EFFECT OF DEPLETED-URANIUM DIOXIDE PARTICULATE FILL ON SPENT-NUCLEAR-FUEL WASTE PACKAGES

RADIOACTIVE WASTE MANAGEMENT AND DISPOSAL

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The use of depleted uranium dioxide (DUO_2) particulates as fill material for repository waste packages (WPs) containing light-water reactor (LWR) spent nuclear fuel (SNF) was investigated. A repository WP would be loaded with SNF, and small DUO_2 particulates (0.5 to 1.0 mm) would be added to fill the void space inside the WP—including the coolant channels inside SNF assemblies. The DUO_2 fill slows release of radionuclides from the SNF by (a) creating a local chemically reducing environment that slows degradation of the SNF UO_2 and (b) reducing groundwater flow through the WP. The depleted uranium (DU) fill minimizes the potential for long-term criticality in the repository by isotopic dilution of ^{233}U and ^{235}U. The potential for criticality is primarily determined by ^{235}U (a) originally in the SNF and (b) from decay of ^{239}Pu. The use of DU consumes excess DU from the production of enriched uranium. The mechanisms for improvements in repository performance with DUO_2 fill are defined, but additional work is required to fully quantify the benefits and costs of such an approach.

I. INTRODUCTION

Spent nuclear fuel (SNF) is highly radioactive. However, the radionuclides in SNF decay, in time, to nonradioactive isotopes. Consequently, the approach for safe disposal of SNF is to isolate the SNF from the environment until the radioactive decay reduces the hazards to low levels.

The strategy adopted worldwide for disposing of SNF is to bury the SNF in waste packages (WPs) hundreds of meters underground in a geological repository. The expected geological-repository failure mode is (a) WP failure by corrosion, (b) the dissolution of radionuclides into the groundwater and formation of colloids that are transportable by groundwater, and (c) the ensuing movement of the groundwater to the open environment. The addition of barriers to slow radionuclide dissolution and groundwater movement aids repository performance by providing time delays for the radionuclides to decay.

A new approach[1] to improve repository performance and to potentially lower fuel cycle costs has been identified. Waste packages are filled with SNF. Depleted uranium dioxide (DUO_2) particulates are then added to fill the void spaces. The DUO_2 particulates (a) create barriers to slow the release of radionuclides from the repository, (b) reduce the potential for nuclear criticality in the repository, and (c) minimize long-term management costs associated with depleted uranium (DU).

The results herein are from a series of investigations[2–5] and recent work. The studies primarily addressed disposal of light water reactor (LWR) SNF in a repository above the water table with oxidizing geochemistry—such as the proposed Yucca Mountain (YM) repository in the United States. Most of the results are applicable to other geological environments.

II. PHYSICAL DESCRIPTION OF THE WP CONCEPT

The proposed WP with DUO_2 fill would be similar in design to the current YM repository WP that accepts 21 pressurized-water-reactor (PWR) fuel assemblies or 40 boiling-water-reactor fuel assemblies. The loading sequence for the WP (Fig. 1) starts with placing the SNF into the canister. A cover with holes is placed over the SNF and the WP is then filled with DUO_2 particulates with sizes from 0.5 to 1.0 mm. The particulate size is sufficiently small to fill void spaces in the WP (corners

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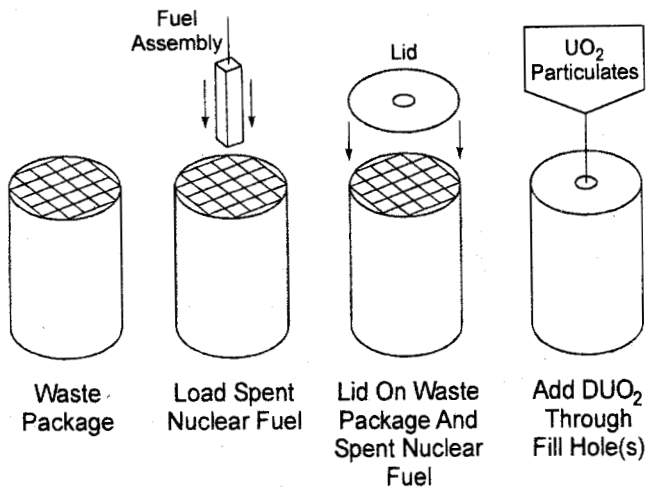

Fig. 1. WP loading sequence.

between the circular WP and square basket structure) and the coolant channels within each SNF assembly.

The analysis herein used the multipurpose canister (MPC) as a basis[6] for investigation of issues associated with the use of fill materials. The MPC is a basket that can be loaded with SNF. The MPC can then be placed (a) in a storage overpack for storage, (b) in a transport overpack for transport of SNF, or (c) in a repository overpack to create a repository WP. Since this design was completed, the YM program has integrated the separate basket and overpack structures into a single WP. These changes in the detailed WP design do not significantly impact the use of DUO_2 fill.

Most of the space in the WP is void space that can be filled with particulates. For the WP designed for 21 PWR SNF assemblies, the WP internal volume is 7.9 m^3, and the SNF internal basket structure has a solid volume of 1.1 m^3. The 21 PWR SNF assemblies have a solid volume of only 1.6 m^3 and are mostly empty coolant channels. Thus, 5.2 m^3 of the 7.9 m^3 of internal WP volume can be filled with 36.7 t of DUO_2 particulates. With most nuclear fuels, most of the canister volume is void space and available for DUO_2 fill. Table I shows a nominal design for use of DUO_2 fill in the MPC.

TABLE I

Representative WP Design for 21 Fuel Assembly PWR SNF Assemblies with DUO_2 Particulate Fill

Property	Value
SNF, MTIHM	9.96
Solid particulate density, g/cm^3	10.96
DU, wt%	88
DU mass, t	32.3
Ratio of DU to SNF	3.33
DUO_2 mass, t	36.7
Theoretical fill density, %[a]	65.0
Assay (wt%) of DU ^{235}U	0.2
Equivalent ^{235}U assay (wt%) of SNF	1.6
Equivalent ^{235}U assay (wt%) of WP	0.53

[a]For uniform spheres in a face-centered cubic array, the spheres would occupy 74.048 vol% of the void space. A particulate packing fraction of 100% implies that 74.048 vol% of the void space is filled with solid particulate and that the remainder of the space is unavoidable void space between particulates. Higher fill fractions are only possible with the use of multisize spheres where the smaller spheres fill the voids between the larger spheres.

III. CONTROL OF RADIONUCLIDE RELEASE RATE FROM THE WP

The use of DUO_2 fill in an oxidizing repository environment such as YM can improve radionuclide isolation by several mechanisms.

III.A. Reduction of Groundwater Flow Through the WP

Groundwater is the mechanism that transports radionuclides from SNF to the environment. Therefore, reduction and elimination of groundwater flow through the SNF minimizes release of radionuclides. DUO_2 fill can help accomplish this task by two mechanisms: (a) diverting groundwater around the WP and (b) creating WPs with low permeability to groundwater flow.

III.A.1. Diverting of Groundwater Around the SNF

Fill materials that support the WP wall and exterior barriers to radionuclide migration help divert water around the SNF. This characteristic applies to all fill materials that can support the WP exterior walls. An example demonstrates this function. One design option for the proposed YM repository is a Richards barrier[7] around the WP. This barrier consists of a gravel layer next to the WP with a sand layer above and horizontal to the WP (Fig. 2). Capillary forces hold the water in the sand, and gravity diverts water flow around the WP through the sand layer. When the groundwater is diverted away from the WP, radionuclides in a degraded WP cannot be transported by groundwater to the environment.

The successful operation of such a barrier requires long-term control of WP geometry. A WP without an internal fill material is >60% empty space—such as SNF coolant channels. When the WP ultimately fails because of corrosion, consolidation will alter the geometry of the Richards barrier and cause its partial failure (Fig. 2), thus diverting water to the degraded SNF[8] and allowing transport of radionuclides from the degraded SNF by groundwater.

