U reduces the TRU plus some REE to metal that dissolves into the Cd phase. The salt can then be passed through zeolite A to remove the REE. The clean salt then can be passed through another pyrocontactor with a counter flow of Cd + TRU + residual REE versus salt + $CdCl_2$, which oxidizes the TRU + REE content out of the molten Cd and into the salt. This salt with lower REE content would then be processed using the Cd cathode.

The LWR fuel cladding is normally Zircaloy, which is an alloy composed of about 98.6% zirconium and 1.4% tin. Since the fuel matrix in this concept for plutonium burning is zirconia, it may be advantageous to use zirconium from the cladding to make the fuel. Uranium and zirconium can be electrotransported in the same electrorefiner at different potentials. It has been shown [11] that uranium can be electrotransported in the presence of zirconium, without transporting zirconium, when the cell potential is maintained below 0.5 V. By moving the potential up to 1.0 V, zirconium can be electrotransported as well. Deposition of pure zirconium would probably require a separate electrorefiner with a salt phase containing no UCl_3 in the electrolyte. It is feasible to use this process to separate zirconium from the LWR cladding to make matrix zirconia for the new fuel.

In the IFR fuel cycle, the metal TRU product would be used to fabricate new metal fuel; however, fabrication of oxide fuel would require that the metal product be oxidized and mixed with zirconia and other oxide fuel components. The mixed oxides would then be pressed and sintered to make pellets for fuel fabrication.

The fuel baskets, which became anode baskets in the electrorefiner, would be melted, along with noble metal fission products and any cladding material not processed to be used for new fuel, to make the metal waste form. The corrosion rate of this metal waste form is extremely low, having been measured at about one millimeter per 1000 years.

A ceramic waste form is used to incorporate the fission products that reside in the molten salts of the reduction step and the electrorefiner. The molten salts, along with the soluble fission products, are absorbed in the alpha cage of zeolite A. The resulting free-flowing dry zeolite powder is mixed with a suitable borosilicate glass frit and hot pressed to make glass-bonded zeolite. This ceramic (or glass-ceramic) waste form is a very fine-grained (1 μm particle size), two-phase system having zeolite grains dispersed in a glass matrix. The leach rate of this waste form has been found [12] to be comparable to that of 'standard' borosilicate glass planned for disposal of high-level waste from Purex processing of spent fuel.

A study was done in 1993 to determine the size of plant required to achieve a throughput of three metric tons of heavy metal per day (MTHM/d) of LWR spent fuel [13]. This study was based on the equipment concepts available at that time. Major equipment innovations have been made since that time, which will result in significant reductions in hot cell space requirements. The 1993 study estimated that 600 m^2 of process cell area would be required for a 3 MTHM/d throughput. This throughput could handle the spent LWR fuel from fifteen 1000 MWe plants. Other support area, including fuel receiving and storage, services, and product storage would, of course, be required in accordance with normal hot cell operations. The output from such a processing plant would be about 30 kg TRU/d, for an annual production of six MTHM. The equipment is designed so that smaller plants with lower throughput can be built and run without undue economic penalty.

3. Non-fertile fuel for burning plutonium

A non-fertile fuel, also called inert-matrix fuel, is one that does not allow the possibility to create more plutonium under irradiation in the reactor. The fuel must contain well-balanced proportions of inert matrix and fissile materials, as well as neutron absorbers (burnable poisons) that will control the reactivity of the fuel during the irradiation cycle.

A new fuel was recently suggested for light water reactors by a group at the Paul Scherrer Institute (PSI) [14,15]. They focused attention on oxides because they are chemically more resistant than metals. The elements considered for the inert matrix and the neutron absorber components were Be, Mg, Ca, Sr, Al, Y, rare earth elements (La to Lu), Si, Ti, Zr, Hf, Cr, and Sn.

The criteria for inert matrix selection were:

– thermal neutron absorption cross section smaller than 0.2×10^{-24} cm^{-2},

– phase stability over a large temperature range and under severe irradiation doses,

– inertness with regard to transmutation products, cladding, and reactor water,

– acceptable thermophysical properties (thermal conductivity, thermal expansion coefficient),

– reasonable cost,

– ease of integration into existing technology.

