

MAINTAINING CHEMICALLY REDUCING WASTE-PACKAGE CONDITIONS

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Maintaining Chemically Reducing Waste-Package Conditions

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ABSTRACT

Most fission products and actinides in spent nuclear fuel (SNF) are trapped in the uranium dioxide (UO_2) crystal structure and cannot escape until the UO_2 is oxidized. Oxidation destroys the crystal structure, exposes the radionuclides to groundwater, and creates the potential for dissolution. For a repository in an oxidizing geochemical environment, the potential exists to delay the release of radionuclides for hundreds of thousands to millions of years by using a combination of excess depleted uranium dioxide and iron in the waste package (WP) to locally maintain chemically reducing conditions. This approach limits the rate of oxygen transport to the SNF after WP failure. Alternative methods of oxygen transport to the SNF were investigated, including transport by groundwater, diffusion through air, and diffusion through water.

INTRODUCTION

It has been proposed [1] that spent nuclear fuel (SNF) storage, transport, disposal, and multipurpose casks be constructed of a depleted uranium dioxide (DUO_2)-steel cermet. Cermets consisting of DUO_2 particulates embedded in a continuous-steel phase (Figure 1) replace the steel components (structural shell and the basket) in the cask. For the multipurpose-cask application, the SNF would be loaded at the reactor and the cask would then be used for storage, transport, and disposal. For all waste package (WP) applications, the cermet cask would become the inner container of the WP, with an overpack of a corrosion-resistant metal. Cermets are a means of making a ductile form of DUO_2 suitable for use as a cask material of construction.

Cermet casks have several attractive features. The DUO_2 cermet is an excellent shielding material and may be the best shielding material that could be used in a repository. High-performance shielding materials maximize the SNF cask capacity for any given weight and size limits. Cermets are used in armor; thus, they offer the potential for better assault protection of the SNF. The use of DUO_2 provides a method for beneficial use of the 500,000 tons of excess depleted uranium (DU) in inventory.

In the repository, the iron and DUO_2 may potentially reduce and delay release of radionuclides from the WP. The DUO_2 can be incorporated into a cermet or be used as a particulate fill [2] for the void spaces in and around the SNF assemblies within the WP. Several potential mechanisms may improve repository performance. The DUO_2 and iron can act as sacrificial reagents to maintain chemically reducing conditions next to the SNF. Most radionuclides in SNF are incorporated within the SNF UO_2 crystal structure and cannot be released until the UO_2 is oxidized. The DU in and around the SNF saturates the groundwater and thus eliminates the concentration gradient for dissolution of uranium. The DUO_2 and iron oxide degradation products chemically and physically sorb various radionuclides and delay their release. Finally, isotopic mixing of the DU with fissile uranium isotopes in the SNF reduces the long-term potential for nuclear criticality.