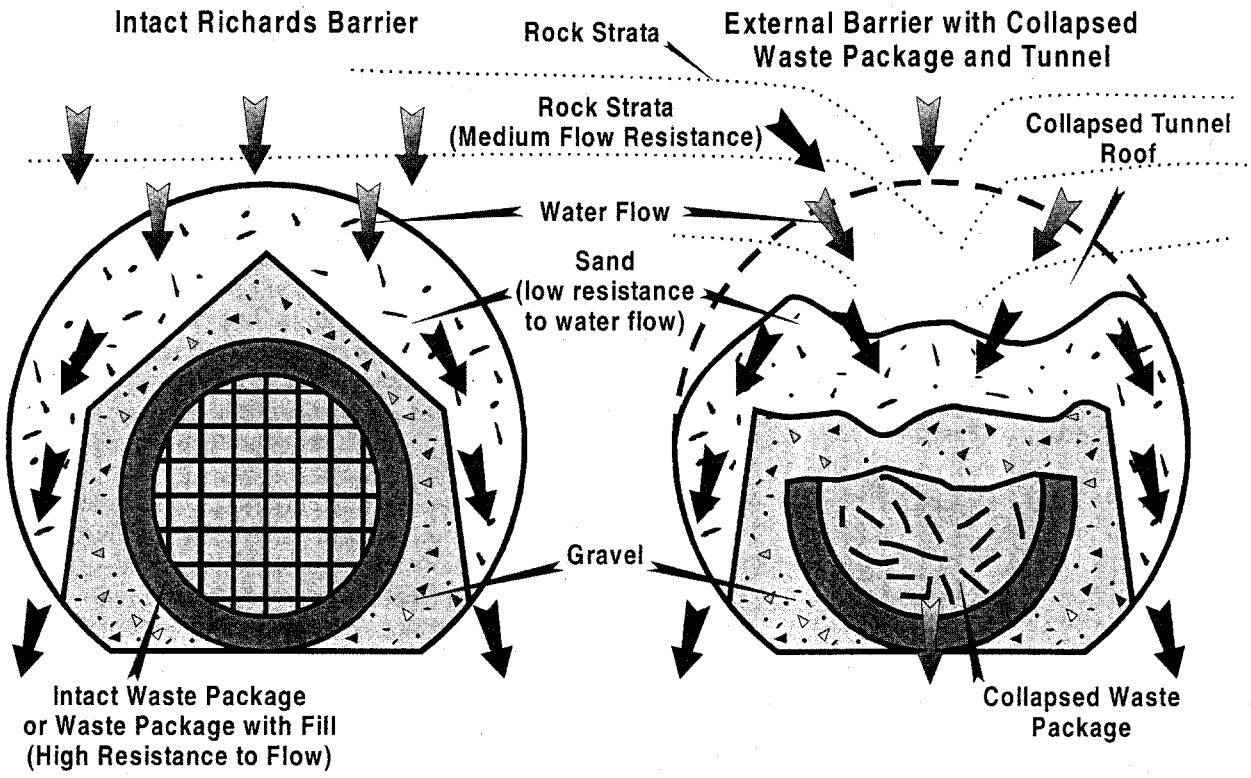

Fig. 2. Impact of WP collapse on exterior barrier performance.

Water does not simply flow through rock. It preferentially flows through cracks. If the tunnel can collapse, there will be collapse of the rock above the tunnel. This will intercept more cracks with water flow and preferentially divert water toward the SNF. This is observed in the mining industry, where tunnels drain water from large zones of rock. This phenomenon is parallel to the problem of early, shallow-land, low-level-waste (LLW) disposal sites, where radioactive waste consolidation caused surface depressions that diverted surface and groundwater through the wastes and brought about an increased release of radionuclides to the environment.

The technical solution is to use a fill material inside the WP to support the external WP wall and thus support external radionuclide barriers and tunnel backfill. Voids inside the WP are minimized. This technology using inert fills has been developed and demonstrated in Canada and elsewhere (see the following). The DUO_2 particulate fill will also perform this function.

III.A.2. Creating WPs with Low Permeability to Groundwater Flow

Water follows the path of least hydraulic resistance. To minimize groundwater flow through the SNF, the WP and its contents should have the lowest permeability to water flow of any component (external WP barriers or geology) in the repository. If the WP has low hydraulic permeability and is surrounded by more permeable rock or barriers—such as a Richards barrier—a true hydraulic cage is created to divert water. The use of DUO_2 may create such an option.

After WP failure in a repository with oxidizing air or groundwater, the DUO_2 fill will oxidize to higher valence-state, hydrated uranium oxides, which have lower densities.[9] The resultant higher specific-volume hydrated uranium oxides (U_3O_8 and $UO_3 \cdot xH_2O$) (a) fill the void spaces between particulates in the WP and (b) consequently reduce WP permeability to fluid flow. If the WP basket is made of a nonnoble metal, such as steel, the metal will also oxidize. The metal oxides are less dense than the metals and thus will also fill the void spaces. These chemical reactions create a self-sealing system that minimizes air and water flow through the SNF. The SNF UO_2 remains as UO_2 embedded in the oxidized DU_3O_8 and $DUO_3 \cdot xH_2O$ (schoepite) for very long times. Figure 3 graphically shows the intermediate oxidation process that fills the void spaces.

The use of DUO_2 fill to reduce WP permeability requires a backfill material between the exterior of the WP and the tunnel walls. (In the current YM design, the use of a backfill is a design option.) If there is no backfill,

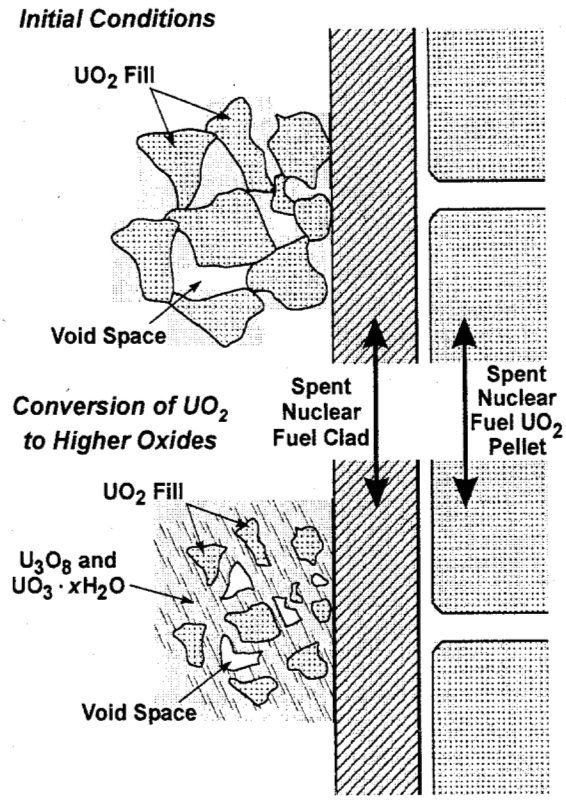

Fig. 3. Conversion of UO_2 to U_3O_8 and $UO_3 \cdot xH_2O$ resulting in a reduction in WP water and air permeability.

the WP will ultimately break open, voids will open between the fill material and SNF, and the WP contents will spread out over the floor of the disposal drift.

There are three important characteristics of this fill material: fill properties, protection of the SNF, and long-term behavior.

III.A.2.a. Fill Properties. For the specific example herein, the final volume of the basket and fill material, if oxidized, would be ~110% of the initial basket, DUO_2, and void space volume. This assumes (a) no outer WP or SNF oxidation, (b) the basket is made only of iron, (c) the DUO_2 and basket are fully oxidized, and (d) the oxidation products are at their theoretical densities. In any real situation, there will be partly oxidized materials. The fill is expected to have low permeability to groundwater.

The fill expansion and reduced permeability are a consequence of the chemistry of uranium oxidation. Under oxidizing conditions, both pure UO_2 and SNF UO_2 will chemically react with oxygen in air and groundwater; however, there are differences.[9,10] In dry air, UO_2 oxidization can be best represented as a two-step process beginning with initial oxidation to U_3O_7 followed by oxidation to U_3O_8. LWR SNF UO_2 oxidation is best represented by a different two-step oxidation process: initial oxidation to U_4O_9 followed by oxidation to U_3O_8. The initial oxidation step for both materials results in small volume changes; however, the second oxidation step results in large volume increases. This oxidation process also converts the UO_2 particulate into smaller U_3O_8 particulates with the final particulate size primarily controlled by the initial grain size of the UO_2 in the fill material. In total, the oxidation of UO_2 to U_3O_8 results in a 36 vol% increase and a corresponding decrease in density. Under humid conditions or in oxidizing groundwater, the products are initially a mixture of U_3O_8 and $UO_3 \cdot xH_2O$. The creation of smaller particles during oxidation that fills the void spaces (versus simple growth in the size of the fill particles and void spaces between the particles) assures low permeability of the fill to groundwater flow.

