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Depleted Uranium Dioxide Waste Package for Spent Nuclear Fuel

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ABSTRACT

Depleted uranium dioxide (DUO₂) 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 DUO₂ is incorporated into the WP as (1) a particulate fill for void spaces within the package and (2) a component of a DUO₂-steel cermet (DUO₂ embedded in steel) that replaces the steel components of the WP. Depending upon the design, there is 3 to 8 times as much DUO₂ as SNF UO₂ in the WP. The radionuclides in the SNF cannot be released until the UO₂ crystal structure is destroyed. The depleted UO₂ surrounding the SNF slows the degradation of the SNF UO₂ in the interior. This behavior is similar to the mechanisms that slow the degradation of natural uranium ore bodies containing UO₂. 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% ²³⁵U in ²³⁸U. Natural uranium (0.7% ²³⁵U in ²³⁸U) is separated into (1) low-enriched uranium that is used to fabricate nuclear fuel and (2) DU. The DU typically has 0.2 to 0.4 wt % ²³⁵U. The SNF is highly radioactive; however, its radioactivity decreases with time. Five to seven tons of DU is generated for every ton of low-enriched LWR fuel that is produced. Over 10⁶ 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. Disposal in a repository ensures its safe isolation from humans. Because of the identical geochemical behavior of all uranium isotopes, DU can be safely 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.

Depleted uranium dioxide 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-pressurized-water reactor (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.

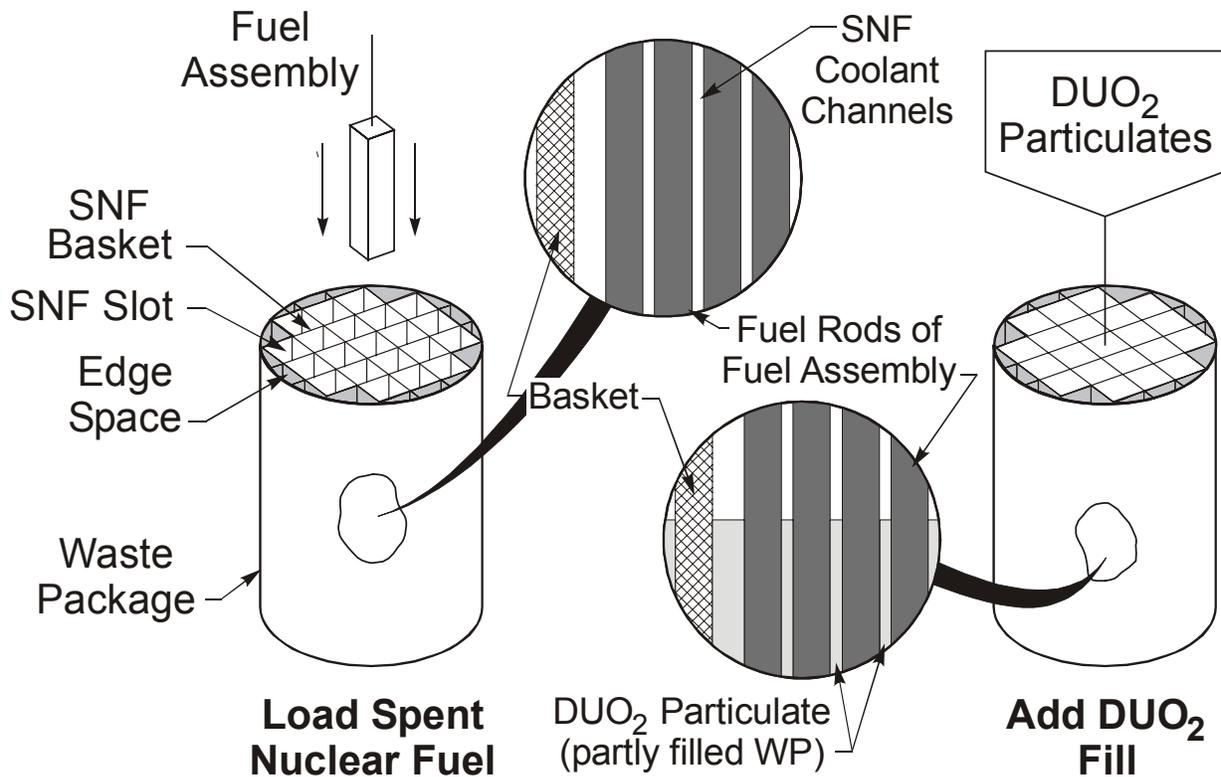


Fig. 1. Loading of DUO_2 fill into a WP.