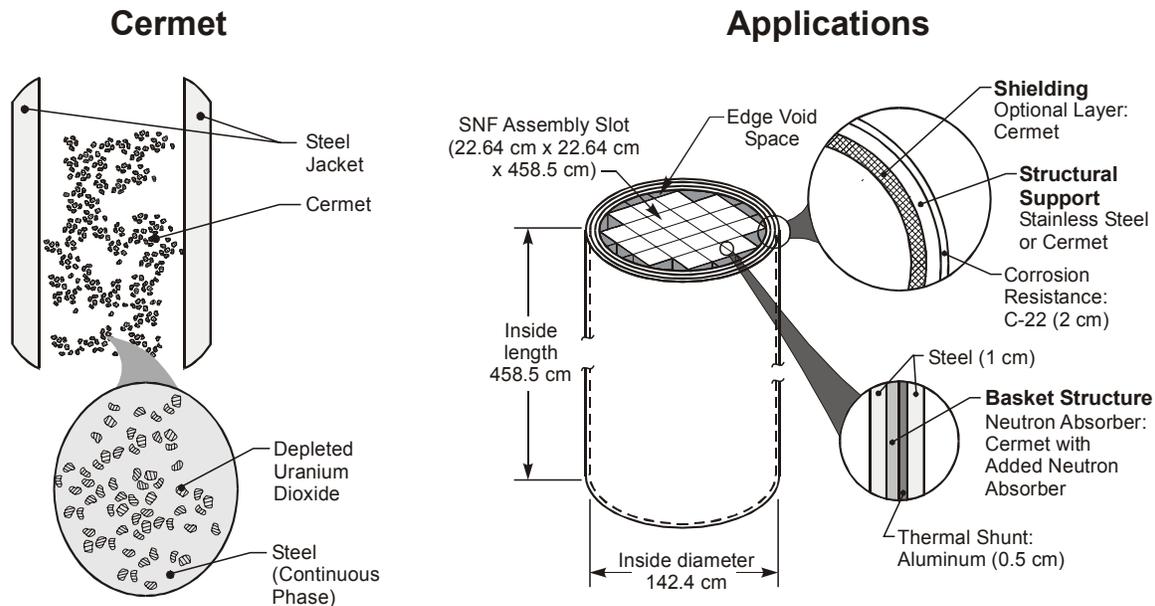


Figure 1. Cermets waste package.

This paper examines the ability of DUO_2 -steel cermets to maintain chemically reducing conditions within the WP by creating a barrier to external sources of oxygen and thus to reduce and delay release of SNF radionuclides from the WP. Other investigators have addressed oxygen produced internally by radiolysis and other mechanisms [3]. This subject is examined from three perspectives: natural analogs, oxidation by water containing dissolved oxygen, and oxidation from air in the disposal drift.

NATURAL ANALOG EXPERIENCE

The world and its crust are not at thermodynamic equilibrium. Many ore deposits and man-made artifacts exist that require chemically reducing conditions to survive, even though they are surrounded by an oxidizing geochemical environment. In these cases, the pockets of chemically reducing conditions exist, embedded in oxidizing horizons, because the mass transfer of oxygen is a very slow process in liquids and solids. Such examples demonstrate that chemically reducing conditions are sometimes maintained in a small zone within a larger oxidizing geochemical environment for extended periods of time and suggest the potential to create a long-lived reducing WP environment in an oxidizing geological horizon. Much can be learned from the specific conditions that have preserved these sites.

- *Roman nail piles.* Shallow piles of buried nails from the Roman Empire have been found in which the nails in the interiors of the piles have remained in good condition [4]. The near-surface environment was oxidizing and wet. Because iron was used for weapons, retreating armies would bury iron that could not be transported to prevent this strategic material from falling into enemy hands.
- *Uranium ore deposits.* Although the surrounding formation has an oxidizing geochemistry, many very old uranium ore deposits still contain UO_2 . The UO_2 in these deposits would have been expected to oxidize.

In each case, the iron or UO_2 on the outer surfaces of the deposit acted as a sacrificial anode that reacted with the oxygen and that prevented more oxygen from entering the center of the deposits. The oxidation [2] of (1) DUO_2 to higher uranium oxides and their ultimate transformation to silicates and (2) iron to various higher iron oxides results in volume expansion. This expansion restricts and slows the flow of groundwater through such deposits by filling the adjacent void spaces and reducing the permeability. Furthermore, upon wet oxidation, some materials, such as iron, tend to form gels that stop all fluid flow. Under humid repository conditions, these iron oxides can form fine-grained, water-saturated semisolids that also greatly reduce the diffusion of O_2 through the outer corrosion-product layers. All of these mechanisms slow oxidation by many orders of magnitude.

In addition to the experience with concentrated deposits of UO_2 and iron, a large body of literature exists on scavenger precipitation of uranium, rare earths, strontium, and other compounds by various iron oxyhydrides in natural systems [5] and water treatment plants [6]. This literature shows the capability of iron compounds in a variety of environments to retard heavy metals and many other species. The iron oxide precipitates from these scavenger-removal technologies leave stable, saturated colloidal matrices [7,8].

SNF OXIDATION BY OXIDIZING GROUNDWATER

The proposed Yucca Mountain (YM) repository site is above the water table, with oxidizing conditions. Groundwater percolates downward through the unsaturated repository horizon to the saturated water table below. Oxygen dissolution in groundwater and subsequent groundwater flow through the WP are the most obvious mechanisms for transport of oxygen to a failed WP and to the SNF.