In addition to oxidation of UO_2, most metallic WPs and basket structures will oxidize. Steel is the most common material of construction.[11] When iron—the primary component of steel—oxidizes to either Fe_2O_3 or Fe_3O_4, its volume increases by ~2.1. Oxidation of the basket will typically fill ~20% of the void space in a WP. The sequence of oxidation (UO_2 versus Fe) will be determined by what first contacts oxygen and what basket material is selected. Experimental data indicates[12,13] that mild steel preferentially reacts with oxidizing groundwater before UO_2.

III.A.2.b. Protection of SNF. The fill preferentially oxidizes and reacts with groundwater. This is desirable so to delay degradation and subsequent release of radionuclides from the SNF. Five factors favor oxidation of DUO_2 over SNF UO_2, described in the following.

1. *Location*: The fill surrounds the SNF; thus, oxygen first contacts the DUO_2 before it can reach the SNF UO_2.

2. *Mass*: For a typical design, the mass of DUO_2 is more than three times the mass of SNF UO_2. If all other conditions are equal, most of the oxygen will react with the DUO_2.

3. *Particulate size*: The small DUO_2 particulates have a large surface area compared to the SNF UO_2. Chemical reaction rates are proportional to surface area.

4. *Clad barrier*: The zircaloy clad provides an added barrier to oxidation of SNF UO_2 compared to the DUO_2.

5. *Oxidation rates*: Low temperature oxidation experiments have been conducted with pure UO_2 and irradiated SNF UO_2. These experiments[9,10] show that the first step in the oxidation process is faster for SNF UO_2 than is the first step in the oxidation process for UO_2. This step does not involve significant volume changes. The second oxidation step—with large volume changes that can break up the SNF—is much faster for DUO_2. Rare earths and actinides stabilize the SNF UO_2 from oxidation to U_3O_8. The SNF UO_2 will oxidize last.

III.A.2.c. Long-Term Behavior. Once a low-permeability zone is created, the water would be expected to flow around the SNF—not through it. There would be the dissolution of the uranium on the outside surfaces of the fill material. This dissolution process is slow because of the formation of lower-solubility uranium silicate compounds and the buildup of insoluble iron oxides from the WP. Groundwater contains dissolved silica. In the presence of this dissolved silica, the uranium oxides further evolve to lower-density, hydrated uranium silicates using the dissolved silica in groundwater. Figure 4 shows the long-term evolutionary sequence for UO_2 as it has been observed with oxidizing groundwater in natural uranium ore bodies,[14] in the laboratory with UO_2 (Refs. 15 and 16), and in the hot cell with SNF UO_2 (Ref. 17).

A simplified calculation can provide some perspective on the impact of a low-permeability matrix of uranium oxides and silicates around the SNF. Assume that groundwater is not diverted from the WP but rather flows by the WP and is saturated with uranium; that is, any water that would have intercepted the WP dissolves uranium from the outside surface and becomes saturated in uranium. In this case, the consequence of the low permeability is to ensure congruent dissolution, which is dissolution of the uranium from the upstream side to the downstream side of the uranium mass with release of actinides and fission products only when the uranium matrix is dissolved. No barrier of insoluble materials builds up. Such a WP has different behavior than does a WP with high permeability to water flow.

1. *Releases spread out over time*: In a degraded WP with high-surface-area degraded SNF, more soluble elements such as cesium, iodine, and technetium are quickly leached and released from the SNF rubble.[18] If the DUO_2 fill results in low degraded-WP permeability and blocks groundwater flow, radionuclide releases are proportional to the uranium dissolution rate and are low.

2. *Delayed time of first release of fission products and actinides*: The initial release of radionuclides depends on the time to dissolve the DUO_2 between the SNF and the interior WP wall. Increasing the DUO_2 in the WP increases the time before release of nonuranium isotopes.

Using the previous assumptions (WP with 42.26 t of uranium and an interior WP cross section of 7.5 m^2), the current estimate of uranium solubility in groundwater[19] at YM (7.6 g/m^3), and a long-term average groundwater flow rate of 3.25 cm/yr (Ref. 19), it will take >20 million yr to dissolve all the uranium and release all the radionuclides from the WP. Mechanisms such as diffusion of soluble radionuclides from the WP will accelerate releases, but the release rates will be low compared to any failed WP with SNF that is permeable to groundwater flow.

III.B. Chemical Effects of DUO_2 Fill on WP Performance

The DUO_2 fill slows release of radionuclides from the SNF because of several chemical mechanisms.

III.B.1. Maintenance of Chemically Reducing Conditions to Minimize SNF UO_2 Degradation

Because uranium in DUO_2 is in the +4 valence state, chemically reducing conditions are ensured within the WP

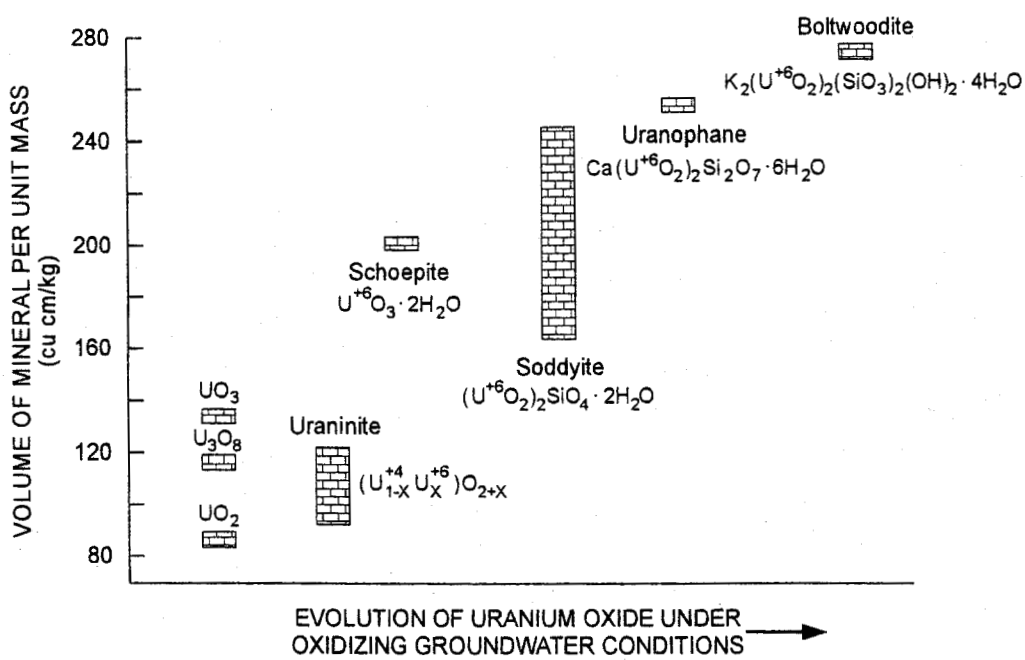

Fig. 4. Specific volume of selected uranium minerals versus evolution over time in oxidizing groundwater.

for an extended time independent of external groundwater chemistry or air. As discussed earlier, after a WP failure, any oxygen in air or groundwater would first react with the DUO_2 fill before it encounters the SNF. The DU in the +4 chemical state would be oxidized to the +6 chemical state through a series of oxidation steps, thus removing the oxygen. If both the WP and basket are made of metal, an additional mechanism is provided for oxygen removal. The removal of oxygen and maintenance of chemically reducing conditions minimize the release of fission products and actinides from the SNF by several mechanisms, described in the following.

1. *Chemical Stability*: SNF UO_2 is thermodynamically stable under chemically reducing conditions. Fission products and actinides that are trapped in the SNF UO_2 crystal structure cannot escape until the crystal structure is destroyed.[17,20]

2. *Uranium Solubility*: The solubility of uranium in groundwater under chemically reducing conditions[21,22] is about four orders of magnitude less than the solubility of uranium under oxidizing conditions with solubilities <1 ppb. Consequently, radionuclide release caused by dissolution of the SNF UO_2 is extremely slow.

3. *Actinide and Fission Product Solubilities*: Chemically reducing conditions minimize the solubility and transport of several other long-lived radionuclides (e.g., neptunium and technetium) and reduce formation and transport of radionuclides as colloids.

III.B.2. Reduction of SNF Radionuclide Release Rate by Saturation of Local Environment with Uranium

Filling the WP with DUO_2 fill creates a local groundwater environment saturated in uranium species. The small particulates (with their high surface areas) saturate the groundwater with DU without fission products rather than with uranium with fission products from the SNF. This phenomenon slows the dissolution of the UO_2 in the SNF.