In addition, if the fuel is to be used in a 'once-through' fuel cycle, the following properties are required:

– minimum radionuclide release from the matrix under storage and disposal conditions,

– good durability under geologic disposal conditions,

– long term stability under radiochemical, mechanical, chemical, and thermal changes,

– minimum accessibility of actinides to diversion.

Among the inert matrix candidates, only ZrO_2, along with trivalent rare earth oxides and CeO_2 were initially selected because they form solid solutions with actinide dioxide compounds (AnO_2). Since none of the other proposed inert materials have this property, and since Ce poses difficulties because it can have more than one valence state, stabilized ZrO_2 was selected. In its stabilized form, this material has excellent thermodynamic properties, which are comparable to those of UO_2 and $(U, Pu)O_2$ (i.e., mixed oxide fuel, MOX).

Pure ZrO_2 is not a good candidate for the inert matrix because it is monoclinic at room temperature and this crystal structure has a limited stability region, easily transforming into other phases. Also, pure monoclinic ZrO_2 has limited capability for solid solution with additives of interest for the fuel. The monoclinic structure of ZrO_2 can be transformed into a cubic structure by a variety of means such as increasing temperature, increasing chemical potential by adding chemical stabilizers, increasing physical energy by phase size restriction, and by nuclear irradiation. For this reason, the cubic phase with solid solution already present through the use of stabilizer elements was chosen.

ZrO_2 stabilized with 10 at.% Y in the form of Y_2O_3 was selected as the basis for our fuel because of its high melting point (~ 3000 K) and because once the solid solution is created, there is no phase transition from room temperature to its melting point [16,17]. The material is stabilized in a cubic structure as a solid solution that is able to dissolve additional components that would be generated from actinide fission and transmutation. The zirconia solid solution is essentially inert with respect to the Zircaloy cladding and hot water. The aqueous solubility of ZrO_2 at 100 to 200°C is only of the order of 10^{-10} M [18]. The absorber material chosen for the case of pure plutonium as the fissile material was 5 at.% Er in the form of Er_2O_3 because of its excellent neutronic behavior, which allows optimal burn-up of Pu over five reactor cycles and because the presence of erbia further stabilizes the cubic structure, complementing the effect of yttria [16].

The final reference fuel selected for burning pure plutonium was $(ZrO_2)_{0.75}(0.5Y_2O_3)_{0.1}(0.5Er_2O_3)_{0.05}(PuO_2)_{0.1}$, which is shown in the phase diagram in Fig. 2 as point A. For simplicity, this composition will be written as ZrO_2–10%Y_2O_3–5%Er_2O_3–10%PuO_2 in the future. This fuel has a cubic structure and forms a solid solution in which ion conductivity is rather large, allowing charge reorganization during irradiation. Since other actinide dioxides behave chemically in a manner similar to Pu, we may include Np, Am, Cm, and U in substitution for Pu. In this case the mixed actinides will be designated $TRUO_2$. Both fuel systems, ZrO_2–Y_2O_3–Er_2O_3–PuO_2 and ZrO_2–Y_2O_3–Er_2O_3–$TRUO_2$, have been studied extensively at PSI using a range of actinide loadings. For loadings less than 10 at.% TRU, the balance is made up by additional ZrO_2.

Paratte et al. [15] calculated the comparative performance of the zirconia-based fuel with that of mixed U–Pu oxide fuel under the same reactor conditions for a burn-up of 60 MWd/kg Pu from the LWR as measured in the MOX fuel. We now extend this comparison to zirconia-based fuels containing pure Pu obtained by Purex reprocessing of first cycle UO_2 fuel and to zirconia-based fuels containing the mixed actinides and REE obtained by reprocessing using the electrochemical methods discussed in the previous section. The calculations of actinide burning were done assuming standard PWR fuel geometry, with solid pellets of radius 0.4565 cm, cladding external radius 0.54576 cm, pitch of 1.50582 cm. Both cladding radius and pitch were slightly increased to take into account the guide tubes of the fuel assembly. In practice, the zirconia-based fuel would probably use annular pellets [14]; this does not significantly affect the results of the present calculations.

