DEPLETED URANIUM DIOXIDE AS A SPENT–NUCLEAR–FUEL WASTE–PACKAGE PARTICULATE FILL: FILL BEHAVIOR

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File Name: DuFill.Behavior.WM01.article.final

Article Prepared For
Waste Management 2001 Symposium
Tucson Convention Center
Tucson, Arizona
February 25–March 1, 2001

Paper Number: 48
Session: 14: Advances in Depleted Uranium Technology
Session CoChairs: Steve H. Brown and William J. Quapp
Presentation Date: February 26, 2001

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ABSTRACT

Depleted uranium (DU) dioxide (DUO_2) particulate fills are being investigated for use in repository waste packages (WPs) containing spent nuclear fuel (SNF). The sand-like particles would fill all void spaces in the WP, including the cooling channels in the SNF. The particulate fill may improve repository performance by (a) maintaining chemically reducing conditions in the WP to preserve the long-term integrity of the SNF, (b) reducing water flow through the SNF and thus slow migration of radionuclides from the WP, (c) slowing radionuclide releases by adsorption of species from groundwater and filtration of colloids, and (d) minimizing the long-term potential for nuclear criticality in the repository. This DU application may potentially use half or more of the entire U.S. inventory of DU.

A baseline scenario of expected fill behavior over geological time has been developed. The expected behavior has been compared to a WP without fill material. This model provides a starting point for the development of a detailed performance assessment model of WP performance and a basis for defining required experiments to understand system behavior. The model is described herein.

INTRODUCTION

DUO_2 particulate fills are being investigated for use in repository WPs containing SNF. The particulate fill may improve repository performance and provide a means of disposal of excess DU. The WP (Fig. 1) would be first filled with SNF and then filled with DUO_2 particles ranging in size from 0.5 to 1 mm. The particles fill void spaces in the WP and the coolant channels within each SNF assembly.

For the proposed Yucca Mountain (YM) repository, the most common WP will be that for 21 pressurized-water reactor SNF assemblies—as shown in Figure 1. The WP contains about 10 t of SNF. Assuming no changes in the WP, there is sufficient void space (1) for ~33 t of DUO_2. About half the DU generated in producing a fuel assembly would be required for use as a fill material for disposal of the same fuel assembly. The YM repository is designed for ~10,000 WPs and thus using DU fill would consume about half of the DU inventory in the United States. Larger quantities could be used if the basic WP design was modified. The other large-scale potential application of DU in a repository, making the WP from a DUO_2-steel cermet (1), would consume an equivalent amount of DU. The cermet consists of DUO_2 particulates embedded in steel. While this report only discusses fill applications, many of the behaviors of fills and cermets in a repository environment will be similar or identical because the same materials are used in each proposed DU application.
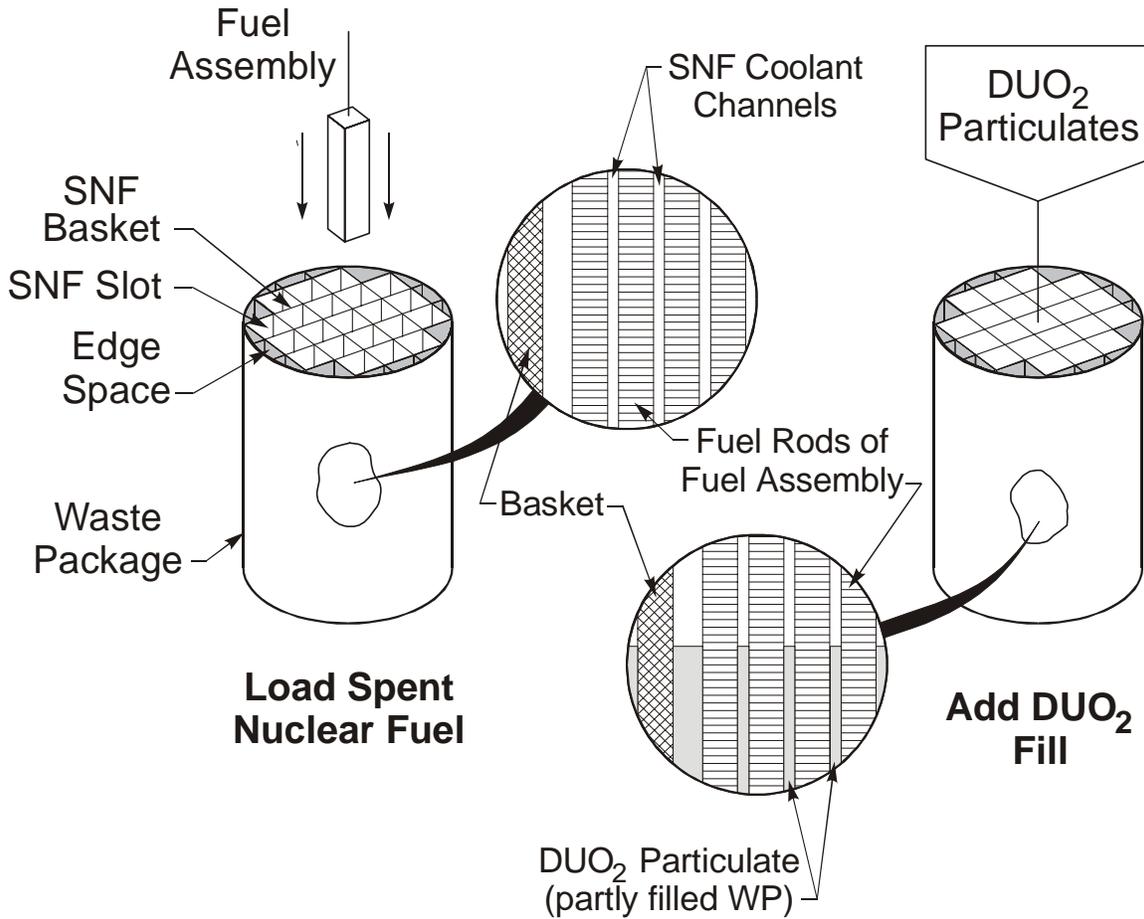
Fig. 1. WP loading sequence with SNF and DUO$_2$ fill.

