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Safe disposal of surplus plutonium

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Abstract

About 150 tons of weapons grade and weapons usable plutonium (metal, oxide, and in residues) have been declared surplus in the USA and Russia. Both countries plan to convert the metal and oxide into mixed oxide fuel for nuclear power reactors. Russia has not yet decided what to do with the residues. The US will convert residues into a ceramic, which will then be over-poured with highly radioactive borosilicate glass. The radioactive glass is meant to provide a deterrent to recovery of plutonium, as required by a US standard. Here we show a waste form for plutonium residues, zirconia/boron carbide (ZrO_2/B_4C), with an unprecedented combination of properties: a single, radiation-resistant, and chemically durable phase contains the residues; billion-year-old natural analogs are available; and criticality safety is given under all conceivable disposal conditions. ZrO_2/B_4C can be disposed of directly, without further processing, making it attractive to all countries facing the task of plutonium disposal. The US standard for protection against recovery can be met by disposal of the waste form together with used reactor fuel. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The directive resulting from the 1996 Moscow Summit between President Clinton and President Yeltsin calls for surplus plutonium to be converted into forms resistant to reuse in nuclear weapons. Both the US and Russia plan to convert the plutonium metal (pits) and its oxide into mixed-oxide fuel for use in nuclear power reactors. Standards in the US for assuring a sufficient deterrent to recovery (the so-called ‘spent fuel standard’) [1] would be met by the radiation field provided by the fuel after burn-up in a reactor, thus requiring no further treatment prior to geologic disposal.

For plutonium residues, i.e., impure forms of plutonium not suitable for mixed-oxide fuel, the US plans to fabricate a ceramic-in-glass (can-in-canister) waste form [1–4]. First, the residues will be converted into a ceramic consisting of zirconolite/pyrochlore, brannerite, and actinide oxides [5]. Then, highly radioactive borosilicate glass will be poured into large metal containers into which smaller sealed containers of the ceramic have been placed [1]. This will occur at a defense waste vitrification plant. In this case, the radioactive glass will provide the deterrent to recovery required by the spent fuel standard.

Suitable ceramic host phases for plutonium are closely related to naturally occurring minerals such as apatite, pyrochlore, zirconolite, monazite, zircon, and zirconia. Physical and chemical properties of these minerals, except zirconia, have been reviewed by Ewing et al. [6]. Gong et al. [7] reviewed the properties of zirconia (ZrO_2) and synthesized various solid solutions $(ZrO_2)_{ss}$ as waste forms for plutonium.

The findings by Gong et al. [7] on zirconia as a waste form for plutonium constitute the technical basis of this work. Gong et al. [7] used gadolinium oxide (Gd_2O_3) to stabilize zirconia's cubic modification and Ce^{4+} (10 mol%) to simulate plutonium. Gadolinium was used because it is an efficient absorber of thermal neutrons. Uranium, an important impurity in plutonium waste and decay product of ^{239}Pu, was added along with iron, calcium, magnesium, and silicon. To demonstrate one of several conceivable methods of fabrication, oxide powders of the starting materials were cold-pressed into pellets and reaction sintered at 1400–1600°C. Homogeneous, single-phase $(ZrO_2)_{ss}$ of cubic structure was obtained.

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Here we show that addition of small amounts of boron carbide to $(ZrO_2)_{ss}$ yields a waste form that is criticality-safe under all conditions conceivable during interim storage and in a geological repository. When B_4C is used, gadolinium is not needed. Boron carbide moderates and absorbs neutrons.

2. Experimental

We have mixed yttria-stabilized zirconia (YSZ) and B_4C powders in various mass ratios and sintered the material for 40 min in argon at 1400°C under a pressure of 10 MPa. YSZ is commercially available as a powdered material with an average grain size of 1 μm. B_4C powder is also a commercial product. It had an average grain size of 7 μm. B_4C powder was ground and the average grain size was decreased to 5 μm. Both powders were mixed in a ball mill for 8 h at low speed, to avoid uncontrolled changes of particle size. Various samples were prepared with B_4C concentrations up to 6 wt%. The sintered samples were polished and investigated by scanning electron microscopy using back-scattered electrons. The sole purpose of these experiments was to prepare samples with low porosity and to show that B_4C particles are homogeneously dispersed and in good phase boundary contact with the continuous YSZ phase. Therefore, plutonium was simulated by zirconium and not by cerium as in previous experiments [7].