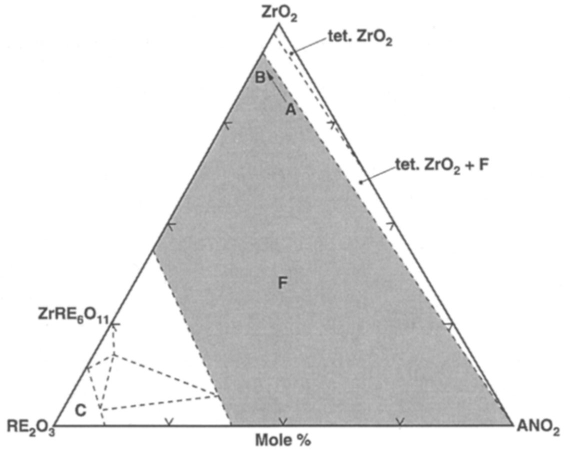

Fig. 2. Tentative phase relations of the ternary ZrO_2–RE_2O_3–AnO_2 system at 1400°C. F = fluorite structure; tet. ZrO_2 = ZrO_2 with tetragonal structure; C = rare earth C-type structure; An = Pu or TRU; RE = Er, Y, or REE from TRU product. Point A is the initial composition and point B is the composition after five reactor burning cycles.

The input parameters for the Pu and minor actinide (MA) compositions are given in Table 2. For MOX fuel calculations, a fuel with 7.0 wt% plutonium mixed with depleted uranium (0.25% ^{235}U) was used. This MOX fuel had a theoretical density of 10.17 g/cm^3 and a total Pu density of 0.7089 g/cm^3. For the zirconia-based fuel with Pu from Purex reprocessing, the assumed fuel composition is total Pu = 0.788 g/cm^3 and Er_2O_3 = 0.143 g/cm^3 in solid solution with zirconia, with a theoretical density for the fuel of 6.48 g/cm^3. For the zirconia-based fuel with mixed TRU coming from the electrochemical separations, the total actinide concentration is assumed to be 1.076 g/cm^3 including Pu, U, Np, Am and Cm in oxide form, which gives the same density of Pu as for the Purex Pu case. A net 0.02196 g/cm^3 of REE is included; this represents the fraction of fission product REE recovered in the metal TRU product when the pyrocontactor is used. With this composition, the reactivity of the fuel is low enough so that no erbium is needed. The theoretical den-

Table 2
Actinide input parameters for fuel calculations in wt% of total Pu or % of total minor actinides (MA)

Plutonium	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
	3.79	49.08	26.54	11.66	8.93
Minor actinides	^{237}Np	^{241}Am	^{242m}Am	^{243}Am	
	50.55	25.55	0.07	16.61	
	^{243}Cm	^{244}Cm	^{245}Cm	^{246}Cm	
	0.04	6.52	0.57	0.09	
Uranium	^{235}U	^{236}U	^{238}U		
	0.6	0.7	98.7		

Rare earths: Y, La, Ce, Pr, Nd, Sm, Eu, and Gd with abundances typical for LWR fuel with burn-up of 60 MWd/kgU.

sity of the TRU fuel including ZrO_2 at 5.44 g/cm^3 is 6.52 g/cm^3.

In the calculations, the temperature during irradiation is assumed to be 600°C. From a neutronic point of view the results would not be very different if the actual temperature were higher. The cell calculation used a constant power density of 90.7 MW_{th}/m^3, which is typical for a modern PWR. Isotopic densities were calculated after 1500 days of irradiation. The reactivity of the reactor cell is plotted as a function of time in Fig. 3. Reactivities of all three fuels are comparable up to 1000 days, but those of the zirconia-based fuels decrease rapidly after 1000 days of irradiation. This occurs because the MOX fuel is generating more fissionable Pu while it is burning the original input Pu. After 1000 days the reactivity of the zirconia-based fuel becomes too low to function alone in the reactor; however, this can be compensated for by inserting fresh fuel assemblies into the reactor.