A baseline description of the expected fill behavior over geological time has been developed using available information from the literature (2–4). This model will be used as a starting point for (a) constructing detailed mathematical models of system performance and (b) planning of experiments. The experiments are to (a) measure key parameters that are unknown, (b) confirm (or disprove) key assumptions about the behavior of the fill, and (c) validate mathematical models of system behavior. A description of the expected fill behavior is provided herein.

MECHANISMS TO IMPROVE REPOSITORY PERFORMANCE

There are several potential repository benefits (5) in using DUO_2 as a fill material. The DU minimizes the potential for long-term nuclear criticality in the repository by lowering the average fissile content of the WP with DUO_2 fill to #0.5 wt % ^{235}U equivalent. The DUO_2 provides added radiation shielding. Last, the fill slows radionuclide releases from the WP by several mechanisms. Slowing the release of radionuclides from the SNF and WP provides more time for the radionuclides to decay to nonradioactive elements and thus reduces long-term releases of radionuclides from the repository. Radionuclide isolation is enhanced by the following mechanisms:

- *Chemically reducing conditions.* SNF UO_2 does not degrade under chemically reducing conditions. If the SNF UO_2 does not degrade, most radionuclides are trapped in the UO_2 crystal structure and can not escape the SNF. The DUO_2 helps maintain chemically reducing conditions in the WP after package failure by reacting with oxygen in air and groundwater to form U_3O_8 and/or $UO_3 \cdot xH_2O$. The removal of the oxygen creates chemically reducing conditions near the SNF.

- *Reduction of groundwater flow.* Radionuclide transport to the accessible environment is by groundwater. The lower the groundwater flow, the lower the possible radionuclide releases. The oxidation of DUO_2 fill, as described previously, results in a 36 vol % increase and a corresponding decrease in particulate density (2). This volume expansion fills interparticulate void spaces and thus reduces bed porosity. This reduction in porosity, in turn, reduces the groundwater flow through the SNF and WP.

- *Saturation of the WP water with uranium.* The high-surface-area DU saturates water entering a failed WP with DU. This saturation process reduces the dissolution rates of SNF uranium with the resultant reduction in a release of hazardous radionuclides.

- *Removal of radionuclides from groundwater.* The particulate bed (a) filters radionuclide colloids escaping from the SNF and (b) absorbs selected radionuclides from the groundwater.

- *Support of WP structure.* A fill material provides internal support against long-term crushing of the WP as the disposal tunnel fails over time.

There have been other investigations of fill materials—but not of DUO_2. Until recently, DU was not considered a potential waste. The Canadians (6) have proposed using a thin-wall corrosion-resistant titanium WP; however, titanium is expensive. To minimize titanium requirements, the Canadian program proposes the use of an inert fill to provide long-term internal support of a thin-wall WP against collapse from external lithostatic pressure in the repository. The Spanish have conducted limited investigations of using inorganic absorbents to reduce long-term radionuclide releases from the degraded SNF. The YM repository project in the United States briefly examined several fill materials with a preliminary evaluation of using iron shot (7). The program is currently examining the use of gadolinium phosphate fill with high-fissile-content SNF as a method to assure long term criticality control (8).

EVOLUTION OF THE WP

Radioactive materials decay to nonradioactive materials over time. A repository functions by delaying the release of radionuclides to the accessible environment until radionuclide inventories have decayed to safe levels. In terms of performance, the value of an alternative WP design is measured by how long it delays the release of radionuclides from the SNF to the groundwater outside the WP. To quantify the potential benefits of using DUO_2 fill, there are two considerations, (a) the evolution of the fill, SNF, and the WP and (b) the subsequent release of radionuclides over geological time-frames. For purposes of discussion, there are four distinct phases in the evolution of the SNF and WP in the repository environment:

- *Intact SNF and WP*

- *Initial WP failure and basket degradation*

- *Oxidation of the fill and SNF*

- *Post-SNF oxidation conditions*

This analysis is for disposal in an oxidizing geological environment similar to that of YM. The repository is above the water table with percolating oxidizing groundwater. The evolution of SNF and the WP would be considerably different under different geological conditions such as a geology with a chemically reducing environment.