A series of idealized calculations [9] compared the chemical evolution of (1) the proposed YM WP with 21-pressurized-water-reactor (PWR) SNF assemblies, (2) a cermet WP containing 21-PWR SNF assemblies, and (3) a cermet WP with 21-PWR SNF assemblies and DUO_2 particulate fill of all void spaces inside the loaded WP. The 21-PWR assemblies have 41 kmol of SNF UO_2 (11 tonnes) and 25 kmol of zirconium (2.23 tonnes). The YM WP is made of stainless steel. The cermet WP contains 137 kmol of DUO_2 and 475 kmol of iron. The addition of a DUO_2 fill to the void spaces adds another 143 kmol of DUO_2 .

The results shown in Figure 2 reflect conditions typical of YM: oxygen-saturated (8.86-mg/L) groundwater with a linear flow rate of 32.5 mm per year and a degraded WP cross section of 21.45 m². (The actual cross section is 9.78 m².) The oxygen is initially consumed by the less noble metals in the different WPs. Only after the oxidation of these metals is complete is the UO₂ oxidized. This idealized model shows that UO₂ oxidation will begin to occur - 400,000 years after failure of the proposed YM WP and 900,000 years after failure of the cermet WP. Because the cermet WPs have more metal, oxidation of any UO₂ is delayed compared with that occurring in the existing YM WP. If one assumes full oxidation of the DUO₂ before that of the SNF UO₂, the cermet WP (Figure 2) delays SNF UO₂ oxidation until 1.4 million years after WP failure. For the cermet WP with DUO₂ fill, SNF UO₂ oxidation is delayed until 2.3 million years after WP failure. The large quantities of uranium will also tend to saturate the local groundwater with some secondary impacts [2]. Generally these impacts appear to be beneficial with respect to slowing the migration of radionuclides.