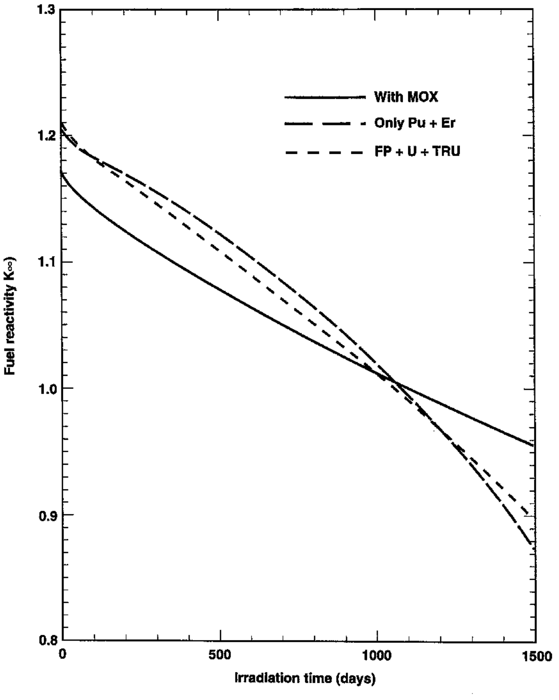

Fig. 3. Reactivity of fuel as a function of irradiation time.

Table 3 gives the results of the burn-up calculations. The fissile isotope ^{239}Pu after 1500 days of irradiation is reduced to 32% of the residual Pu in the case of MOX fuel, while total Pu at the end of burning is 69% of the amount originally loaded into the reactor. For the Pu–zirconia fuel, ^{239}Pu is reduced to 5% of the final Pu and the total Pu becomes only 34% of that originally loaded. With the TRU–zirconia fuel, ^{239}Pu comprises 11% of the final Pu and the amount of total Pu is reduced to 46% of that initially loaded. Almost no Np is created during use of the zirconia-based fuel, and the amounts of Cm and Am created in both zirconia-based fuels and MOX through transmutation reactions are comparable. Degueldre et al. [14] calculated cases for use of zirconia-based fuels that included weapons-grade Pu. In this case only 4% of ^{239}Pu and 23% of total initial Pu remained after 1300 days of irradiation.

Table 3
Comparison of final plutonium and minor actinide contents relative to amounts present at beginning of life and isotopic composition in % for Pu and minor actinides (MA). Note: for MA isotopes, data are given as ^{xyz}MA/ΣMA. Conditions calculated were for 1500 days of irradiation at a power density of 90.7 MW_{th}/m^3 in a cell typical of a modern PWR

Element/isotope	MOX fuel	ZrO_2–RG Pu	ZrO_2–TRU
Final concentration/initial concentration for actinide elements			
U	0.964	na	0.821
Pu	0.688	0.337	0.461
Np	na	na	0.371
Am	na	na	0.748
Cm	na	na	4.496
Total MA/TRU$_0$	0.059	0.059	0.103
Plutonium isotopic composition in %			
^{238}Pu	4.2	6.3	14.3
^{239}Pu	32.1	5.5	10.8
^{240}Pu	31.1	33.6	31.4
^{241}Pu	17.0	18.1	17.5
^{242}Pu	15.6	36.5	25.9
Minor actinides isotopes as % to total MA			
^{237}Np	4.2	–	22.5
^{239}Np	1.5	–	–
^{241}Am	18.3	7.5	8.4
^{242m}Am	0.5	0.2	0.2
^{243}Am	43.5	47.8	29.5
^{242}Cm	3.7	4.8	4.0
^{243}Cm	0.1	0.2	0.2
^{244}Cm	25.0	35.6	30.5
^{245}Cm	2.9	3.1	3.5
^{246}Cm	0.3	0.8	1.1

Table 3 clearly shows that the efficiency of destruction of both ^{239}Pu and total plutonium in the zirconia-based fuel is far greater than for the MOX fuel. This is because there is little or no uranium in the zirconia-based fuel, so no in-growth of new plutonium occurs. The final concentration of plutonium in the case of reactor grade plutonium in the zirconia-based fuel is about 4 wt%, which is much higher than in conventional light water reactor fuel (about 1%); however, it contains very little of the fissile ^{239}Pu isotope. This is a distinct advantage with respect to waste disposal performance analysis because it will simplify considerations related to the potential for criticality to occur in the repository over long periods of time.