While a baseline scenario for WP evolution is provided herein, it is important to recognize the real-world variability in how a WP will preform. There will be - 10,000 WPs in YM. While some will fail early in their lives, others will last far beyond their expected lifetimes. These different lifetimes will reflect differences in WP fabrication history and different local repository WP environments. There will be different thermal histories, groundwater flows, groundwater compositions, air flows, and air compositions across the repository. Ultimately, corrosion will cause all the WPs to fail. After a WP failure, different parts of each SNF assembly and the WP will evolve at different rates; thus, the different mechanisms may be simultaneously occurring within a single WP. One zone of the SNF may be fully oxidized, while another section may have somewhat intact SNF.

STAGE I: BEHAVIOR OF INTACT SNF AND WPs

The WPs filled with SNF will be emplaced in parallel disposal drifts. A titanium drip shield will be placed over each WP to delay contact between the WP and groundwater. When the repository is closed, a backfill material may be placed over the titanium drip shield (Fig 2) to help protect the drip shield and WP against long-term rock falls, which could damage either the drip shield or WP.

The WPs are designed to last many thousands of years. During this time, the decay heat will decrease resulting in decreases in SNF and WP temperatures. From the perspective of the SNF, there is little difference between a WP with or without fill material. The fill material does not have a significant impact on SNF temperatures (9). This is a consequence of two factors:
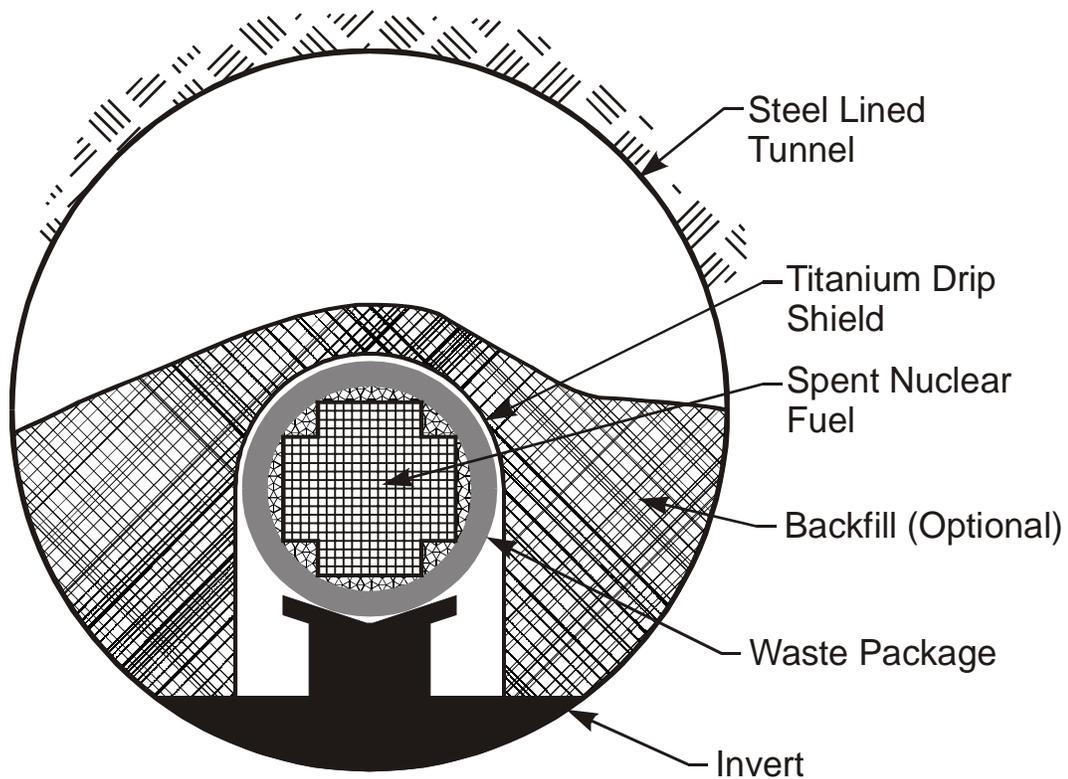
Fig. 2. Schematic of YM disposal drift with SNF WP.

- *WP design*. The heat transfer path in a WP is from the SNF, to the basket that holds the SNF assemblies (Fig. 1), to the cask wall, through the cask wall, and into repository. To minimize SNF temperatures, the basket structure contains a high thermal conductivity metal that efficiently transfers heat from the SNF to the inside WP wall. As a consequence, the use of a fill material primarily impacts the temperature drop between the fuel assembly and the basket. Heat does not transfer through multiple fuel assemblies or long distances through fill. This limits the thermal impact of any fill material—good or bad.

- *Thermal conductivity*. In the current WP designs, heat transfer from a fuel assembly to the basket is a combination of helium thermal convective currents and thermal conduction. The thermal conductivity of UO_2 particulate beds have been experimentally measured by several investigators for various applications. It is significantly greater than the thermal conductivity of helium and thus the fill improves heat transfer by conduction. The fill effectively eliminates thermal convective currents in the fuel assembly; however, thermal convective currents are small in a horizontal SNF assembly with the small dimensions between the fuel rods. Under these conditions, the DUO_2 fill may slightly reduce temperature drops between the SNF and the basket. However, the differences in temperature drops between SNF and the basket for the fill and no fill cases are small compared to the temperature drops elsewhere in the WP; thus, this has no significant impact on SNF temperatures.

