DEPLETED URANIUM DIOXIDE WASTE PACKAGES FOR SPENT NUCLEAR FUEL

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Paper: JJ11.41
File Name: Repository: MRS.Boston.2001.revised
Publish Manuscript Date: February 8, 2002

Article prepared for

2001 Materials Research Society Meeting
Symposium JJ: Scientific Basis for Nuclear Waste Management XXV
Boston, Massachusetts
November 26–30, 2001

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*Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725.

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ABSTRACT

Depleted uranium dioxide (DUO_2) waste packages (WPs) for disposal of spent nuclear fuel (SNF) are being investigated to (1) reduce radionuclide releases from WPs, (2) decrease the potential for repository nuclear criticality events, (3) provide radiation shielding, and (4) provide a means to beneficially use excess depleted uranium (DU). The DUO_2 is incorporated into the WP as (1) a particulate fill for void spaces within the package and (2) a component of a DUO_2-steel cermet (DUO_2 embedded in steel) that replaces the steel components of the WP. Depending upon the design, there is 3 to 8 times as much DUO_2 as SNF UO_2 in the WP. Most radionuclides in the SNF cannot be released until the UO_2 crystal structure is destroyed. The DUO_2 surrounding the SNF slows the degradation of the SNF UO_2 in the interior. This behavior is similar to the mechanisms that slow the degradation of natural uranium ore bodies containing UO_2. The results of initial investigations and the expected thermodynamic WP behavior are described.

INTRODUCTION

There are two primary waste streams from the light-water reactor (LWR) once-through fuel cycles: SNF and DU. LWRs are fueled with low-enriched uranium with 3 to 5% ^{235}U in ^{238}U. Natural uranium (0.7% ^{235}U in ^{238}U) is separated into (1) low-enriched uranium (3 to 5% ^{235}U) that is used to fabricate nuclear fuel and (2) DU (0.2 to 0.4 wt % ^{235}U). Five to seven tons of DU is generated for every ton of low-enriched LWR fuel that is produced. Over 10^6 tonnes of DU have been generated worldwide from military and commercial applications of nuclear energy. There are incentives to co-dispose of these two potential waste forms:

- *Safe disposal*. DU is a long-lived, chemically toxic, radioactive (300 to 500 nCi/g) material. Repository disposal ensures its safe isolation. Because of the identical geochemical behavior of all uranium isotopes, DU can be co-disposed with SNF [1, 2].
- *Improved repository performance*. The use of DU in a geological repository may improve the repository performance [3] by reducing the potential for release of radionuclides from SNF in the WP (see below).
- *Long-term strategy*. At the current time, uranium resources are sufficient to meet all demands. Sometime in the future, however, it may be necessary to process SNF to recover fissile materials and recycle DU into advanced reactors. Use of DU in SNF WPs provides a means of safely disposing of both materials as well as co-locating them should future generations require these fissile and fertile materials.

DUO_2 is the preferred form for DU in a repository environment. This is the same chemical form as found in SNF and thus is the best understood form of uranium in a repository environment. It is the preferred form to enhance repository performance (see the following discussion). It avoids known difficulties associated with other forms of uranium [2].

The DUO_2 may be used as a fill for all void spaces in the WP—including SNF coolant channels (Fig. 1). Using the 21-PWR WP proposed for the Yucca Mountain (YM) repository, ~3.5 tons of DUO_2 fill [3] can be added per ton of SNF. This assumes a 65% volume packing density for a particulate fill with diameters between 0.5 and 1.0 mm.