III.B.3. Reduced Radionuclide Release Rates by Ion Exchange and Sorption with Hydrated DU Oxides

Experimental work has shown that many hydrated metal oxides act as ion exchangers or absorbers 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.[23] Such ion exchangers are now leading candidates at the Hanford and Savannah River Sites in the United States for cleanup of highly radioactive liquid waste streams.

It has 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 (Ref. 24). This phenomena is a consequence of the ion-exchange capability of hydrated uranium oxides (created by the oxidation of SNF UO_2) and other mechanisms. The relative importance of the different mechanisms are not well understood.

The first phenomenon is also a mechanism of radionuclide retention with the use of DUO_2 fill independent of other mechanisms. 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 into the fill. The limited existing data suggest that this is potentially a major mechanism for retention of radionuclides in a WP, but significant additional experimental work is required to quantify the effect. Historically, no one considered hydrated uranium oxide as an ion exchanger to remove radionuclides; thus, it is one of the few hydrated metal oxides that has not been extensively investigated as an ion exchanger.

III.B.4. Protection from Variable Groundwater Chemistry

The use of DUO_2 provides a mechanism to counteract any unexpected changes in groundwater that may accelerate the degradation of the SNF. Groundwater chemistry can change because of climatic changes and human activities (e.g., irrigation, groundwater pumping, liquid waste injection, etc.). DUO_2 has the same basic chemistry as SNF UO_2. The DUO_2 acts as a sacrificial chemical to absorb changes in groundwater chemistry and delay their effects on the SNF. DUO_2 is the only material that can be used as a sacrificial protective material if the future chemical conditions can not be predicted. All other sacrificial materials are sacrificial only in some types of environments relative to SNF UO_2.

III.C. Repositories with Reducing Environments

The preceding analysis is for repositories under oxidizing conditions. With chemically reducing groundwater, such as the proposed Swedish, Canadian, British, French, German, and Belgian repositories, UO_2 does not change its chemical form: It is thermodynamically stable. The fill material assists isolation by support of the WP wall. The DUO_2 saturates groundwater in the WP with uranium and suppresses SNF UO_2 dissolution. Degradation of SNF is very slow under these conditions.

The dissolution rate of UO_2 is determined by total water flow and the difference between the uranium concentration in the groundwater and the solubility of uranium in groundwater. However, the solubility of uranium in the reducing groundwater is very low. Studies of granite[25] predict uranium solubility limits between 23.8

and $<3 \times 10^{-5}$ ppb with measured values from <0.01 to 44.5 ppb. The values depend upon other elements in the rock. Typically ~1 ppb (Ref. 21) is used as a representative value for uranium solubilities. These solubilities are orders of magnitude lower than the solubility of uranium in oxidizing groundwater.

IV. AVOIDANCE OF POSTCLOSURE REPOSITORY NUCLEAR CRITICALITY

Nuclear criticality while placing SNF into the repository can be prevented using traditional engineering techniques (geometry control, neutron absorbers, etc.). However, such techniques do not necessarily ensure criticality control after repository closure. Eventually, the WPs and SNF will fail, and groundwater will preferentially dissolve selected elements. This certainty implies that the geometry of fissile materials and the relative amounts of fissile materials and neutron absorbers change over time. Engineered criticality control techniques may or may not work. The use of DUO_2 provides an alternative criticality control strategy.

IV.A. Potential For Nuclear Criticality

The historical geological record[26–28] shows that nuclear criticality has occurred in natural uranium ore bodies. Sixteen natural nuclear reactors have been identified at Oklo, Gabon, Africa. Nuclear chain reactions began when the ^{235}U enrichment of natural uranium on earth was about 3.6% and after natural geochemical processes concentrated the uranium into large, concentrated uranium ore bodies. After operation and the ensuing generation of heat and fission products, ^{235}U enrichments of the uranium at shutdown were as low as 1.3%. Today natural uranium deposits have a ^{235}U enrichment level of 0.71% because of the long-term decay of ^{235}U. Nuclear criticality can no longer occur in natural uranium ore bodies because of these low enrichment levels (Fig. 5).

The average fissile content of LWR SNF in the United States is equivalent to 1.5 wt% ^{235}U (Ref. 29). Most of the fissile material is ^{235}U and ^{239}Pu; however, the ^{239}Pu decays to ^{235}U. This fissile enrichment is significantly greater than the fissile content of naturally occurring nuclear reactors. Planned repositories contain several orders of magnitude more uranium than do typical ore deposits. Consequently, the potential exists for future nuclear reactors to be created from enriched uranium in a repository by the same mechanisms that have created natural uranium ore bodies that in turn became natural nuclear reactors.

There is no consensus on how common natural criticality events were in the past; thus, there is no consensus on the probability of such events in SNF repositories in the future. The discovery of the Oklo natural reactors showed that geochemical processes could create natural reactors. The latter discoveries of uranium isotopic anomalies in ore deposits worldwide suggest that nuclear criticality probably occurred in many locations. Because mountain ranges are created and destroyed over a period of several hundred million yr, many uranium ore deposits are formed and destroyed over a similar time period with the ultimate destruction of most of the natural reactors. The most logical explanation for the small uranium isotopic anomalies among current uranium ore bodies is that different amounts of uranium in these ore bodies came from uranium in earlier reactors. Recent analysis of atmospheric xenon isotopic anomalies[30] suggests that ~2.5% of the xenon in the atmosphere is from neutron-induced fissioning of ^{235}U—implying that natural nuclear reactors may have been common.

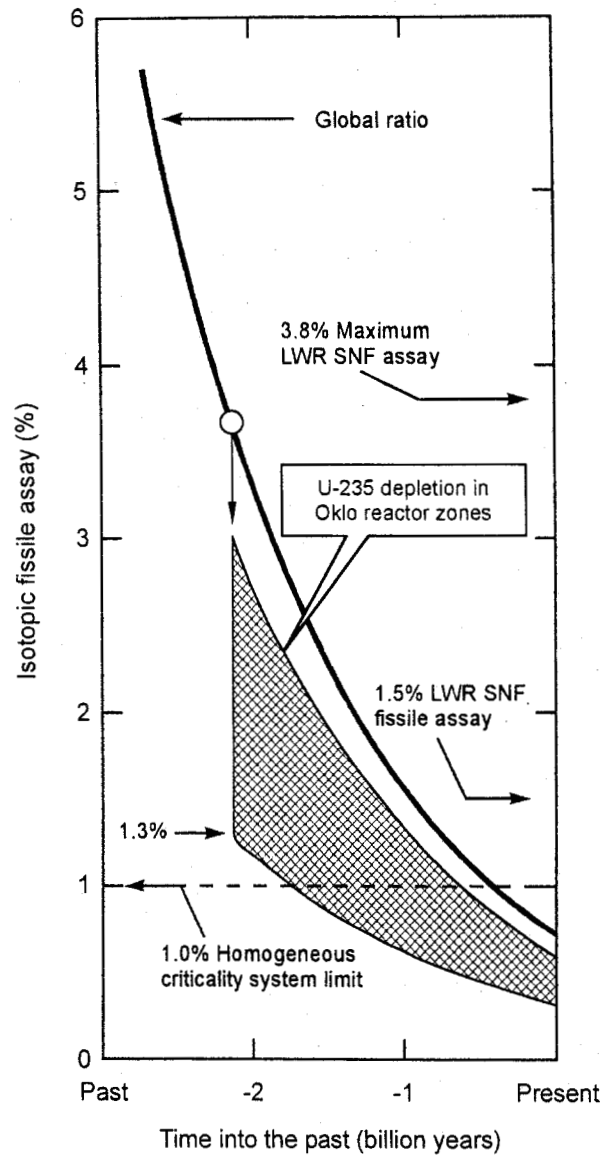

Fig. 5. Natural uranium enrichment levels over geological time.

IV.B. Consequences of Nuclear Criticality

Naturally occurring nuclear reactors generated radioactivity and heat over hundreds of thousands of years. In a repository, the heat generated from nuclear criticality would increase repository temperatures that (a) accelerate chemical reactions, which in turn, accelerate degradation of SNF; (b) cause water movement within a repository that may transport radioactivity to the environment; and (c) create added uncertainties in repository performance. Water movement can be accelerated by heat in both unsaturated[31] and saturated geological environments. This potential is coupled with the following two other considerations.

1. *Timing*: Nuclear criticality, if it occurs, will happen after WP failure and selective movement of fissionable materials (see the following). The WP barrier to radionuclide movement will no longer exist to prevent radionuclide migration that is accelerated by the existence of hot water.