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. The quantity of cermet used depends upon the application. 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 primarily 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 very large volumes.

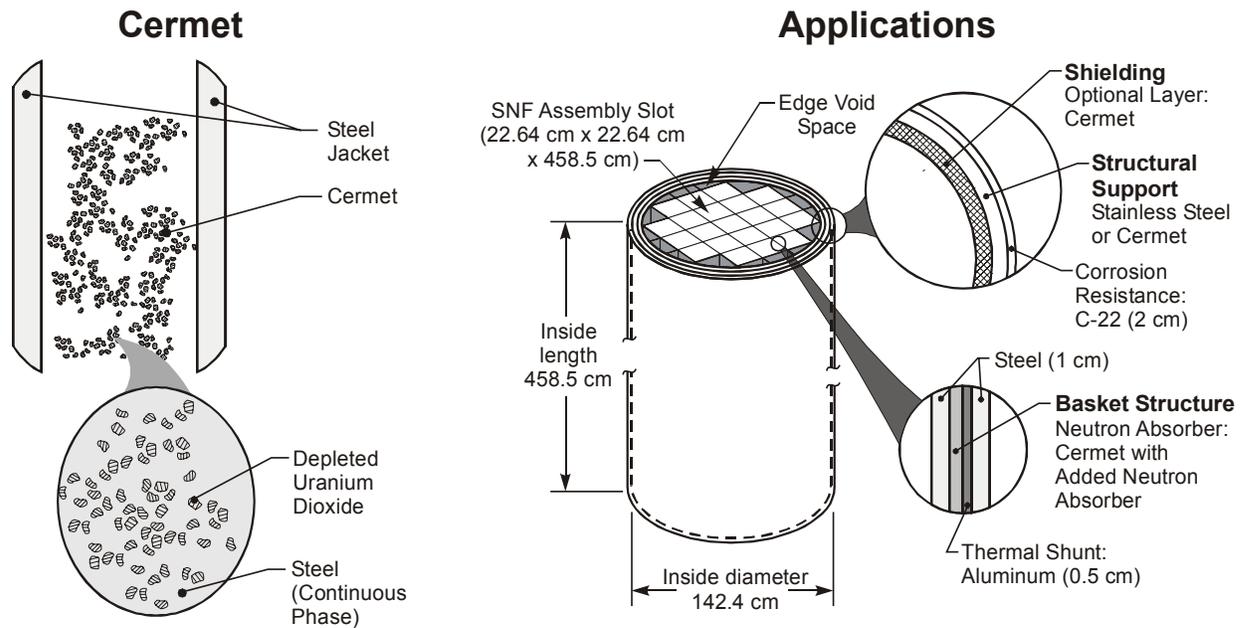


Fig. 2. Characteristics and uses of cermets in SNF WPs.

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 (low weight, small thickness) available because the better shielding materials

have been disqualified. Gold, tungsten, and similar materials are unacceptable because of cost. The Resource Conservation and Recovery Act (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.

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 mix with the SNF-enriched uranium through dissolution, ion exchange, and coprecipitation of the different uranium isotopes in the WP. The uranium enrichment will be lowered sufficiently that nuclear criticality can no longer occur [3].

PRESERVATION OF WP GEOMETRY

The use of fill helps maintain the WP geometry even as the package degrades. If no void spaces exist inside the WP, it cannot collapse. 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, 6]. The Canadian repository program has extensively investigated the specific advantages of different fill materials.