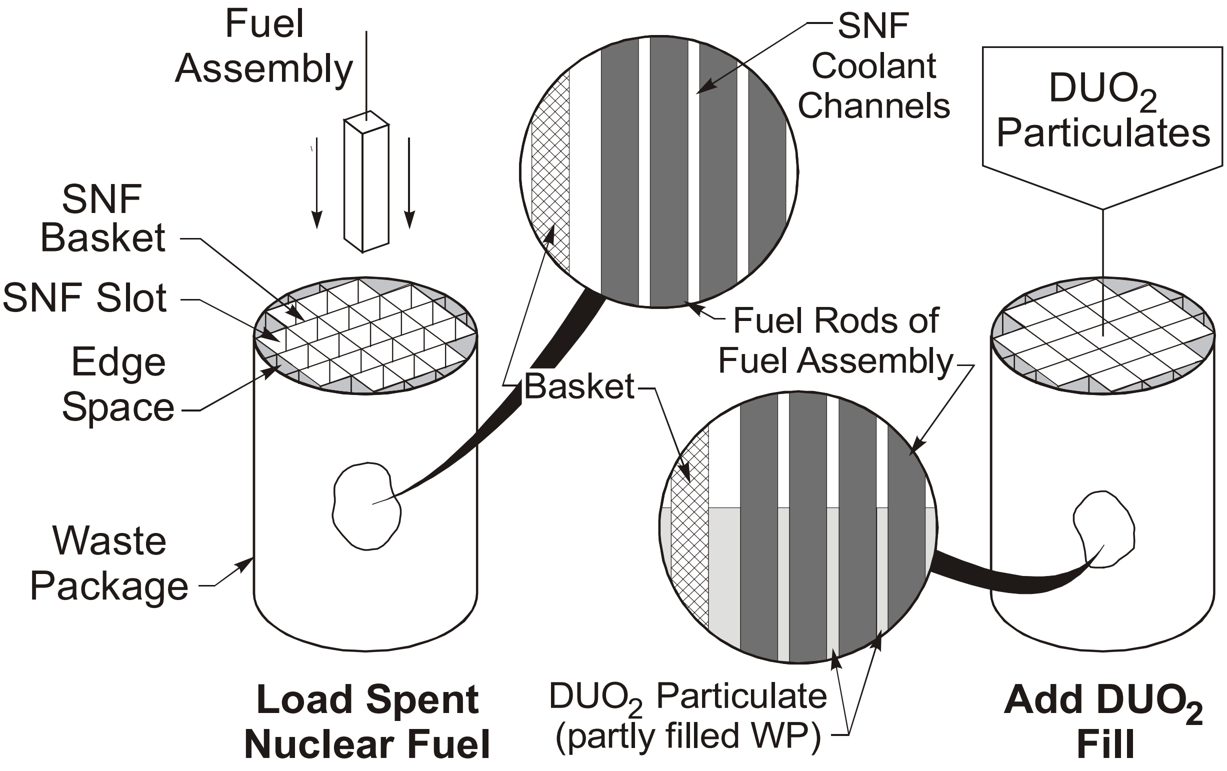

Fig. 1. Loading of DUO_2 fill into a WP.

The DUO_2 may be used as a component of a cermet WP (Fig. 2). Cermets (4) are a mechanism to create a strong ductile form of DUO_2. The cermet contains 40 to 65 vol % DUO_2 particulates embedded in steel and substitutes for the steel components (shell and basket) of the WP. For shielded WPs, 3 to 8 tons of DUO_2 would be used per ton of SNF. In all WP designs, the cermet would be covered with a corrosion-resistant metal layer (C-22, copper, etc.) to delay failure of the WP. Cermet properties depend upon the choice of metal and the ratio of DUO_2 to metal. In the 1950s, cermet fuels were investigated and used in 11 research and test reactors in the United States [5]. Low-cost, nonnuclear cermets have been produced in large volumes.