2. *Location*: The fissionable materials may be transported beyond the repository boundaries. Nuclear criticality—with generation of fission products—may occur beyond the specific geology chosen to contain the radionuclides.

IV.C. Fissile Uranium Isotopes: The Dominant Criticality Concern

Two factors, described in the following, determine whether a fissile isotope may cause nuclear criticality in a disposal site: radioactive decay half-life and geochemistry.

IV.C.1. Radioactive Decay Half-Life

Only long-lived fissile materials can realistically cause nuclear criticality in a disposal site. For operational safety, SNF is packaged to avoid the potential for "near-term" nuclear criticality events. WPs are designed to last several thousand yr. Geological processes that can dissolve and reprecipitate fissile materials into a critical mass (CM) require significant time. Short-lived fissile isotopes decay before they can cause nuclear criticality.

The primary isotopes of concern [^{233}U ($T_{1/2} = 1.6 \times 10^5$ yr), ^{235}U ($T_{1/2} = 7.0 \times 10^8$ yr), ^{237}Np ($T_{1/2} = 2.0 \times 10^6$ yr), and ^{239}Pu ($T_{1/2} = 2.4 \times 10^4$ yr)] were derived by examining the half-lives and decay schemes for all fissile isotopes with half-lives in excess of 1 yr, as shown in Fig. 6. The figure also shows the subcritical mass limits (SCMLs). The CM for a specific isotope is just above the SCML. The fissile uranium isotopes are the primary criticality concerns because of their long half-lives and the decay of other fissile isotopes (including ^{239}Pu) into fissile uranium isotopes.

IV.C.2. Geochemistry

The repository design and geochemical considerations determine which long-lived fissile isotopes are most likely to create potential long-term criticality concerns. Because chemical behavior determines the potential for concentrating specific elements in the geology, the analysis must be done element by element.

IV.C.2.a. Neptunium. Neptunium is not a major criticality concern.[3] Neptunium is a significant radionuclide of concern in the design of a repository because of its tendency to migrate in groundwater.[19] The same chemical behavior that allows its transport in groundwater also makes the concentration of neptunium into a CM unlikely. Furthermore, neptunium (Fig. 6) has a large CM; it would be difficult to precipitate from groundwater a sufficient mass of neptunium to cause criticality.

IV.C.2.b. Plutonium. It is possible, but unlikely, that plutonium in LWR SNF would cause nuclear criticality to occur in a repository environment. However, the primary plutonium isotope ^{239}Pu has a half-life of 24 000 yr (i.e., the decay rate is 3×10^{-5}/yr) and decays to ^{235}U. The ^{235}U decay product of plutonium is a potential criticality concern in a repository environment. There are several reasons why plutonium in LWR SNF is not likely to be of significant concern in terms of nuclear criticality. (The analysis herein may not apply to wastes with high plutonium concentrations.)

1. *Historical Data.* Theoretical, laboratory, and field data from naturally occurring reactors[26,27,32,33] indicate that in most environments the plutonium will decay to uranium before the uranium or plutonium can be transported from the waste form. These data must be used with caution. Most of the data are from studies of uranium ore deposits under reducing conditions where the plutonium is trapped in stable UO_2 crystal structures. For these conditions, the scientific case for minimal plutonium transport is strong. The data are less clear for repositories under oxidizing conditions where the UO_2 may be oxidized with the release of plutonium colloids.

2. *WP Performance.* For the proposed YM repository, it is estimated[19] that the first WP failure will occur at ~2500 yr but that the median age at WP failure will be ~150 000 yr. For most proposed WP systems worldwide, most of the plutonium will decay to ^{235}U before complete WP failure occurs and fissile materials are transported from the WP.

3. *Effects of DUO_2 fill.* Transport of SNF UO_2 and plutonium by groundwater is delayed by the mechanisms previously discussed.

IV.C.2.c. Uranium. The primary mechanisms to create uranium ore bodies and the potential for nuclear criticality are results of planetary geochemistry. The planet exists under chemically reducing conditions and initially

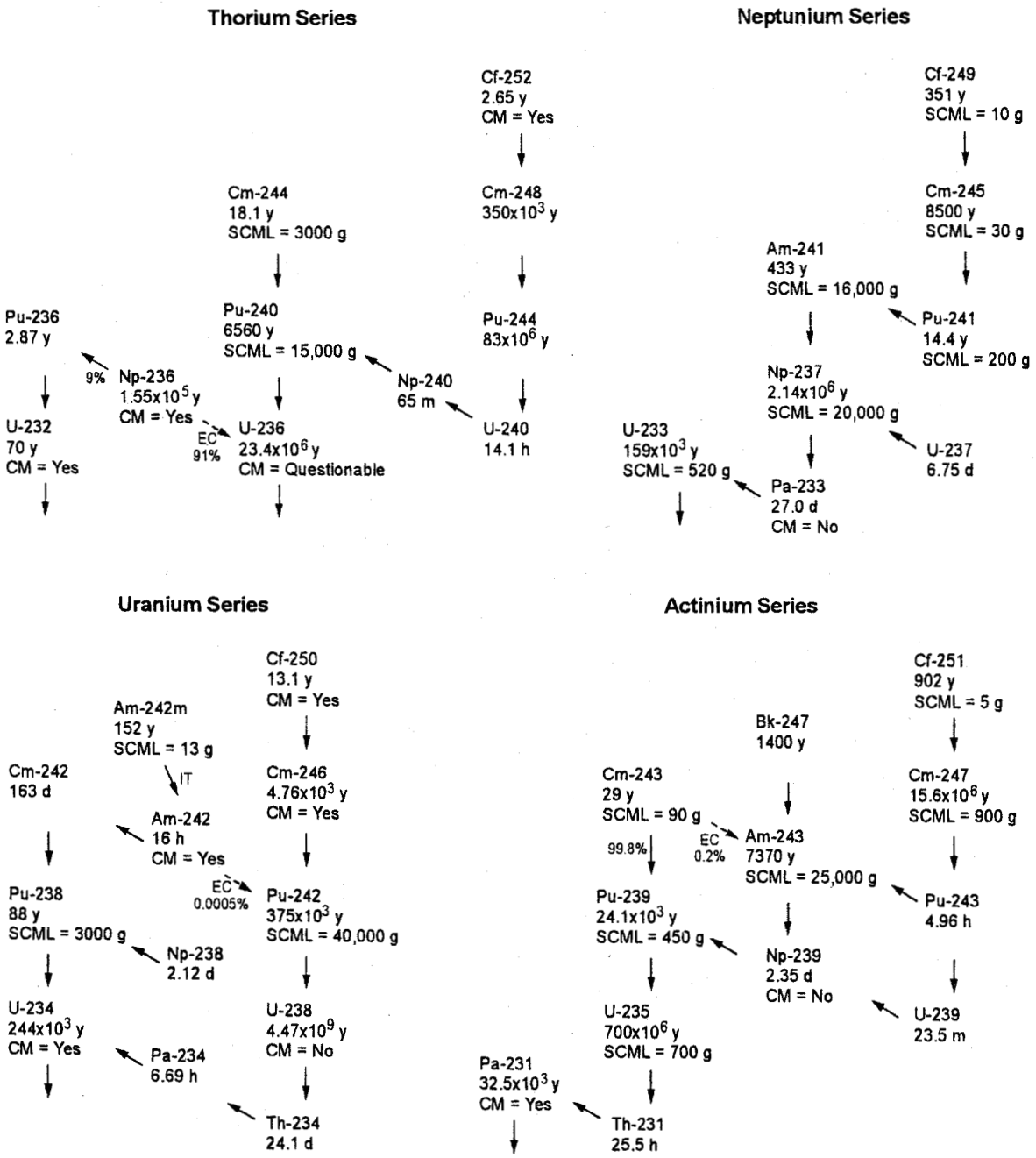

Fig. 6. Decay pathways, half-lives, and subcritical mass limits of fissionable isotopes.

had a chemically reducing atmosphere. About two billion yr ago, with the evolution of life and photosynthesis, the atmosphere evolved from a reducing atmosphere to an oxidizing atmosphere.[34] On land, the oxidizing conditions extend from the atmosphere to below the earth's surface for distances measured from <1 cm (coal deposits, swamps, etc.) to >1000 m. The ocean is under oxidizing conditions, but sludges on the bottom are, for the most part, under chemically reducing conditions because of the decomposition of organic material.