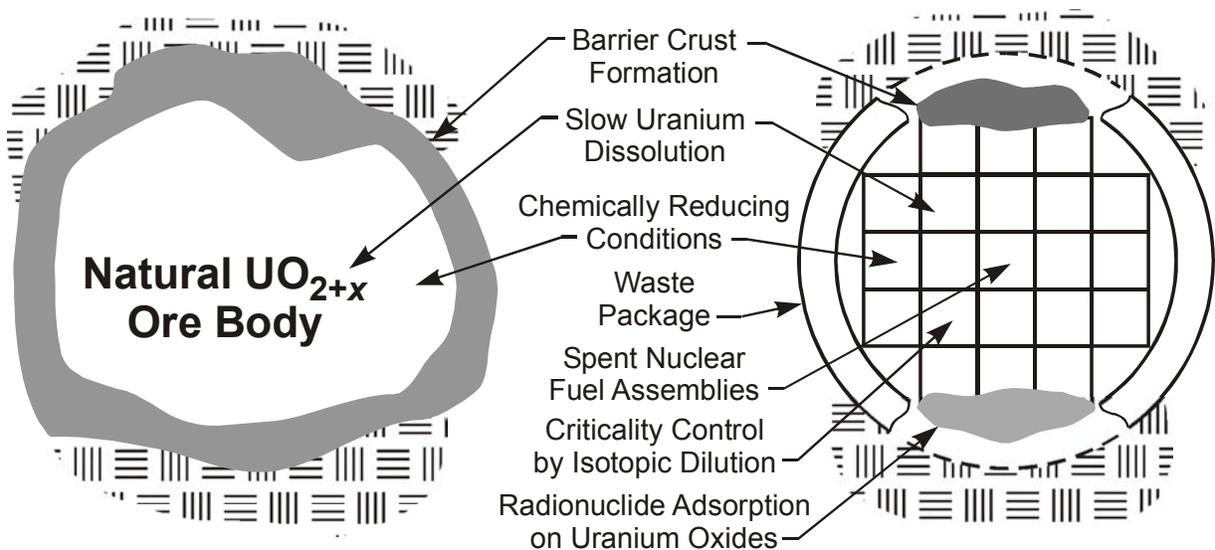


Fig. 3. Similarities in long-term behavior between uranium ore bodies and SNF WPs with DU.

SLOW RELEASE OF RADIONUCLIDES FROM THE REPOSITORY

Natural ore bodies containing UO_2 have remained intact for millions of years. In naturally occurring nuclear reactors, many fission products have not migrated from the original locations of the reactors. 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. The mechanisms [3] that can assist in the isolation of radionuclides in SNF are complex.

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 pellets and cannot escape until the SNF UO_2 is oxidized and dissolved in 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 quantities of iron and DUO_2 in the proposed WPs 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 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 summarizes the amounts of iron, uranium dioxide, and zirconium in these two cases.

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, 0.26, and 0.04. In the case where 143 kmol of DUO_2 fill (38.5 tonnes) is

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
mole fraction	0.70	0.26	0.04
DUO_2-Fill			
cermet	475	137	
21 PWR Assemblies		40.70	25
DUO_2-Fill		143	
Total (fill)	475	320	25
mole fraction	0.58	0.39	0.03

added, the respective mole fractions are 0.58, 0.39, and 0.03. 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 [7]. The degraded WP cross section is assumed to be 21.45 m² (actual cross section is 9.78 m²). The imaginary flow through or over the WP is 6,971,000 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 O₂ represents the amount of oxygen transported to the package by saturated groundwater over 250,000 years.

Therefore, each kmol of O₂ represents 5000 years of groundwater flow. No oxidation of UO₂ occurs in the cermet or SNF until about 12 kmol of O₂, which represents 60,000 years of groundwater flow, passes through the WP horizon. The iron that oxidizes first (as confirmed in experiments) initially consumes the oxygen. Then the UO₂ begins to form compounds of higher oxides. After groundwater transport of an additional 16 kmol of O₂ (80,000 years) to the WP, the first 137 kmol of DUO₂ is reacted, and the reactions then begin with the remaining 41 kmol of UO₂ in the SNF. The first significant soluble species of uranium [UO₂(CO₃)₃(-4a)] appears between 125,000 and 130,000 years.

A second cermet WP was analyzed with a 140 kmol of DUO₂ fill added to the inside of the cermet WP. With the added DUO₂, it takes 175,000 years before the UO₂ of the SNF begins to react with the groundwater. The first appearance of significantly soluble uranium species occurs at nearly 200,000 years.

The simplified analysis indicates the potential for cermet WPs and fills to provide a significant improvement in performance that is independent of that of the outer corrosion-resistant layer of the WP.