The in-pile performance of nuclear fuel pins is also governed by the thermophysical properties of the pellet material. Thermal conductivity is a very important parameter because it determines the fuel temperature for a given energy generation rate. It would be desirable to have the thermal conductivity for the zirconia-based fuels be as high as those of standard UO_2 and MOX fuels. If this cannot be achieved, the fuel centerline temperatures would exceed those generally accepted for standard reactor fuels. Since the thermal conductivity of stabilized zirconia is of the order of 1.5 to 2.0 W/m K, and since fissile and neutron absorber materials would account for only about 15% of the composite fuel, we cannot anticipate a thermal conductivity higher than 2.0 W/m K for the fuel. Therefore, the design of the fuel pellet must be modified to avoid temperatures that are higher than normal. One method to achieve this would be to use annular fuel pellets. There are also other, less attractive, methods for reducing fuel inner temperatures such as reducing the diameter of the fuel pins, which implies a corresponding increase in the number of pins, and using a zebra configuration of fuel pellets in the pins, in which fuel pellets are alternated with dummy pellets of material with a higher thermal conductivity.

In order to estimate the fuel temperature as a function of radius to be expected at the beginning of life in the reactor, calculations were carried out for both solid and annular pellets using the PINTEMP code. Results for a linear power of 400 W/cm and a thermal conductivity of 2.0 W/m K are presented in Fig. 4. This clearly shows the advantage of the annular pellet, for which the peak temperature is 600°C lower than for the solid pellet. An annular design with a diameter ratio of 0.5 is acceptable, using a pre-fill of inert matrix material in the hole to avoid the potential for fuel fragments to fall into the hole during preparation or use of the fuel.

Zirconium is a by-product of the nuclear industry. Specifically, the spent fuel cladding material constitutes a significant radioactive waste stream when fuel is reprocessed using the Purex process. This zirconium could easily be recovered if the electrochemical reprocessing method is used. Used cladding material or zirconium can be dissolved in nitric acid when traces of fluoride are added. Yttria and erbia are available at reasonable price from commercial rare earth element suppliers.

4. Irradiation testing

Fuel pellets for radiation testing are currently being prepared by a wet mixing process using nitrate solutions of each element (Zr, Y, Er, and Pu). This solution can be added to a vigorously stirred solution of concentrated ammonia, which precipitates the fuel precursor as mixed oxides. The solution containing the precipitate is filtered and the precipitate is washed to remove ammonia and nitrates, and then dried. The dried oxide is milled in a zirconia bowl vessel, pelletized into the annular design pellets and sintered at 1600°C for 5 h. Pellets prepared by this method would have a porosity of less than 10% and the material would be entirely in a cubic phase. These

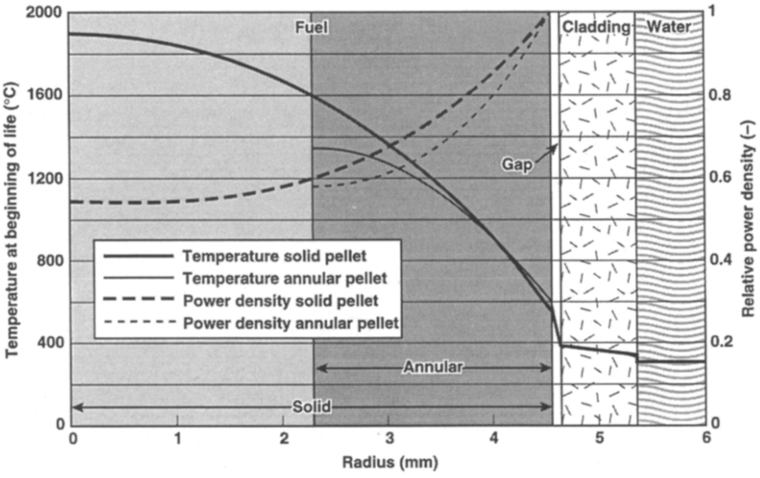

Fig. 4. Temperature profiles for solid and annular pellets at 400 W/cm linear power. Assumed thermal conductivity = 2 W/m K.