The fill does absorb gamma radiation and thus reduces radiation levels within and outside the WP. Over the lifetime of the repository, there will be rock falls, partial or full collapse of the drifts and tunnels, and eventual failure of the drip shields. Ultimately, groundwater will reach the WP surface. Once this occurs, corrosion will begin to degrade the WP, and ultimately the WP will fail.

Fill material may delay WP failure by providing internal support to delay collapse of the WP as the walls thin from corrosion. Without any fill, over half the internal volume of the WP is void space. Therefore, debris from tunnel collapse can squeeze the WP as the walls thin and accelerate WP failures.

STAGE II: BEHAVIOR DURING INITIAL WP FAILURE AND BASKET DEGRADATION

Once a WP fails and air or water enters, the WP basket structure will be the first component to corrode and rapidly fail. The WP body is made of stainless steel with an outer layer of C-22, a corrosion-resistant nickel alloy. The SNF is clad in zircalloy. The basket structure is made of carbon steel, which will oxidize rapidly as compared to these other metals. A WP without fill has an open structure. Most of the volume in an SNF assembly consists of empty coolant channels, which are filled with gas. Once the WP is breached, this characteristic allows rapid air flow to the entire basket structure and causes rapid corrosion. Following the failure of the basket structure, the SNF will collapse into a pile.

If DUO_2 fill is used, a somewhat different sequence of events occurs. Thermodynamic and experimental data indicate (2,10,11) that mild steel preferentially reacts with oxidizing groundwater or air before DUO_2 fill is oxidized to higher uranium oxides. However, the rate of oxidation will be much lower. With fill, air and water flow are limited. The oxidation of iron and the resulting lower-density iron oxides fill void spaces in the WP. When iron—the primary component of steel—oxidizes to either Fe_2O_3 or Fe_3O_4, its volume increases by - 2.1. This will fill the inter-particulate void spaces further and will slow the movement of air and oxidizing water. Oxygen must diffuse through the fill and iron oxides toward the SNF. Oxygen will preferentially react with the basket, but much of the oxygen will react with DUO_2 before it can diffuse to all parts of the steel basket structure.

The fill also acts as a packing material to protect the SNF from large mechanical deformations caused by tunnel convergence and subsequent WP collapse. The Canadian repository program that has examined the use of fill as a structural support mechanism (6) has done significant work on these factors.

STAGE III: BEHAVIOR DURING OXIDATION OF THE FILL AND SNF

DUO_2 and SNF UO_2, under oxidizing conditions, will oxidize to higher uranium oxides. YM has oxidizing conditions: the gas phase is air, and the groundwater is saturated with oxygen. All uranium will ultimately be oxidized to higher uranium oxides. The rates of the oxidation process determine how fast this happens and subsequently how fast radionuclides can escape the WP system. As long as the uranium in the SNF remains as UO_2, most of the radionuclides will remain trapped in the SNF UO_2 crystal structure and can not be released from the SNF and thus can not be released to groundwater for transport to the accessible environment. One goal of the fill DUO_2 is to delay the SNF UO_2 oxidation process to allow time for radioactive decay.

Overview of Expected Oxidation Process

The following events are expected to occur after WP failure.

- *Oxidation*. The DUO_2 fill begins to oxidize.

- *Fill swelling*. The DUO_2 oxidation products have lower densities than does DUO_2. Particulate bed void spaces fill up, and the permeability of the bed to gas and groundwater decrease.

- *Reducing conditions*. The initial oxidation removes oxygen from air and groundwater. This results in chemically reducing conditions near the SNF. With no free oxygen, SNF UO_2 remains intact. Radionuclides are trapped in the SNF UO_2 grains in fuel pins.

- *Reduced oxygen transport*. As the bed permeability decreases, the rate of oxygen diffusion into the bed decreases. With less oxygen, oxidation rates decrease. Less DUO_2 must be oxidized to maintain chemically reducing conditions. Ideally, chemical reaction rates, including SNF degradation, rapidly decrease, and chemical reducing conditions are maintained for very long times.

The DUO_2 fill reacts before the SNF does. The high-surface-area particulate implies faster chemical reactions than the lower-surface-area SNF. The SNF UO_2 is protected by the zircalloy clad, which takes considerable time to fail. The DUO_2 is exterior to the SNF and thus sees the oxygen in the gas phase or groundwater before the SNF.

Mechanistic Description

When the WP fails, air and oxidizing groundwater will enter. The air and water will first react with the DUO_2 at the point of WP failure. As time progresses, air and water will penetrate further and further through the fill toward the SNF. Figure 3 shows this progression and the expected behavior.