The solubility of uranium compounds is strongly dependent upon the oxidation conditions of the environment. Under reducing conditions, uranium is in the +4 valence state, is highly insoluble in water (<1 ppb), and is often found as UO_2. Under oxidizing conditions, uranium is in the +6 valence state, is two to four orders of magnitude more soluble than under reducing conditions, and is almost always found as a uranyl (UO_2^{+2}) ion. Oxygen dissolved in water will oxidize uranium from the +4 to the +6 valence state. Because of these chemical

characteristics, many uranium ore deposits are formed by the oxidation of uranium from the +4 to the +6 valence state by oxidizing groundwater (from rain), the subsequent dissolution in groundwater, its transport in groundwater, and its reprecipitation when the groundwater flows through a chemically reducing environment, which reduces uranium from the +6 back to the +4 valence state (Fig. 7). Reducing environments are primarily, but not exclusively, created by organic materials and iron in the +2 valence state and the metal state.[13]

This relatively unusual redox chemistry implies that unlike most other types of ore deposits, many uranium ore deposits migrate over time.[35] Flowing oxidizing groundwater will also oxidize other reducing agents within the rock. Uranium precipitated by chemical reduction will then be reoxidized, dissolved, transported, and reprecipitated. The uranium remains at the boundary between chemically oxidizing and reducing rock conditions and moves as oxidizing groundwater alters the location of this chemical interface. Such uranium ore deposits are known as "roll-front" deposits, and some of these roll-front deposits have moved many kilometers over longtime periods.

These and other mechanisms have extracted uranium from rock at concentrations of a few parts per million and created ore bodies with uranium concentrations of several tens of percent by weight. The concentration process separates uranium from most other elements, including boron, cadmium, and rare earths. The only elements consistently found with natural uranium ore bodies are silicon, oxygen, and hydrogen in the chemical forms of silica, silicates, and water. There are three competing processes that determine the fate of enriched uranium. They are:

1. *Fission.*

2. *Isotopic dilution with natural uranium*: As the enriched uranium is transported by groundwater, it will isotopically exchange with natural uranium in the rock and be isotopically diluted to ~0.7 wt% ^{235}U, and trace quantities of ^{233}U, if the enriched uranium contains ^{233}U. This process eliminates the potential for nuclear criticality.

3. *Radioactive decay*: Fissile uranium isotopes decay to nonfissile isotopes. Radioactive decay eliminates the potential for nuclear criticality.

The half-life of ^{235}U is 7×10^8 yr. However, geochemical processes that result in mountain building and destruction from erosion are an order of magnitude faster

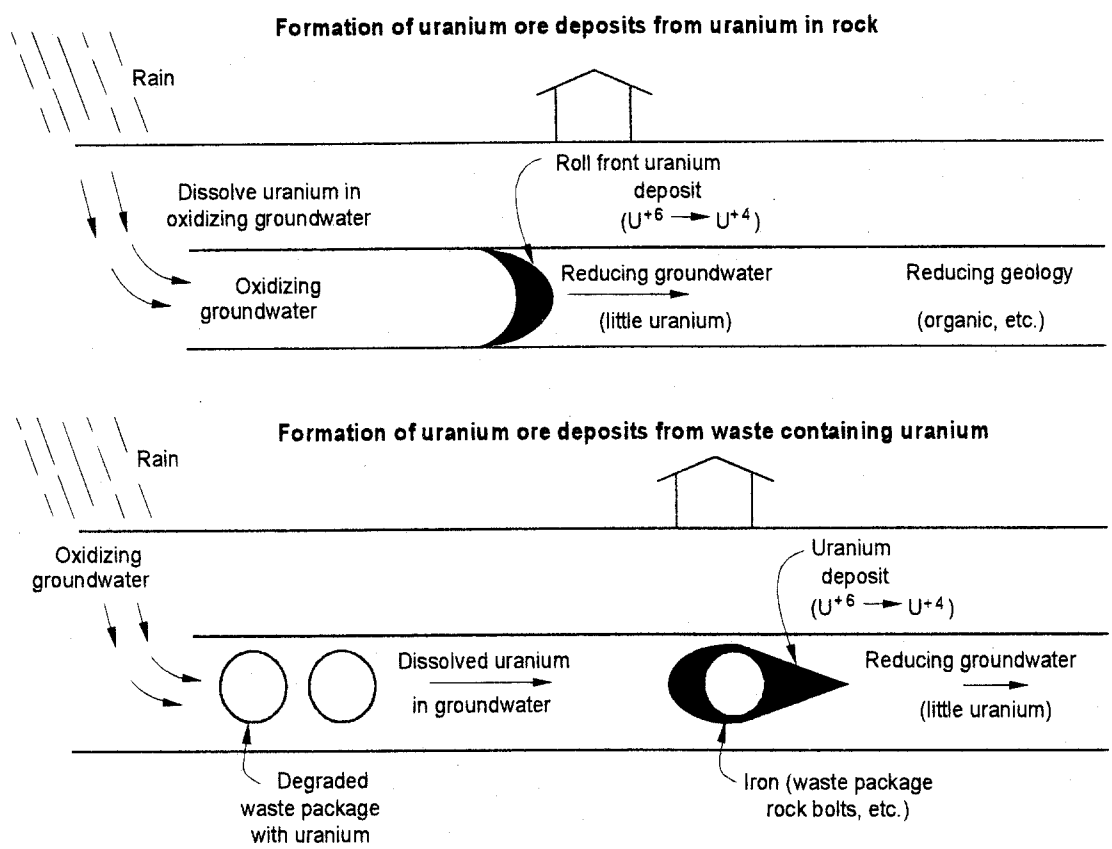

Fig. 7. Natural and man-made formation of uranium ore deposits.

than this; thus, enriched uranium is destroyed by fission or by isotopic dilution before significant radioactive decay occurs.

IV.D. Basis to Demonstrate Criticality Control

Long-term repository criticality control can be assured by (a) demonstrating that as enriched uranium migrates, it will be isotopically diluted with natural uranium in the rock before nuclear criticality can occur or (b) adding DU as a fill around the SNF. For DU to be used for criticality control there are two requirements: (a) defining how much DU is required and (b) ensuring that the DU mixes with the enriched uranium before natural processes can concentrate the uranium into a CM.

IV.D.1. Defining How Much DU Is Required

Nuclear criticality in natural environments can be prevented by isotopically diluting ^{235}U to <1 wt% ^{235}U in ^{238}U (Ref. 3) and isotopically diluting ^{233}U to <0.66 wt% in ^{238}U (Ref. 36). These values are based on multiple considerations: (a) experimental measurements of the uranium enrichments in natural reactors at shutdown,[28] (b) analysis of uranium ore bodies to determine what uranium enrichments would be required for existing uranium ore deposits to become nuclear reactors,[37] (c) geochemical modeling of disposal sites,[38] (d) criticality experiments,[39] and (e) industrial standards.[40]

IV.D.2. Ensuring Isotopic Dilution

Preventing nuclear criticality in and beyond the WP requires that DU isotopically mix with the SNF UO_2 as the WP degrades. This mixing is accomplished by several mechanisms, described in the following.

1. *Mass Action*: The void spaces within a WP and the SNF result in the addition of >3 t of DUO_2 per ton of SNF UO_2 (Table 1), at which WP enrichment levels (~0.53 wt% ^{235}U in ^{238}U) are far below the 1 wt% ^{235}U in ^{238}U needed to assure criticality control.

2. *Simultaneous Dissolution*: For isotopic dilution to be successful, the DUO_2 and SNF UO_2 should dissolve at similar rates to avoid one form of uranium being selectively leached away from the second form of uranium. This simultaneous dissolution is assisted by three characteristics of this system. First, the DUO_2 and SNF UO_2 are intermixed on the scale of a fuel rod (1 cm). Second, the dissolution kinetics for different chemical species of uranium are almost identical. Uranium in a WP will be found in multiple chemical forms over time.[41] The dissolution process is a multistep process. Fortuitously, laboratory and hot-cell experiments[42] indicate that the dissolution-rate-limiting step is the same for different uranium compounds. The prerequisite oxidation of UO_2 to higher oxides before dissolution is, in comparison, a fast process for both DUO_2 and SNF UO_2. Third, congruent dissolution of the SNF and DU is expected because the low permeability of the package prevents water flow through the WP with selective leaching of WP contents.

3. *Effects of Dissolved DU*: The DUO_2 saturates the local environment with DU. If it is assumed that in a particular WP, because of some special local conditions, the ^{235}U is not isotopically diluted with DU to critically safe isotopic concentrations, it is likely to become isotopically diluted as it migrates because most of the surrounding environment is saturated with DU.