3. Results

Waste form compositions are listed in Tables 1 and 2. Fig. 1 shows the microstructure of the ceramic waste form. In this sample, 2 wt% of B_4C (black) are dispersed in the YSZ matrix phase with an average particle distance of about 20 μm between B_4C crystals. The microstructure is typical of all waste form compositions listed in Tables 1 and 2, except the last composition in Table 2, whose B_4C concentration (10 wt%) exceeds the experimental range (2–6 wt%). The phase boundaries are in good contact. No void space has been detected between the matrix phase (YSZ) and the dispersed phase (B_4C). The light gray areas in Fig. 1 are either B_4C particles within the YSZ phase beneath the surface or spots where flaky B_4C crystals were removed during polishing.

At higher magnification some micropores (0.1–1 μm wide) were detected. Porosity was found to depend on

Table 1
Waste form compositions and neutron multiplication factors k_{eff}; zirconia solid solution/boron carbide

Waste form composition $Zr_{0.8-x}Pu_xY_{0.2}O_{1.9} + yB_4C$				Neutron multiplication factor k_{eff}		
Pu (mol%)	Pu (wt%)[a]	B_4C:Pu (molar ratio)	B_4C (wt%)[b]	Canister filled with pellets; 50% void space		100% waste form
x		y/x	y	Void = air	Void = H_2O[a]	No void[c]
5	9.3	0.330	0.71	0.3274	0.8981	0.7031
10	17.6	0.350	1.40	0.5588	0.8860	1.0458
15	25.3	0.375	2.12	0.7356	0.8906	1.2654

[a] In $(ZrO_2)_{ss}$.
[b] In the canister.
[c] Canister surrounded by 15 cm H_2O reflector.

Table 2
Waste form compositions and neutron multiplication factors k_{eff} for double batching of plutonium; zirconia solid solution/boron carbide

Waste form composition $Zr_{0.8-x}Pu_xY_{0.2}O_{1.9} + yB_4C$			Neutron multiplication factor k_{eff}		
Pu (mol%)	B_4C:Pu (molar ratio)	B_4C (wt%)[a]	Canister filled with pellets; 50% void space		100% waste form
x	y/x	y	Void = air	Void = H_2O[a]	No void[b]
10	0.350	1.40	0.5588	0.8860	1.0458
20	0.375	2.67	0.8800	0.9129	1.4295
30	1.110	10.00	0.9034	0.6697	1.3240

[a] In the canister.
[b] Canister surrounded by 15 cm H_2O reflector.

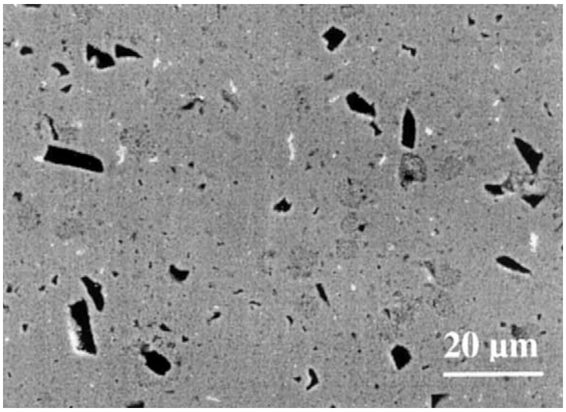

Fig. 1. Back-scattered electron image of a hot pressed ceramic (98 YSZ–2B_4C; wt%); gray matrix phase is ZrO_2 (YSZ); dispersed phase is B_4C (black); dark gray spots are either crystals beneath the surface or residues of flaky B_4C removed by polishing.

sintering conditions. No effort was made to optimize these conditions to further decrease porosity. At the relatively low sintering temperature of 1400°C, no chemical reaction between B_4C and YSZ was observed. However, at temperatures above 1000°C, sintering should take place in an inert atmosphere to avoid oxidation of B_4C.

We calculated mixing ratios of $B_4C{:}(ZrO_2)_{ss}$ to make nuclear-criticality-safe ceramics. Nuclear criticality is measured by the neutron multiplication factor k_{eff}. A system with $k_{eff} < 1$ is subcritical, with $k_{eff} = 1$ critical, and with $k_{eff} > 1$ supercritical. We define criticality safety by two criteria: (1) The neutron multiplication factor must be less than 1, if the waste form and the container are soaked in water and surrounded by it; (2) k_{eff} must be less than 1 under the conditions of the first criterion, if the plutonium concentration in the waste form is doubled. To test the effectiveness of B_4C, assumptions were made about the quantity and geometry of the waste form. The assumptions are examples showing the variation of k_{eff}. The assumptions comprise: (a) nominal plutonium concentrations 5, 10, and 15 mol% in $(ZrO_2)_{ss}$; (b) nominal plutonium concentrations accidentally doubled (double batching); (c) metal container 3 m high and 0.6 m in diameter; (d) container filled with pellets, leaving 50% void space between them or completely filled with a monolith. A particular size and shape of the pellets was not selected for this study.