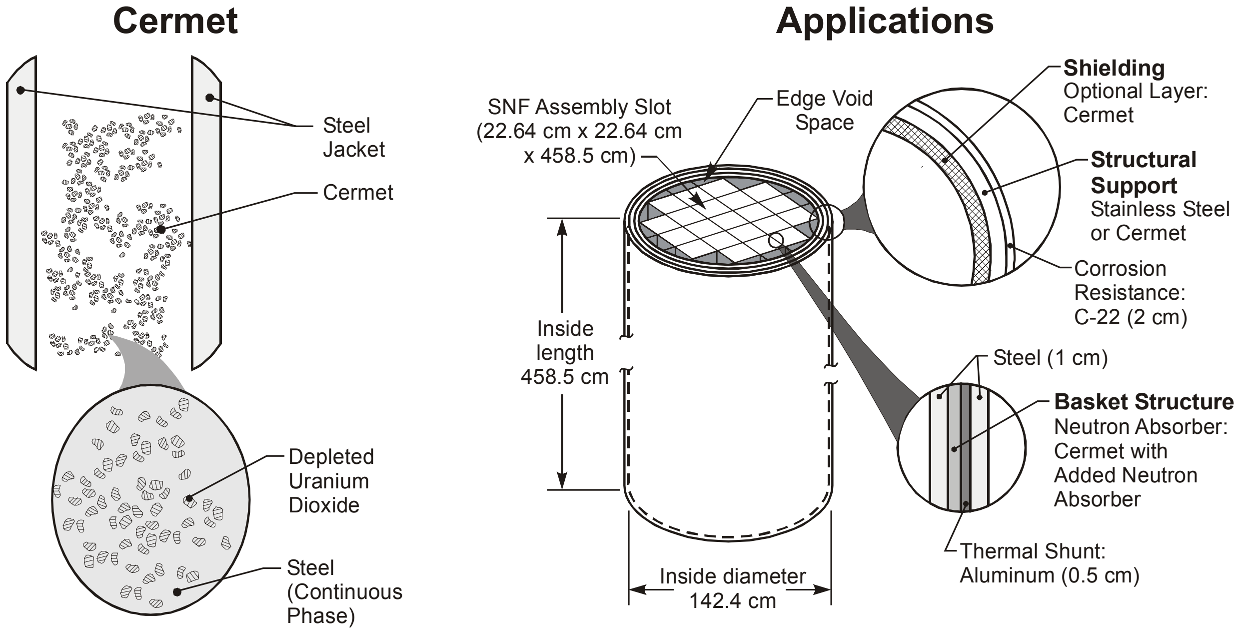

Fig. 2. Characteristics and uses of cermets in SNF WPs.

The option exists for a combined storage, transport, and disposal packaging system in which the cermet cask is also used as both a storage cask and a transport cask (with transport overpack). At the repository, the transport overpack would be replaced with a corrosion-resistant repository overpack before underground disposal.

The characteristics of using DU to aid SNF disposal are described herein.

SHIELDING

Repository designers are considering both shielded and unshielded WPs. Shielded WPs have significant advantages: (1) the WPs can be used to store SNF to allow the radioactive decay heat to decrease before placement in the repository, (2) the WPs provide lag storage between surface and underground facilities to decouple these two operations, (3) underground operations are simplified, and (4) radiation interactions between the waste form and the geology are minimized. The wall thickness for a shielded WP [4] would be 25 cm assuming (1) the cermet contained 50 vol % DUO_2 and 50 vol % steel and (2) the WP interior and SNF were identical to those of the proposed YM 21-PWR WP (SNF burnup of 40,000 MWd/ton, WP loaded 25 years after discharge from the reactor). The cermet weight would be ~70 tons.

High-performance shielding materials are desired to minimize WP diameter and thus tunnel size. Cermets are excellent shielding materials because they have higher densities than steel for gamma shielding and sufficient oxygen to act as a moderator to improve neutron shielding.

Cermets may be the best WP shielding material (4) available because the better shielding materials have been disqualified. Gold, tungsten, and similar materials are unacceptable because of cost. RCRA (hazardous waste regulations) eliminate materials such as lead from the repository. Potentially adverse impacts on repository performance at YM have eliminated the use in the repository of such materials as uranium metal, concrete, and organics.