The SNF UO_2 is encapsulated in zircaloy cladding. In principle, this cladding could allow selective leaching of the DUO_2 before the SNF UO_2 is exposed to groundwater after cladding failure. However, the cladding is expected to fail[41] in thousands to a few tens of thousands of years by clad oxidation caused by air and water and by mechanical stress on the clad. WP basket failure results in high stresses on the zircaloy cladding that accelerate clad failure. These mechanisms operate much faster than does the uranium dissolution, as was described earlier.

IV.E. Autocatalytic Criticality

In recent years, speculation has arisen that in addition to the thermal-neutron criticality events that occurred at Oklo, autocatalytic, high-energy criticality events might occur in geological repositories because of the presence of plutonium or highly enriched uranium. Analysis indicates that the use of DU eliminates these theoretical criticality concerns.[43,44]

V. ANALOG DATA ON LONG-TERM REPOSITORY PERFORMANCE

Natural analog data were examined to provide a second approach for understanding system performance. A 46-t mass of UO_2 (the contents of the WP) is similar to a uranium ore deposit. The most intensely studied[45–49] uranium ore deposit in an environment similar to YM is the Nopal I uranium ore deposit in the Pena Blanca District, Chihuahua, Mexico. This low-assay (~0.5 wt%) uranium deposit formed ~ 8×10^6 yr ago as uraninite. Uraninite (Ref. 50) is naturally formed UO_2. The ore deposit was initially under chemically reducing conditions in groundwater. Uplift of the land resulted in the deposits being placed in a unsaturated oxidizing environment similar to that of YM. The uraninite that has been exposed to the oxidizing environment is slowly being converted to higher uranium oxides and silicates of uranium, leaving some uraninite remaining in the deposit.

The central question in terms of radionuclide releases from the WP is, "How fast can air and water penetrate a mass of UO_2 when the chemical behavior of the

uranium oxides plugs flow channels?" A comparison of laboratory and geological data, described in the following, suggests that with large masses of uranium, the oxidation process is slowed.

1. *No barriers to air or groundwater flow*: If the WP has high permeability, water can flow through the WP and rapidly oxidize the SNF UO_2 oxidation. Based on laboratory experiments,[18,19] it is estimated that bare SNF UO_2 pellets exposed to air and oxidizing groundwater will be oxidized within 500 yr. SNF has a high surface-to-volume ratio. This surface area, which is required for efficient heat removal from the fuel in a nuclear reactor, potentially allows for rapid chemical reactions between the SNF and fluids in the repository after WP and clad failure.

2. *Uranium dioxide barriers to air and groundwater flow*: In contrast, studies of the Nopal I uranium ore deposit indicate that uraninite oxidation and degradation is slow in a confined system with mass-transfer barriers to air and groundwater. Pearcy et al.[47] observed that some uraninite remained and had not been oxidized because of the formation of higher uranium oxides and silicates around concentrated deposits of uraninite that protected the interior uraninite. These are the self-protective mechanisms that were described earlier. The depth of penetration of the oxidation front into the natural uraninite masses at Nopal I measured up to several centimetres.

Such deposits provide another method to estimate the time for oxidation of the outer few centimetres of a DUO_2 bed that is 148 cm in diameter (inside of WP) and contains SNF embedded within it. Several types of bounding estimates for oxidation times at Nopal I can be made. Field studies[51,52] show that parts of the ore body have been under oxidizing conditions for at least 3×10^6 yr. The minimum period of time the entire deposit has been under oxidizing conditions is 1.0×10^4 yr assuming rapid uplift of the land (1 cm/yr) with respect to the water table.[46]

Nopal I is a low-uranium–assay deposit. The uranium concentration in a WP is ~100 times larger, which implies ~100 times more expansion of UO_2 upon oxidation with resultant shutdown of air and groundwater movement in the WP. This would suggest that the oxidation rate of UO_2 in a WP would be 100 times slower than in an ore body similar to Nopal I. Using these estimates for oxidation times, DUO_2 fill may delay the large-scale release of radionuclides from a WP by millions of years.

Analog data also exist for iron (Ref. 45). In the 1950s, archaeologists found over a million nails buried in a 5-m pit in Inchtuthil, Scotland. This was the most northerly fort in the Roman Empire. When it was abandoned in 87 A.D., the Romans buried the nails to prevent the iron from falling into the hands of their enemies. The groundwater there is highly oxidizing, but nails on the inside of the pile show little corrosion. In contrast, a solid crust of rusted nails existed on the top of the pit. This crust apparently protected the nails lower in the pit.

This and other evidence[45] suggest that while a thick, steel WP may be water tight for 10^2 to 10^4 yr, such containers can maintain chemically reducing conditions to preserve SNF UO_2 up to 10^5 yr. However, the maintenance of chemically reducing conditions with the iron does require a low-permeability fill material to eliminate rapid air or oxidized groundwater flow through the degraded WP.

Unfortunately, there are weaknesses in analog data. We observe only the ore deposits or human artifacts that survived. The conditions which preserve artifacts or uranium ore bodies are not fully known, and only a limited number of studies have been completed.

VI. MANAGEMENT OF DEPLETED URANIUM

There is sufficient DU for use of DUO_2 as a fill material. To manufacture LWR fuel, natural uranium with a ^{235}U content of 0.71% is separated into a DU fraction and an enriched uranium fraction. The enriched uranium (3 to 5% ^{235}U) is fabricated into fuel. Typically, 4 to 6 t of DU with a fissile content of 0.2 to 0.35 wt% ^{235}U are produced per ton of enriched uranium nuclear fuel. Worldwide, about 47 000 t are produced annually. Currently, DU consumption is at somewhat less than 1000 t/yr (Ref. 53). Approximately 1×10^6 t are in storage with no identified use, and ~40% of that inventory is in the United States.

Performance assessments have been done on disposal of DU in shallow-land disposal facilities[54] and in the proposed YM repository.[55] These assessments indicate that if DU is considered a waste, there are significant advantages of disposal of DU in a repository.[56] The beneficial use of DU in a repository is consistent with this perspective. Depleted uranium has some unusual characteristics as a radioactive waste. The chemical toxicity (230 mg may produce 50% lethality in a 70-kg person) exceeds the radiotoxicity[54] and is similar to other heavy metals. The radioactivity increases for the first 2 million yr after disposal because of the buildup of decay products from ^{238}U (^{234}U, ^{230}Th, ^{226}Ra, etc.). Last, the quantities are very large compared to other radionuclides (see earlier discussion).

If there are large quantities of SNF to be disposed of, there will be large quantities of DU requiring disposal. From a long-term perspective, the world will either develop new energy sources (e.g., fusion) or deploy breeder nuclear reactors. If breeder reactors are deployed, there will be no SNF or DU to dispose of. The SNF will be processed to obtain fissile material for the breeder reactors, and the DU will be used as a fertile

material. If breeder reactors are not deployed, it will be necessary to dispose of the SNF and DU. The option does exist to recover both the SNF and DU from the WP—if desired (see the following). By coincidence, a minimum-volume WP uses most of the DU that is generated as a by-product of fuel manufacturing.

VII. DESIGN ISSUES

A series of studies were completed to examine engineering issues associated with DUO_2 fill. They are discussed in the following.

VII.A. Particulate Loading of the WP

This concept requires efficient loading of the WP with a small particulate fill. Substantial theoretical, experimental, and industrial experience[4,57,58] exists in filling packages with small particles for different applications. Canada[59] has conducted extensive tests to fill void spaces with small particles within WPs that contain simulated Canadian Deuterium Uranium (CANDU) SNF. The Canadian repository program is considering a high-performance, thin-walled titanium WP. Titanium has excellent performance under the expected Canadian repository conditions; however, the material is expensive and difficult to weld into thick sections. To avoid these problems, a thin-walled WP was chosen. In this WP, the SNF and fill material support the external WP wall against external hydrostatic and geostatic pressure after the WP is buried. This approach avoids the need for thick-walled WPs to withstand compressive external hydrostatic or geostatic pressures in the repository.