The oxygen in air or water will react with the DUO_2 fill to produce higher oxides. The removal of the oxygen results in a nitrogen atmosphere (the other primary component of air) with smaller quantities of argon and other noble gas constituents of the atmosphere. This in turn creates chemically reducing conditions in the WP. Oxygen from air outside the WP must diffuse through the nitrogen to react with the DUO_2; however, the diffusion process is slow, and thus the rate of oxidation of fill is slow. The bed creates complex and long pathways from the exterior of the WP through the breach in the WP to where oxygen can react with DUO_2. Oxygen can also be dissolved in the groundwater, enter the WP with the groundwater, and be transported to unreacted DUO_2. Oxygen in groundwater will be in equilibrium with the local atmosphere.

The detailed fill oxidation process depends upon the water content in the WP. At sufficient times into the future, the badly degraded WP will be wet; that is, there will be a drip flow of water through the WP with water in interstitial locations. If WP failure occurs early, there may be dry-to-semidry conditions, particularly if the level of decay heat generation is sufficient such as to raise local temperatures and lower the relative humidity in the WP. Two types of oxidation can occur under two different conditions, respectively.
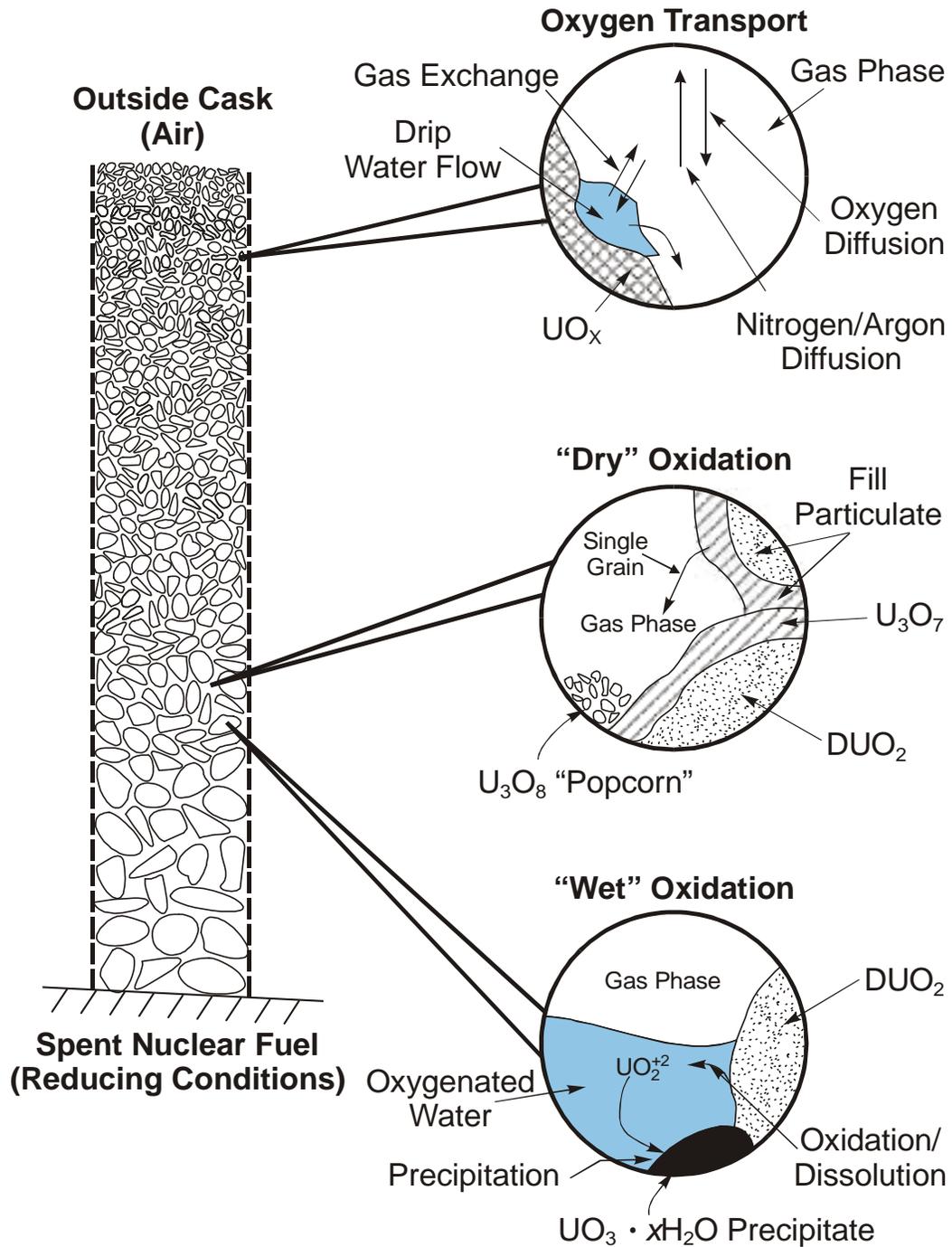
Fig. 3. Oxidation mechanism inside DUO$_2$ fill bed.

- *Dry conditions*. The DUO_2 goes through a two-stage oxidation process from UO_2 to U_3O_7 to U_3O_8 (2). While gamma-phase UO_3 is in the thermodynamically stable state in air up to 700EC, in practice, the oxidation does not go beyond U_3O_8 because of kinetic constraints.