SLOW RELEASE OF RADIONUCLIDES FROM THE REPOSITORY

Natural ore bodies containing UO_2 have remained intact for millions of years (3). In naturally occurring nuclear reactors, many fission products have not migrated. In some cases, the UO_2 has remained, although the particular geological environment would be expected to quickly degrade the UO_2. These different lines of evidence suggest that the UO_2 on the outer edges of the ore deposits have acted as a sacrificial material to preserve the UO_2 within the interior zones of the deposits and that various other mechanisms associated with uranium chemistry helped preserve the deposits. The same approach (Fig. 3) is proposed here to help ensure the long-term preservation of SNF until most radionuclides have decayed to very low levels. The SNF is packed in DUO_2 in the form of fill or cermet. The DUO_2 provides SNF protection in all types of groundwater. Whatever happens to the SNF first happens to the DU in the cermet and fill.

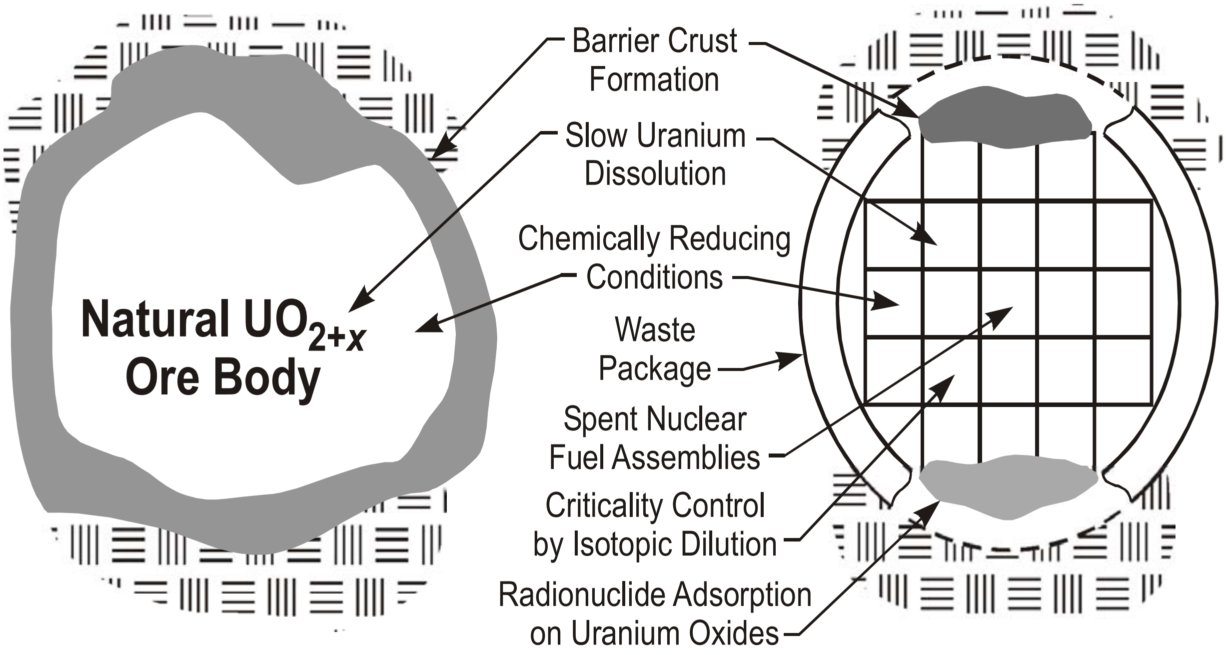

Fig. 3. Similarities in long-term behavior between uranium ore bodies and SNF WPs with DU.