Table 2 Amount of ground water constituents for YMP site's long-term flow (32.5 mm/y) with a package zone-of-influence cross-section of 21.45 m² and an oxygen saturation (25°C, 1 Atm).

			Upper Bound: 6,971,000 liter per 1,000y
	mg/l	kmole/l	kmole/1000y
H ₂ O	1.00E+06	0.056	3.87E+04
O ₂ (Sat'd)	8.86E+00	2.77E-04	1.93E-01
Ca ⁺⁺	58	1.45E-06	1.01E+00
Mg ⁺⁺	4	1.64E-07	1.15E-01
SiO ₂	50	8.33E-07	5.80E-01
Na ⁺	184	8.00E-06	5.58E+00
Al ⁺⁺⁺	1	3.71E-08	2.58E-02
HCO ₃ ⁻	400	6.56E-06	4.57E+00
CO ₃ ⁻⁻	138	2.30E-06	1.60E+00

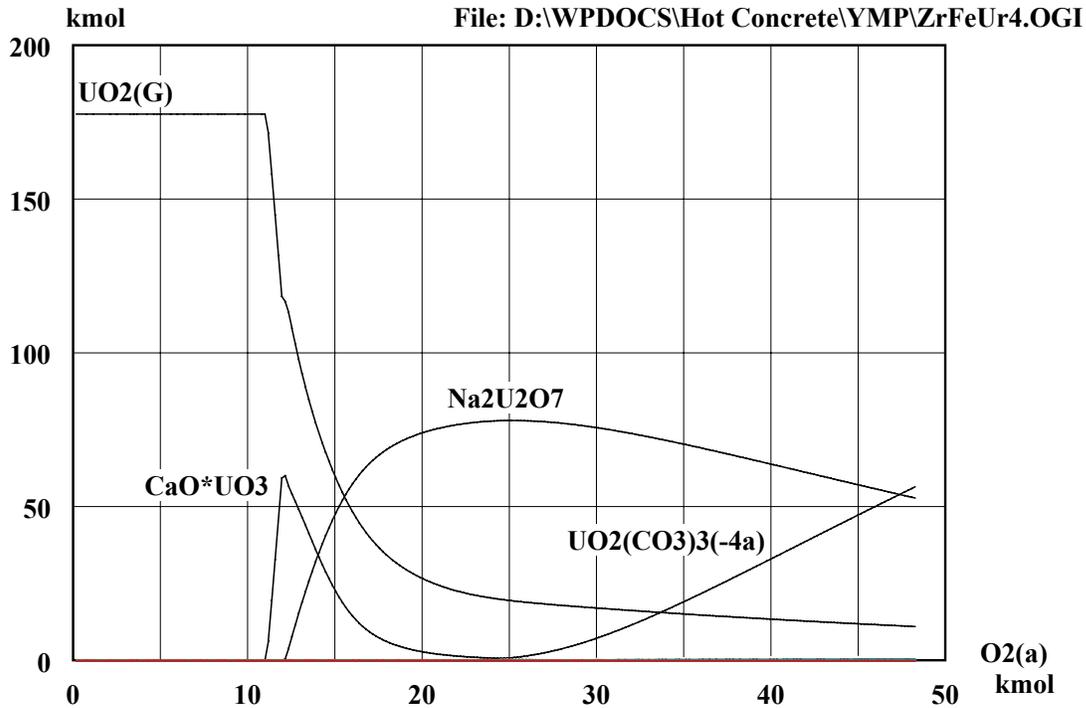


Fig. 4. Groundwater flow of 32.5 mm/y for 250,000 years with 143 kmole of DUO₂ in the Cermet canister and 41 kmole of UO₂ in the 21 PWR assemblies.

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 DUO₂. Hydrated iron oxides (hydroxides) will also retain a variety of radionuclides by several mechanisms. In addition, the various degradation products will filter various radioactive colloids (small particulates) from the groundwater. These specific radionuclides are those that control repository performance [8]. 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.

ACKNOWLEDGMENTS

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Additional information on DU applications in a geological repository can be found at the following URL: “web.ead.anl.gov/uranium/uses/index.cfm.” Copies of many of the references are also available at this site.

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