  The first oxidation reaction results in a very small reduction in volume (2%). Because of this behavior, much of the particulate fill can be partially oxidized with the consumption of significant quantities of oxygen without causing major changes in bed properties. The U_3O_7 forms a discrete layer on the surface of the UO_2. The oxidation process is diffusion controlled—with the depth of oxidation proportional to the square root of time. This results in a parabolic reaction kinetics. There is some evidence that the shrinkage creates cracks, which then accelerate oxygen diffusion to unreacted UO_2.

  Below 250EC, the intermediate product is U_3O_7. As the oxidation temperature increases, a similar (but different) intermediate is formed—U_4O_9. Over a range of oxidizing conditions, both structures are found.

  In much of the literature, no distinction is made between these two uranium oxide forms. In SNF, at burnups above 6- to 12-MWd/kg, low-temperature oxidation of SNF UO_2 yields U_4O_9 rather than U_3O_7. This phenomenon is a result of stabilization of the crystal structure by rare-earth fission products and the higher actinides. Furthermore, fission products that migrate to the grain boundary appear to allow faster diffusion of oxygen along the grain boundaries. Because of these differences, SNF UO_2 behavior is not identical to clean UO_2 behavior; therefore, SNF UO_2 data must be used with caution.

  The second oxidation step to U_3O_8 results in a major change in the crystal structure and in a large volume expansion (- 36%). The expansion causes stresses, which break U_3O_8 grains away from the particulate (i.e., popcorn effect). This breakup accelerates oxidation by reducing the thickness of the U_3O_7 layer, which retards diffusion of oxygen to the UO_2 surface. The smaller oxidized grains are expected to fill the void spaces between the larger UO_2 particulates.

  The size of the fine particulates is similar to the grain size of the original UO_2. The second-stage kinetics can be represented by a nucleation and growth model. The term *powder formation time* refers to the time when visual observation can detect the change. Experimentally, U_3O_8 is observed at - 25 h at a temperature of 260EC—with powdered UO_2 as the starting material. With sintered pellets, the powder formation time under identical conditions is - 100 h.

  Above 350EC, the intermediate U_3O_7-U_4O_9 is not observed in significant quantities. The bulk oxidation appears to proceed directly to U_3O_8. Above 500EC, the oxidation kinetics slow down, and dramatic changes occur in the characteristics of the U_3O_8 product. The U_3O_8 grain size increases rapidly. It is believed that this behavior is a result of the UO_2 and U_3O_8 becoming sufficiently plastic such that oxidation can occur without particulate breakup. The changes in the oxidation mechanisms place clearly defined limits on how much a bed-oxidation experiment can be accelerated by increasing the bed temperature.

- *Wet conditions*. In oxygenated water (bulk liquid or condensed film), DUO_2 oxygenation proceeds by an alternative mechanism. The oxidation kinetics are faster. The UO_2 is oxidized to UO_2^{+2}, the ion goes into solution, and the ion is then precipitated as schoepite ($UO_3*2[H_2O]$ or other UO_3–H_2O forms). Various other oxidized uranium mineral forms can be formed if the groundwater contains

other cations. This behavior begins to appear when the relative humidity exceeds 40%—with ensuing changes in the products with relative humidity. The YM project has assembled the existing data (7) for such conditions, and an empirical relationship for oxidation rates has been developed at Lawrence Livermore National Laboratory.

Both dry and wet reactions increase with surface area. It is hypothesized that smaller UO_2 particulates in the bed will more rapidly accelerate oxidation in partly wetted UO_2 beds, as compared to dry beds. With small particulate sizes, water tension will create liquid water zones, where particulates touch and dissolution and precipitation are accelerated. Flooded beds (as compared to partly wetted beds) will have slower oxidation kinetics because of the slower diffusion of oxygen through water, as compared to air, slows oxygen transport from outside the WP to the uranium surface. The fastest kinetics are expected to occur in a bed that is wet but which has sufficient air spaces such as to allow movement of gaseous oxygen.

There are several important observations based on the literature data for either mode of oxidation.

- *Fill permeability*. DUO_2 oxidation is expected to selectively fill the interparticulate void spaces. In the dry case, small particulates pop off the larger fill particulates. In the wet case, a precipitate forms. In either case, the voids are expected to be filled, and the permeability is expected to decrease. This behavior where the initial particulate is reduced in size during the oxidation process is in contrast with some other materials where oxidation increases the size of the particulates and thus the size of the interparticulate void spaces. If this alternative form of behavior occurred, the fill bed would remain permeable to rapid diffusion of oxygen or movement of oxidizing groundwater through the WP.

- *Low stresses*. In direct contrast to the higher-temperature oxidation of SNF UO_2, the oxidation process is not initially expected to generate high stresses on the SNF or WP because void spaces are filled. It has been observed experimentally that in dry air, SNF pins with clad failures will split because of the oxidation of UO_2 and the resultant expansion. This splitting in SNF is a consequence of two factors that do not apply to fills: (a) no interparticulate expansion void space and (b) higher temperatures, which allow the particulate to oxidize without breakup into fine grain particles (no popcorn effect) that can fill void spaces. By fortunate coincidence, the proposed YM repository has a maximum temperature limit of 350EC to minimize cladding failure. This maximum temperature is below that at which the mechanism of dry UO_2 oxidation changes from (a) breakup of particulates upon oxidation and filling of void spaces to (b) oxidation of whole particulates with the potential to create significant strain via particle expansion.