Canadian fill tests investigated different particle sizes, different mixtures of particle sizes, alternative fill materials, vibratory filling with different vibration frequencies and amplitudes, and other factors. Full-scale WP hydrostatic tests (10 MPa, 150°C) of the filled WP (Fig. 8) showed that there were no voids within the WPs, i.e., no package collapse. Other tests showed no significant damage to the fuel assemblies during such operations. The tests also demonstrated the ability to remove the fill particulate if a defect in the WP was identified and the SNF had to be repackaged. Canada did not evaluate the use of a DUO_2 fill because CANDU reactors use natural uranium and thus Canada has no DU and there are no criticality issues associated with disposal of CANDU SNF. Engineering designs and cost estimates of packaging facilities were also developed for processing 4730 metric tons initial heavy metal (MTIHM) of CANDU SNF per year. The decade-long test and development program provided high confidence in the practicability of using fill materials in WPs.

This experience is directly applicable to LWR SNF. The minimum spaces between fuel pins (Fig. 9) in a CANDU fuel assembly are considerably smaller than the minimum spaces between fuel pins in an LWR fuel assembly. Therefore, it is expected that filling a WP containing LWR SNF with particulates should be easier than filling a WP containing CANDU fuel assemblies.

VII.B. Temperature Limits

A significant repository design constraint is the maximum allowable SNF cladding temperature. It is chosen to minimize clad failure. The current SNF clad temperature limit for YM is 350°C (Ref. 6). Analysis[2] indicates that the DUO_2 fill material is not a major barrier to heat transfer and does not significantly increase the SNF temperature (<15°C). This analysis assumed that air was the DUO_2 fill gas—a conservative assumption. Helium, with better heat transfer properties, is the nominal WP fill gas.

The addition of DUO_2 fill only impacts heat transfer from the fuel pins to the WP basket structure. The fill reduces convective and radiative heat transfer; however, it improves heat transfer by thermal conduction. A crystalline material such as DUO_2 has a thermal conductivity ~50 times higher than that of the helium gas that it replaces. The fill significantly reduces the uncertainties associated with peak SNF repository temperatures. Heat transfer by thermal conductivity is well defined. In contrast, gas-phase convective heat transfer depends on the orientation of the WP (vertical, sloped, or horizontal) and the physical clearances between the SNF and basket structure. Radiation heat transfer depends on the surface properties of the SNF—properties that depend upon the history of the SNF.

VII.C. WP Weight

Scoping calculations were conducted[2] to evaluate the impact of various fill materials on the mass of a self-shielded, 21 fuel assembly PWR MPC in a transport cask. The results indicate that the addition of a fill material for this specific design would increase total weight by several percent. The fill material adds weight but also replaces some of the radiation shielding. As a result, there is little net change in total package weight. This conclusion is dependent upon the size and details of the package design. For repositories with ramp entrances such as YM, package weight is not a significant design constraint.

VIII. ECONOMICS

There are economic benefits and costs. The potential areas for cost savings include an improved repository performance, a simplified and more robust repository licensing case, and an avoidance of costs of disposing of DU. The costs are for those associated with implementing the use of DU in WPs. The costs or savings (independent of repository benefits) are primarily determined by the costs of DU disposal—which are not well defined.

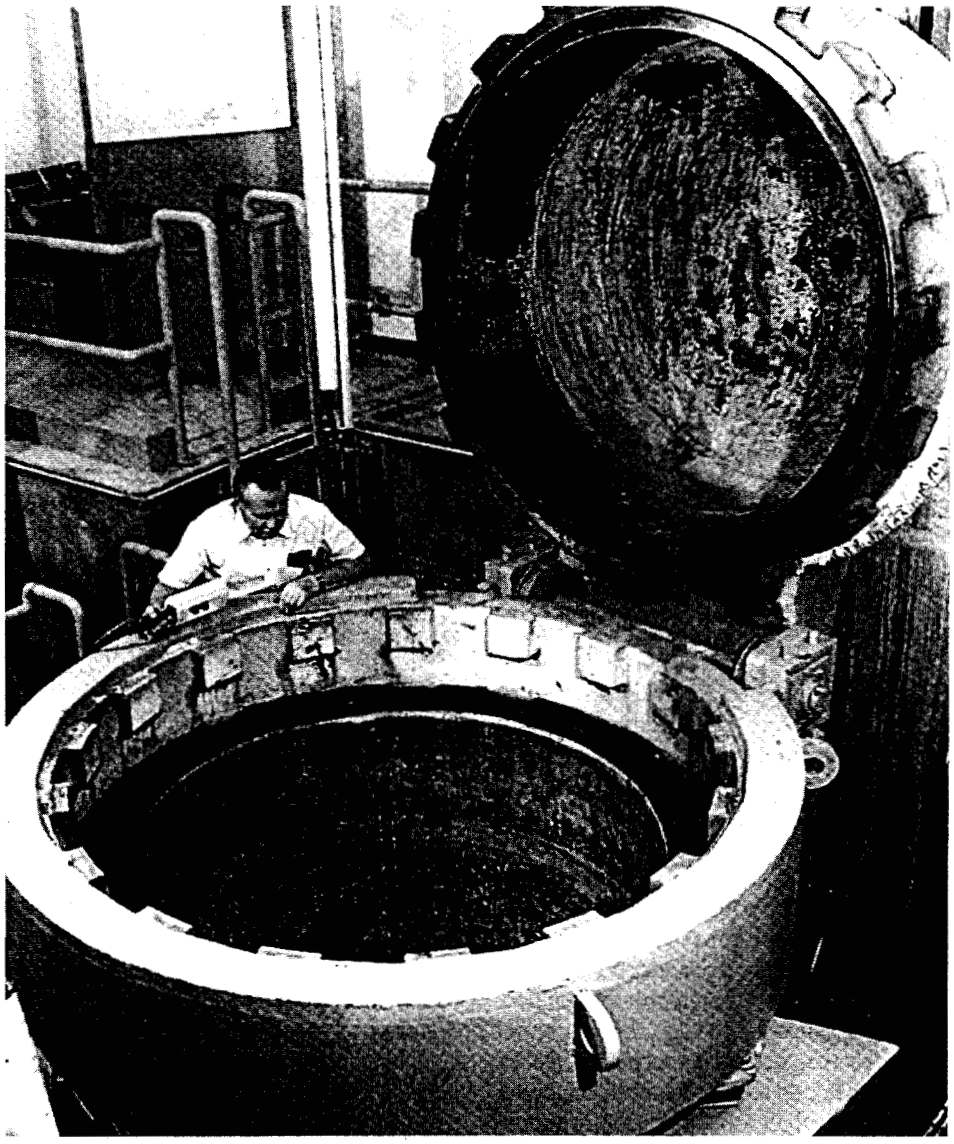

Fig. 8. Whiteshell hydrostatic test facility to test filled WP up to 10 MPa and 150°C (photo courtesy of Atomic Energy of Canada Limited).

IX. UNCERTAINTIES AND FUTURE RESEARCH NEEDS

These investigations indicate the potential for DUO_2 fill. However, significant additional research is required. First, a better understanding is needed of the changes in the permeability of UO_2 beds under oxidizing conditions in a WP and in the natural environment. Permeability to fluid flow is the single most important parameter in terms of repository performance. If the permeability of SNF embedded in DUO_2 to fluid flow is low, the repository performance will be excellent. The coupling of laboratory and natural analog data may provide a much stronger licensing basis for repository performance than any other approach. Second, the ion-exchange capabilities of hydrated uranium oxides must be better understood. Limited data suggest that DUO_2 fill could be a major barrier to radionuclide migration as an absorbent, but definitive data do not exist. Finally, an integrated model of system performance is required.

X. CONCLUSIONS

The use of DUO_2 as a fill material has multiple potential benefits: reduced radionuclide release rates from the WP, reduced potential for nuclear criticality in the

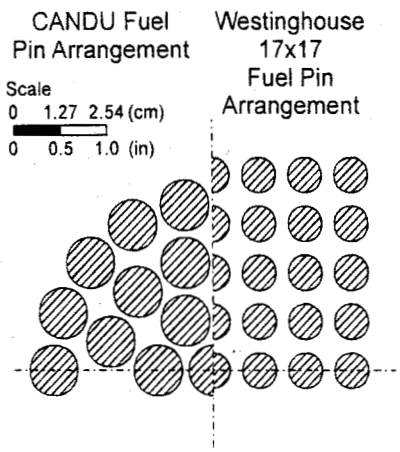

Fig. 9. Cross section of CANDU and PWR fuel assemblies.

repository, and disposal of excess DU. In an oxidizing repository environment, DUO_2 oxidation is used to slow radionuclide transport. In a reducing repository environment, uranium solubility limits are used to slow radionuclide releases from SNF. Significant additional work is required to integrate these results into a complete repository performance assessment, understand the penalties, and have confidence in the benefits of DUO_2 fill.

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