Calculations were conducted with the MCNP code [8] and the results in Tables 1 and 2 verified with the DANTSYS code [9]. In the calculations, we considered B_4C as a homogeneous constituent of the solid solution. In reality, B_4C and $(ZrO_2)_{ss}$ are separate phases. B_4C is homogeneously distributed on a micrometer scale (average particle distance $\leqslant 20$ μm). Differences between the calculated and real k_{eff} are expected to be small.

Columns 1 and 2 of Table 1 show the plutonium concentrations in $Zr_{0.8-x}Pu_xY_{0.2}O_{1.9}$ in mole percent (x) and in weight percent, respectively. Column 3 shows the B_4C/Pu molar ratio (y/x). Column 4 shows the respective amount of B_4C in the waste form in weight percent (y). These additions of B_4C yield the k_{eff} values shown in column 5 for metal containers filled with the waste form as pellets, assuming 50% void space. Filling the void space and the near field around the canister with water considers the event of water contacting the waste form in the repository. This event cannot be excluded over geologic periods of time. The amount of water surrounding the canister may be unrealistically high but it is the one with the highest possible effect on k_{eff}. A cylindrical water reflector of 15 cm thickness was considered. Thicker water layers have no additional effect on k_{eff}. Column 6 shows the k_{eff} values for this scenario. To obtain these values, k_{eff} was calculated as a function of y/x. An upper limiting value of $k_{eff} \approx 0.9$ was selected for this study. Under this condition, the y values in Tables 1 and 2 represent the smallest quantities of B_4C necessary. The last column shows k_{eff} values for a canister filled with a monolith of the ceramic waste form. Even for this technically unrealistic assumption, which results in doubling of the mass of the waste form in the same volume, one obtains a subcritical system with $y = 0.71$ wt% B_4C for $x = 5$ mol% (Table 1). Higher plutonium loading leads to supercritical configurations and would require higher B_4C concentrations than given in Table 1 to achieve subcritical conditions.

Table 2 shows the results obtained, if the designed plutonium concentration in the waste form is doubled (double batching). This assumption is made for safety reasons in the framework of criticality calculations for a plutonium handling facility. Again, $k_{eff} > 0.9$ was not considered. Table 2 shows that this condition can be met for canisters filled with pellets by adding more B_4C. Canisters filled 100% with a ceramic monolith and surrounded by water would be supercritical.

Taking double batching into account for ceramics with nominal compositions listed in Table 1 requires that the respective B_4C concentrations in Table 2 are used to make the ceramics. These B_4C concentrations guarantee that all waste forms are subcritical under all conceivable manufacturing, storage, and disposal conditions. However, a properly manufactured waste form (single batch of plutonium) would have a lower k_{eff} value than shown in Table 1. A plutonium loading of $x = 15$ (30) mol% appears unrealistically high, when considering that the plutonium is associated with other constituents to be accommodated in the ZrO_2 solid solution. Hence, more realistic plutonium loading with $x = 5$ (10) or 10 (20) mol% would yield single-phase ceramic waste forms with a small amount of 1–3 wt% of B_4C dispersed in it.

Calculated neutron spectra showed that moderation in the waste forms was not very strong because of the small amount of moderator (B_4C). Neutrons are moderated, if water reaches the waste form. Comparing moderation and absorption properties and molecular masses of B_4C and Gd_2O_3 shows that the mass of B_4C to be added to the $(ZrO_2)_{ss}$ to create the same calculated k_{eff} is only 40% that of Gd_2O_3.

4. Discussion

We propose an alternative to the two-step process currently envisaged for making plutonium residues suitable for disposal. By providing a directly disposable zirconia ceramic waste form that is more durable than a zirconolite/pyrochlore ceramic, our process would enhance safety and result in important savings in time and money. Addition of boron carbide makes the zirconia ceramic nuclear-criticality-safe. The spent fuel standard can also be met: as space in repositories will be costly and limited, tighter packaging of spent reactor fuel may be necessary before emplacement. This would require disassembling of the fuel bundles, opening the way to mix spent fuel rods with rods containing the plutonium waste form. To fabricate rods with the waste form, standard ceramic densification techniques can be applied, e.g., pelletizing, slip casting, or vibro-compaction together with heat treatment. Even without tighter packaging, fuel bundles with the plutonium waste form could be mixed with spent fuel bundles.