- *Chemically reducing conditions*. The DUO_2 oxidation process is expected to locally maintain chemically reducing conditions, which preserve the SNF UO_2. Some materials, when they oxidize, form protective layers that stop chemical reactions. For example, if aluminum metal were used as a fill material, the outer layer of the aluminum would form a protective layer of aluminum oxide. This layer would stop further oxidation and allow oxidizing conditions in the WP. No such highly protective layers have been identified in earlier experimental examinations of uranium oxidation.

The oxidation process reduces the permeability of the WP to air and groundwater flow and thus the rate of oxygen transport in the WP. The void spaces decrease. In systems with liquid water, capillary forces will result in water between grains. The presence of this water rapidly reduces the potential for convective air flow. The reduced transport of O_2 has several effects:

- *Extended times for reducing conditions.* Only some of the DUO_2 is oxidized in shutting down bed permeability. The remaining DUO_2 can help maintain reducing conditions for extended periods of time.

- *Lower groundwater flow.* The lower permeability reduces transport of radionuclides from the SNF to outside the WP.

The oxidation reactions start at the location of the WP failure. Over time, fill further from the failure location is oxidized. Consequently, the conditions in the WP vary both with time and location in the WP as the package degrades. For much of the history of the WP after initial failure, there will be zones of partly oxidized uranium and of DUO_2. The permeability of the fill will be low near the WP failure locations.

Parallel with the oxidation of the DUO_2, there will be uranium dissolution. Uranium is several orders of magnitude more soluble under oxidizing conditions than chemically reducing conditions. There will be a slow dissolution of uranium from the upstream side of the WP. The groundwater will become saturated in uranium and thus uranium dissolution only occurs on one side of the WP. There is an important geometric characteristic of the oxidized bed. The remains of each SNF rod are surrounded by the oxidized DUO_2. For a typical WP, there will be - 3.5 t of DUO_2 per t of SNF UO_2. The coolant channels in SNF are a significant fraction of the fuel assembly. The masses of DU slow SNF uranium dissolution.

The best-case scenario is blockage of groundwater flow through the WP. If this occurs, the ultimate transport of uranium and radionuclides from the WP will occur by congruent dissolution of the fill and SNF uranium from the upstream side of the WP and flow of the groundwater around the remains of the package. If this occurs there is no selective leaching of soluble radionuclides from the SNF as groundwater flows through the WP. Under these idealized conditions, most of the inventory of radionuclides will be trapped for millions to tens-of-millions of years that are required to dissolve a large package of uranium.

The uranium dissolution from the upstream side of the WP results in the simultaneous transport of both the SNF uranium and the DU. Uranium-235 from the original SNF and from the decay of ^{239}Pu is isotopically down-blended with the DU. This minimizes the potential for long-term nuclear criticality in the repository.

Implications for Experiments, Models, and Design

The uranium oxidation mechanisms described in the literature have implications for design. Overall DUO_2 fill density can be modified by choosing (a) the density of DUO_2 (typical reactor-grade UO_2 pellets have a density of - 95% of theoretical density) or (b) the volumetric fill fraction of the bed. By choice of particulate size range and distribution of sizes, the volumetric fill fraction can be varied from - 50 vol % to 80 vol %. The surface area for chemical reactions can be changed by the particle size distribution. A recent report (9) evaluates fill properties as a function of these and other parameters.

The above mechanisms are based on single crystal and unconfined particulate bed experiments. Confirmatory information on bed behavior in a confined bed is required. The most difficult theoretical and experimental question is the permeability of the WP to groundwater flow as a function of time. If this number is sufficiently small, extraordinary performance is possible.

STAGE IV: BEHAVIOR AFTER FILL AND SNF OXIDATION

The longer-term evolution of the WP will see all of DUO_2 and SNF UO_2 uranium oxidized to higher uranium oxidation states with the formation of complex, mineralized, hydrated uranium oxides. This is a multistep transition where the uranium is ultimately converted to uranium silicates—with the silica provided by the groundwater (Fig. 4). The slow conversion of the hydrated oxides to other uranium minerals will follow that shown in the laboratory (12) and found in natural uranium ore deposits. The conversion to more complex, hydrated, uranium oxides further expands the volume of the uranium compounds.

The WP is expected to collapse and cease to exist as a recognizable container. The geometry of the WP and its contents will change over time. When there are changes in container geometry, un-reacted DUO_2 will become exposed to oxidizing conditions and is expected to reduce the local permeability of the SNF-fill debris bed.