Control of oxidation

SNF degrades under oxidizing conditions but does not degrade under chemically reducing conditions (except by the very slow process of dissolution of U^{+4}). Radionuclides are trapped in the UO_2 grains (>95%) and cannot escape until after the SNF UO_2 is oxidized with potential release of radionuclides to groundwater. The UO_2 must be oxidized to UO_2^{+2} for rapid degradation to occur. For repository sites with oxidizing conditions, chemically reducing conditions may be maintained after WP failure by adding materials to the WP that remove oxygen from the groundwater. For a cermet WP, oxygen is removed from groundwater as the iron oxidizes to rust and—subsequently—the DUO_2 oxidizes. As long as metallic iron or DUO_2 remains, chemically reducing conditions will be maintained in the WP with slow SNF degradation. The iron and DUO_2 may allow maintenance of chemically reducing conditions for very long times.

A thermodynamic analysis of this system was performed to begin to understand the potential benefits of the system. The analysis assumed (Table 1) a SNF containing UO_2 and Zr, a fill of DUO_2, and a cermet of Fe and DUO_2. The analysis provides an indicator of the potential of such systems. Actual performance depends upon the kinetics and other factors. The interactions of two proposed SNF packages with YM groundwater chemistry was simulated using the HSC Version 4.1 thermodynamic code by Outokumpu Research Oy. The first "no-fill case" assumes a shielded cermet WP with 21 PWR assemblies, and the second case assumes that DUO_2-fill is added to the cermet WP. In the "fill case," a shielded cermet WP is used and 3.5 tons of DUO_2 fill is added for each ton of UO_2 in the SNF.

Table 1. Proportions of Fe, UO_2, and Zr in cermet SNF packages with 21 PWR assemblies, with and without DUO_2-fill.

Cases	**Fe, kmol**	**UO_2, kmol**	**Zr, kmol**
No Fill			
cermet	475	137	
21 PWR Assemblies		41	25
Total	**475**	**178**	**25**
DUO_2-Fill			
cermet	475	137	
21 PWR Assemblies		40.70	25
DUO_2-Fill		143	
Total (fill)	**475**	**320**	**25**

The proposed cermet WP has 475 kmol of iron (26.5 tonnes) and 137 kmol of DUO_2 (36.9 tonnes). The 21 PWR assemblies have 41 kmol of UO_2 (11 tonnes) and 25 kmol of Zirconium (Zr) (2.23 tonnes). In the no-fill case, the respective mole fractions are 0.7 (Fe). 0.26 (DUO_2), and 0.04 (Zr). In the case where 143 kmol of DUO_2 fill (38.5 tonnes) is added, the respective mole fractions are 0.58 (Fe), 0.39 (DUO_2), and 0.03 (Zr). Using conditions typical of YM, a generalized representative groundwater composition was selected and oxygen saturation was assumed to be 8.86 mg/L. The groundwater flow rate is assumed to be 32.5 mm per year [6]. The degraded WP cross section is assumed to be 21.45 m^2 (actual cross section is 9.78 m^2). The imaginary flow through or over the WP is 697,100 L per 1000 years. Table 2 summarizes these assumptions and the assumed groundwater composition.

For these two cases, the model takes 250 steps—each step a 1000 years long. Then for each successive step, the model calculates the formation of the predominant compounds in both the solid and aqueous phases by minimizing the Gibbs free energy for a mixture of 353 potential compounds. Figure 4 shows the results for the cermet WP with “no-fill” over 250,000 years for the groundwater described in Table 2. These calculations exclude the corrosion-resistant outer metal layer of the WP; thus, behavior is shown after failure of this long-lived barrier. The span of 50 kmol of O_2 represents the amount of oxygen transported to the package by saturated groundwater over 250,000 years.

Table 2. Amount of groundwater constituents for YMP site's long-term flow (32.5 mm/y) with a package zone-of-influence cross-section of 21.45 m^2 and an oxygen saturation (25°C, 1 Atm).