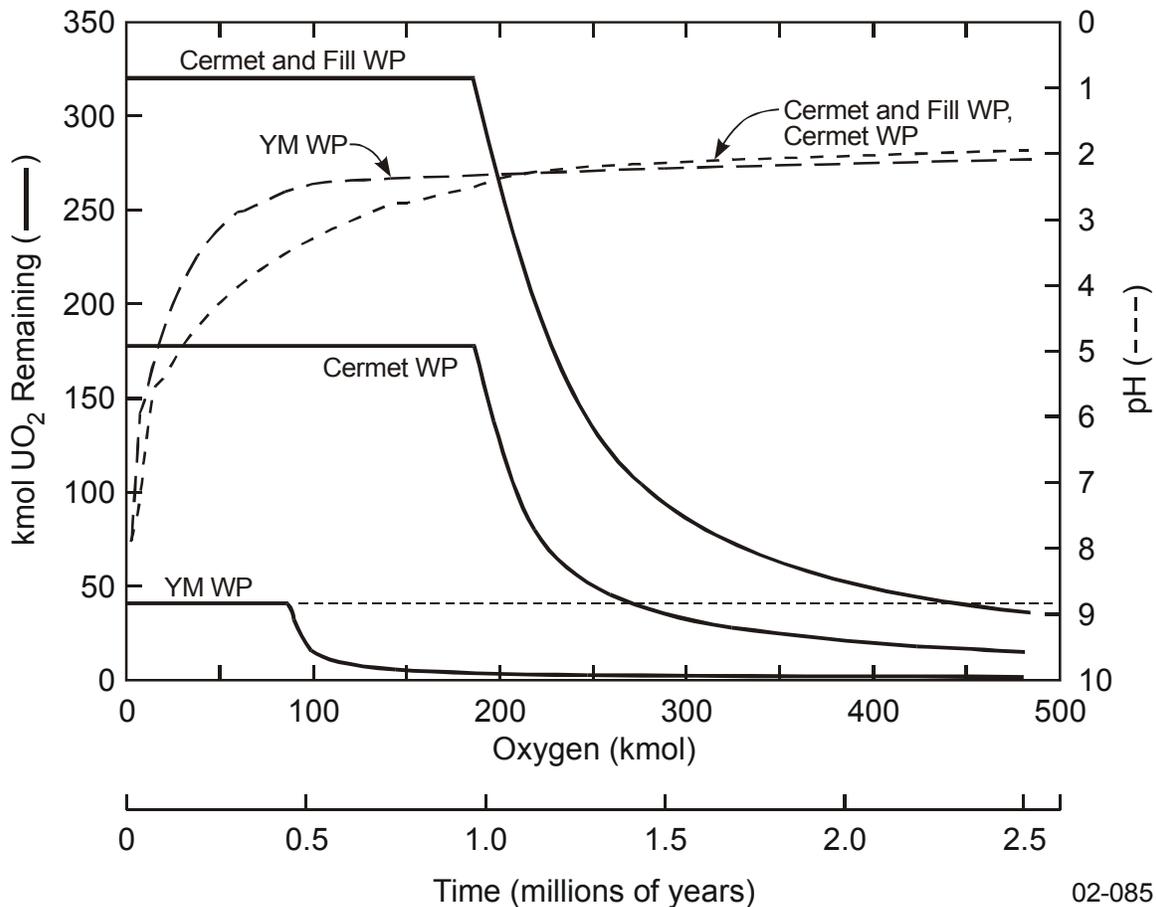


Figure 2. Remaining UO₂ (DUO₂ and SNF UO₂) and variation of pH in a WP versus time.

Thermodynamic equilibrium defines the ultimate chemical species. However, chemical kinetics actually control the rate and order of the oxidation of materials. Experimental evidence shows that the iron has the most rapid oxidation kinetics; thus, the oxidation of the steel in the cermet releases the DUO_2 particulates contained in the DU-steel cermet. Uranium dioxide oxidizes much more rapidly than stainless steel or zirconium. Consequently, if there are clad defects and the SNF UO_2 is exposed to groundwater containing oxygen, the SNF UO_2 will tend to oxidize before the unreacted stainless steel in the WP. For several reasons, however, most of the WP DUO_2 is expected to oxidize before the SNF UO_2 . (1) Whatever the direction of groundwater flow, it first contacts the DUO_2 particulates from the degraded cermet; thus, the oxygen can first react with these particulates. (2) The DUO_2 particulates have a high surface area compared with that of SNF UO_2 pellets, which allows more rapid oxidation of the former. (3) The SNF UO_2 is protected by zircaloy cladding with slow oxidation kinetics. (4) It has been experimentally observed that oxidation of SNF UO_2 is slower than that of unirradiated UO_2 , due to the presence of rare earth fission products and actinides that slow oxidation kinetics.

The conclusion is that the degradation by oxygen in groundwater of a large shielded WP with large inventories of iron and DUO_2 is a very slow process. The corrosion of large quantities of iron with the freeing of the fine DUO_2 particulates will tend to fill void spaces within the WP and fuel assemblies. Large quantities of oxygen are then required to oxidize such large masses of strongly reducing agents.

GAS-PHASE OXYGEN TRANSPORT

Groundwater may not be the only source of oxygen in the WP. The proposed YM site has an unsaturated geology with oxygen in the gas phase, which is exchanged with barometric pressure. The above calculations did not include air as a source of oxygen. The rate of atmospheric exchange of air with the geology is not well understood because of several factors.

- *Barometric pumping.* The daily increases and decreases in atmospheric pressure provide a mechanism of gas transport; however, the long, narrow pathways in the rock imply that the gases will primarily move back and forth, slowing oxygen transport.
- *Thermal convection.* The decay heat from the wastes provides a mechanism for thermal convection of air from below ground to the surface of the mountain. However, the materials in the repository rock are not fully oxidized. Higher temperatures will also accelerate other oxidation reactions in the rock that consume some of the oxygen in the air. This may also change the permeability of the geology.
- *Man-made reducing agents.* After repository closure, the exposed steel surfaces of tunnel liners, rail tracks, and other features will consume large quantities of oxygen.

However, if air is present in the repository drifts, oxygen can be transported to the inside of a degraded WP by diffusion through the gas-phase pore spaces, diffusion through capillary water, and air transport via barometric pumping through the gas phase. The potential impact of each of these transport mechanisms can be estimated.