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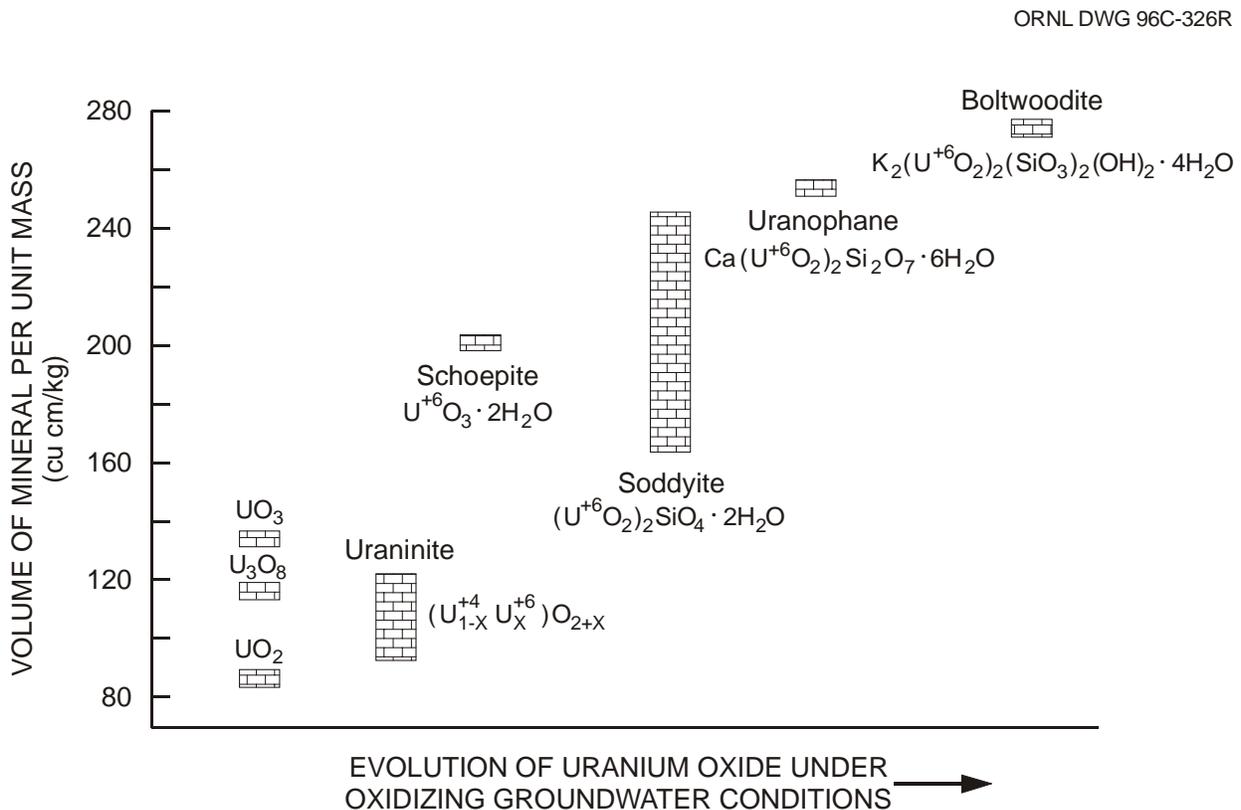
Fig. 4. Evolution of UO_2 over time in an oxidizing environment vs mineral density.

Experimental work has shown that many hydrated metal oxides act as ion exchanges to remove a variety of anion and cation radionuclides with high efficiency. This effect has been observed with iron, titanium, thorium, uranium, and other metal oxides (13). It has also been observed that when SNF UO_2 is leached with oxidizing groundwater, many radionuclides become incorporated into the oxidized, hydrated uranium oxides that form and are not released (or are only slowly released) from degraded SNF. These include difficult-to-isolate radionuclides, such as [237]Np (14). These phenomena are a consequence of (a) the ion-exchange capability of hydrated uranium oxides (created by the oxidation of SNF UO_2) and (b) other mechanisms. The relative importance of the different mechanisms are not well understood.

The hydrated oxidized products of DUO_2 fill oxidation will also retain many radionuclides independent of other mechanisms. There are strong theoretical reasons to expect that the absorption capability of these uranium oxides will exceed the adsorption by the degraded SNF oxides. In the SNF, the ion-exchange capability of SNF hydrated uranium oxides (degraded SNF) is saturated by fission products and actinides. As radionuclides migrate from the degraded SNF into the DUO_2 fill, with its low concentrations of fission products and actinides, many radionuclides that escape the SNF will be absorbed onto the fill. The limited existing data suggest that this is potentially a major mechanism for retention of radionuclides in a WP.

Significant additional experimental work is required to quantify the ion exchange and absorption behavior of DUO_2 fill. Historically, no one considered hydrated uranium oxides as an ion exchanger or absorber to remove radionuclides; thus, it is one of the few hydrated metal oxides that has not been extensively investigated as an ion-exchanger or absorber.

CONCLUSIONS

There have been many major experimental studies of the behavior of UO_2 under various oxidizing and reducing conditions. From this work, there is a basic understanding of the mechanisms of UO_2 oxidation and the kinetics of UO_2 oxidation. That knowledge base provides (a) reasonable confidence that the major mechanisms of uranium oxidation are understood, (b) a basis for initial construction of models of fill behavior, and (c) a basis for design of experiments to address unknowns. Significant remaining unknowns must be addressed before there can be reasonable confidence that the use of DUO_2 fill will result in major improvements in the performance of the repository system. Specifically, additional modeling and experiments are required to understand how fast and how long the various mechanisms operate and thus estimate how long radionuclides remain trapped within the degrading WP.

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