			Upper Bound: 697,100 liter per 1,000y
	mg/l	**kmole/l**	**Kmole/1000y**
H_2O	1.00E+06	0.056	3.87E+04
O_2 (Sat'd)	8.86E+00	2.77E-07	1.93E-01
Ca++	58	1.45E-06	1.01E+00
Mg++	4	1.64E-07	1.14E-01
SIO2	50	8.33E-07	5.80E-01
Na+	184	8.00E-06	5.58E+00
AL+++	1	3.71E-08	2.58E-02
HCO3-	400	6.56E-06	4.57E+00
CO3--	138	2.30E-06	1.60E+00

Therefore, each kmol of O_2 represents 5000 years of groundwater flow. No oxidation of UO_2 occurs in the cermet or SNF until about 12 kmol of O_2, which represents 60,000 years of groundwater flow, passes through the WP horizon. The iron that oxidizes first (as confirmed in experiments and also observed by the precipitation of UO_2^{+2} in the presence of iron) and initially consumes the oxygen (3). Then the UO_2 begins to form compounds of higher oxides. After groundwater transport of an additional 16 kmol of O_2 (80,000 years) to the WP, the first 137 kmol of DUO_2 is reacted, and the reactions then begin with the remaining 41 kmol of UO_2 in the SNF. The first significant soluble species of uranium [UO_2 (CO_3) $_3$ (-4a)], which is an aqueous species, appears between 125,000 and 130,000 years.

A second cermet WP was analyzed with a 140 kmol of DUO_2 fill added to the inside of the cermet WP. With the added DUO_2, it takes 175,000 years before the UO_2 of the SNF begins to react with the groundwater. The first appearance of significantly soluble uranium species occurs at nearly 200,000 years.

This is an idealized case where iron and DUO_2 are sequentially oxidized by oxygen in groundwater. Air ingress is assumed to be small (see below). In the repository, water flow distributions and other factors result in uneven oxidation. While this is a simplified analysis, it indicates the potential for cermet WPs and fills to improve performance.