pellets could be loaded into standard Zircaloy tubes, with the central hole then filled with spheres of suitable non-nuclear material. For commercial application of the zirconia-based fuels, a dry process based on ball-milling of oxide powders would probably be used to prepare the fuel.

The PSI inert-matrix fuel program is planning an irradiation test of the zirconia-based fuel as part of the OECD Halden reactor program. PSI would fabricate test pellets using the procedure described above, but without using inert fill in the annulus of the pellet. A long-term irradiation of two types of uranium-free fuels is planned to start in 1998. The fuels will be (in cation at.%) ZrO_2–11%PuO_2 (Reactor grade)–4 to 5%$ErO_{1.5}$–10%$YO_{1.5}$ and ZrO_2–8 to 11%PuO_2 (Weapons grade)–8 to 11%ThO_2–3 to 4%$ErO_{1.5}$–10%$YO_{1.5}$. In-situ measurements of the temperature in the center of the pellets are planned so that heat transfer can be monitored. Pre- and post-irradiation analysis of fuel pellets will be done at PSI. In preparation for these irradiation tests, inert matrix materials are being tested for radiation damage resistance using accelerated heavy ion bombardment. Tests with I^- and Xe^+ have shown that the material does not lose its crystalline structure and become amorphous under heavy irradiation.

5. Fuel cycle use and safeguards control

The fuel cycle we propose would take spent fuel from LWRs, process that fuel by electrometallurgical separations, make zirconia-based TRU fuel from the separated plutonium and higher atomic number actinides and burn that fuel in a LWR. The spent fuel from 8 to 10 LWRs would provide enough TRU fuel to power one LWR. The zirconia fuel after burning would be the final disposal waste form. Because of the solid solution of U and Zr in the cubic zirconia phase, we anticipate that the fission product elements will behave in a similar fashion in the zirconia-based fuel as they do in uranium dioxide fuel. The zirconia-based fuel would have an advantage as a waste form over uranium dioxide because the zirconium will not change its oxidation state, while the uranium dioxide spent fuel is subject to oxidation and phase changes under oxidizing storage or disposal conditions.

The use of the zirconia-based fuel to close the light water reactor fuel cycle would produce a reduction in total spent fuel requiring geologic disposal if reprocessing were not carried out by a factor of 8 to 10. In the US, this would mean that no more than one high level nuclear waste repository would be needed even if nuclear power generation increased. The metal and ceramic wastes generated from the electrometallurgical separations process could be stored above ground until their activity had decreased to the levels allowed for low level waste disposal.

The electrometallurgical process produces a separated product that includes plutonium and higher atomic number actinides. While this material cannot be used directly to fabricate nuclear weapons, a small solution chemistry plant could separate the plutonium from the other actinides. For this reason, we propose that the separations and fuel fabrication activities occur at the same location and that the TRU be made into fuel as soon as it is separated. Once the fuel is made, the plutonium would be extremely difficult to recover for other uses. In addition, we believe that this fuel cycle should be run under direct supervision of an international safeguards organization such as the International Atomic Energy Agency.

6. Conclusions

Development of a non-fertile fuel based on cubic zirconia combined with a compact electrometallurgical separation of transuranium elements from spent light water reactor fuels would reduce the amount of plutonium held in storage and would use that plutonium to generate energy. An additional advantage would be that the amount of high level radioactive waste that would need disposal would be greatly reduced. The zirconia-based fuel is designed to be burned in standard LWRs, so that development of new reactor types is not needed.

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