The waste form for the plutonium residues in the US is a zirconolite/pyrochlore-based ceramic with additional phases including brannerite and actinide oxides [5]. The designed plutonium content is 11 wt% [5]. Gadolinium is added as the neutron absorber to minimize the risk of nuclear criticality in case of contact of the waste form with water. Plutonium and gadolinium are distributed among zirconolite, pyrochlore, and brannerite.

Zirconolite and pyrochlore are known to undergo a crystalline-to-amorphous phase transition, and so is brannerite (R.C. Ewing, personal communication) when exposed to alpha decay events such as decay of ^{239}Pu [10] or energetic ions simulating alpha decay [11–13]. This phase transition occurs in respective minerals in nature under the influence of alpha decay of uranium, thorium and their daughter nuclides and is known as metamictization. It is generally accompanied by changes of physical and chemical properties causing considerable decrease in density fracture and enhanced leaching [14–17]. With 11 wt% ^{239}Pu, amorphization takes place within a few thousand years. Leaching can lead to partial loss of the neutron absorber and of plutonium. This would deteriorate the long-term confinement and criticality safety of the fissile plutonium and uranium in the ceramic. A waste form for plutonium must confine the fissile radionuclides, ^{239}Pu ($t_{1/2} = 2.43 \times 10^4$ y) and its daughter ^{235}U ($t_{1/2} = 7 \times 10^8$ y) for a very long time and should therefore be as durable as possible. A protective function of the glass surrounding the ceramic would be difficult to establish. The glass provides pathways for water through fractures and corrosions. Natural glasses are always chemically altered, except in rare cases when there is no contact with water.

It should be noted that the deterrent provided by the spent fuel standard becomes ineffective after a few hundred years when most of the radioactivity has decayed. This deterrent as an additional prerequisite for geologic disposal is not stipulated anywhere outside the US or by rules recommended by the IAEA. National disposal criteria in Japan and the European Union, for example, call for indefinite safeguarding of fissile materials, if recoverable. The criterion of recoverability is open to interpretation. Though not yet universally accepted, indefinite custody is part of the IAEA's 'additional protocol' on fissile materials disposal [18].

Zirconia (ZrO_2) occurs in nature and is known as baddeleyite. ZrO_2 forms solid solutions with a large number of oxides including plutonium oxide (PuO_2) and uranium oxide (UO_2) [19]. Solid solubility is usually high (10–40 mol%). There is complete miscibility with PuO_2 [20]. ZrO_2 occurs in three modifications, monoclinic, tetragonal, and cubic. The cubic modification can be stabilized by yttria (Y_2O_3) or other oxides [21] to avoid changes of modifications and related changes of physical properties such as abrupt changes of thermal expansion with temperature. Therefore, most solid solutions are of cubic structure. Baddeleyite is a chemically extremely durable and radiation-resistant mineral [22]. It is the most suitable mineral for geo-chronological dating of igneous rocks from the earth's upper mantle by the uranium–lead method [23]. Total confinement of uranium and its daughter nuclei for billions of years was evidenced by age dating of baddeleyite samples from the upper mantle [23]. Alpha decay does not produce structural damage in baddeleyite. Metamict (amorphous) zirconia is unknown in nature.

Boron carbide exhibits similar resistance against irradiation as silicon carbide (SiC) [24–26]. In the $(ZrO_2)_{ss}$ waste form, B_4C will be exposed to a low α-dose rate (from ^{239}Pu), $\approx 10^5$ cm^{-2} s^{-1}, initially. After total decay of ^{239}Pu (in about 2.4×10^5 y), α-irradiation will have caused between 1 and 2 displacements per atom (dpa) in B_4C. A damage of 1.3 dpa induced by electron irradiation within 19 h at 300 K left B_4C fully crystalline [27]. At a dose rate of 10^{20} cm^{-2} s^{-1} (2 MeV electrons) B_4C became amorphous at total a dose of 10^{24} cm^{-2} at 106 K [28,29]. The same condition applied at 300 K rendered B_4C only partially amorphous. Irradiating B_4C with

16 keV H_2^+ (dose 1.6×10^{18} cm^{-2}, dose rate 2×10^{14} cm^{-2} s^{-1}) at 300 K [30] yielded complete amorphization. No systematic study has been published on dose rate dependence and annealing of radiation effects in B_4C as a function of temperature. We interpret the available data such that an amorphization of B_4C requires radiation dose rates many orders of magnitude higher than those expected in the waste form.

The high chemical durability and the radiation resistance of ZrO_2 and B_4C suggest that selective loss of ^{239}Pu and ^{235}U or boron is negligible and that confinement of the fissile radionuclides and criticality safety are maintained over geologic periods of time.

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