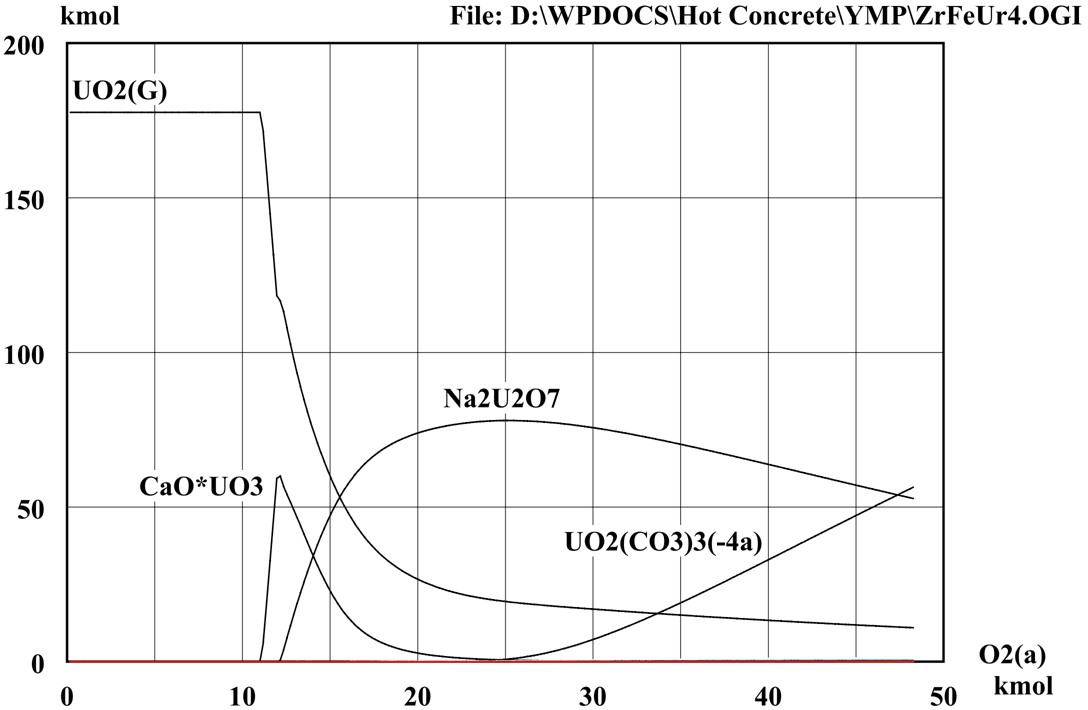

Fig. 4. Groundwater flow of 32.5 mm/y for 250,000 years with 143 kmole of DUO_2 in the Cermet canister and 41 kmole of UO_2 in the 21 PWR assemblies.

Removing radionuclides from groundwater

For repositories with oxidizing conditions (such as YM), the use of cermets and fills creates a redox radionuclide trap that may exist for many tens of thousands of years. Some radionuclides are insoluble under oxidizing conditions. Other radionuclides are insoluble under chemically reducing conditions. The combination of a WP that maintains reducing conditions for long periods of time and an oxidizing geochemistry limits the transport of all radionuclides that are insoluble over a wide range of redox conditions. Insoluble radionuclides are trapped in the WP (reducing conditions) or the geology (oxidizing conditions).

Recent SNF leaching experiments show that certain long-lived radionuclides (e.g., neptunium) are retained by hydrated uranium oxides [3], such as those created by oxidation of DUO_2. Hydrated iron oxides (hydroxides) will also retain a variety of radionuclides by several mechanisms. In addition, the various degradation products may filter various radioactive colloids (small particulates) from the groundwater. These specific radionuclides (^{237}Np and ^{99}Tc) are those that often control repository performance [7]. This is an active area of investigation where preliminary results are encouraging but major additional work is required to understand the chemistry and quantify the potential benefits.

Blocking fluid flow

The oxidation of DUO_2 to higher uranium oxides and the ultimate transformation to silicates result in volume expansion [3]. This expansion can slow the flow of groundwater through the WP and thus slow migration of radionuclides in groundwater from the WP. The filling of the void spaces also reduces the potential for diffusion of oxygen through air into the WP.

PRESERVATION OF WP GEOMETRY

The use of fill helps maintain the WP geometry. If no void spaces exist inside the WP, it cannot easily collapse from rockfalls. As the WP corrodes and weakens, the basic geometry remains intact and any exterior engineered barriers to radionuclide release are not compromised by WP collapse or consolidation of the WP [3, 8]. Over a longer period of time, fill oxidation with lower density reaction products eliminates fill void spaces with positive (lower gas and water flow) and negative impacts (mechanical forces on the degraded WP). The Canadian repository program has extensively investigated the specific advantages of different fill materials.

CRITICALITY

Over geological time, the SNF and the WP will degrade. Fissile materials will change chemical form and migrate. During these processes, fissile materials can become sufficiently concentrated to cause nuclear criticality to take place, as has happened the past [3]. At Oklo, Gabon, Africa, prehistoric natural reactors operated at enrichments as low as 1.3 wt % ^{235}U in ^{238}U. The average enrichment of LWR SNF is equivalent to -1.5 wt % ^{235}U in ^{238}U. Two sources of ^{235}U exist: (1) ^{235}U originally in the SNF and (2) ^{235}U from the decay of ^{239}Pu. Many other SNFs have higher enrichments.

The potential for nuclear criticality can be minimized by addition of DU to the WP. As the WP and SNF degrade (Fig. 3), the DU is expected to isotopically mix with the SNF enriched uranium through dissolution, ion exchange, and coprecipitation of the different uranium isotopes in the WP. Large-scale dissolution (see above) occurs after oxidation of the DUO_2 and SNF and after most of the ^{239}Pu has decayed to ^{235}U. The uranium enrichment will be lowered sufficiently that nuclear criticality can no longer occur [3].

ACKNOWLEDGMENTS

This work was done under the auspices of the U.S. Department of Energy Depleted Uranium Uses Research and Development Program.

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