Oxygen transport by gas diffusion

If the degraded WP is not saturated with water, oxygen can diffuse from the surrounding air to the SNF. The rate of oxygen transported can be calculated, assuming worse case conditions. Under humid repository conditions, the partial pressure of oxygen (p_{O_2}) is between 0.15 and 0.2 atm. At the raw-iron interface, the equilibrium fugacity (f) of O_2 is $<1 \times 10^{-75}$ atm. Therefore, the effective p_{O_2} gradient between the ambient repository atmosphere and the corroding iron surface is 0.15 to 0.2 atm. The oxygen must diffuse from the outside the WP where the composition of the gas is that of air to the corroding iron surface where the oxygen composition is almost zero and the gas is primarily nitrogen. The effective mean diffusion coefficient for O_2 in air is $0.18 \text{ cm}^2/\text{s}$ [10]. With about 8.9×10^{-6} mol of O_2 per cm^3 above the diffusion boundary, the time to diffuse a mol of O_2 across a 1-, 5-, 10-, 50-, and 100-cm-thick ideal stagnant boundary of infinite extent onto a 100-cm^2 area would be about 63 days, 4.3 years, 17 years, 430 years, and 1700 years, respectively. The original model considered that each 500-year time step was as instantly mixed compositions of component reactants and products. For the case of diffusion-controlled reactions, the reaction times are extended beyond the 500-year time steps when the corrosion-product diffusion barrier grows beyond 50 cm.

Oxygen transport by liquid diffusion

It is likely that the corrosion layer of the degraded WP will be saturated by water, because, under the humid repository conditions, the capillary pores in the fine colloidal iron oxide layers will become filled. Therefore, oxygen must diffuse from the surrounding air to the SNF components through this tortuous capillary pore water. The diffusion coefficient for O_2 in water is about $2.0 \times 10^{-5} \text{ cm}^2/\text{s}$ at 20EC, which is 10,000 times smaller than that for air. The rate of oxygen transport can be calculated, assuming idealized conditions. Using Henry's law, the O_2 concentration at the water-air boundary is 3.6×10^{-5} mol/L, or 3.6×10^{-8} mol/ cm^3 . The time to diffuse a mole of O_2 across a 1-cm-thick ideal stagnant boundary of infinite extent onto a 100-cm^2 area would then be thousands of years. In this saturated case, diffusion limitations in the filled capillary pores of the corrosion products extend the life of the WPs by factors of thousands if the repository backfill is designed to stabilize the formation of the protective corrosion-product layers.

Barometric pumping

If the degraded WP has gas voids and the gas pressure varies with barometric pressure, the variations in barometric pressure can pump oxygen into the WP. Regardless of the rate of barometric pumping, the diffusion-limited case of saturated corrosion-product pores overcomes any O_2 transport associated with this phenomenon.

IMPLICATIONS OF ALTERNATIVE OXYGEN TRANSPORT MECHANISMS

For a large shielded WP with a large inventory of iron and DUO_2 , evidence from natural analogs and calculations indicates that SNF oxidation (and subsequent dissolution) by groundwater is a very slow process that occurs on a geological time scale—even if the WP is located in an oxidizing geological environment.

If rapid WP degradation is to occur, the oxygen must come from a dry atmosphere in the disposal drift. The oxidation of iron, DUO_2 , and other materials would be expected to rapidly fill any large void spaces within the WP; thus, oxygen diffusion through air and water into the WP debris becomes the primary transport mechanism. The rate of oxygen diffusion is strongly dependent upon whether the void spaces are filled with air or water. Oxygen diffusion through water is an extremely slow process. The filling of capillary spaces depends upon the wettability of the WP degradation products. Hydrated iron and uranium oxides have wettable surfaces. Independent of these factors is the tendency of hydrated iron oxides to form gels that prevent water movement. Such gels, to the degree that they form, greatly decrease gas transport.

The evidence is sufficient to suggest that large shielded WPs will create a locally reducing environment within an oxidizing geological environment for very long periods of time—potentially hundreds of thousands, even millions of years. There are significant unknowns, and substantial additional work is required. However, the potential benefits of an independent engineered barrier to radionuclide releases that uses a totally different approach is worth careful consideration.

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REFERENCES

1. C. W. Forsberg and M. J. Haire, "Depleted Uranium Dioxide–Steel Cermets for Spent Nuclear Fuel Multipurpose Casks," *Proc. of the Fifth Topical Meeting on DOE Spent Nuclear Fuel and Fissile Materials, Charleston, South Carolina*, (American Nuclear Society, La Grange Park, Illinois, September 2002).
2. C. W. Forsberg, "Effect of Depleted-Uranium-Dioxide Particulate Fill on Spent-Nuclear-Fuel Waste Packages," *Nucl. Technol.* **131**, 337–353 (2000).
3. L. Longcheng and I. Neretnieks, "A Reactive Transport Model for Oxidative Dissolution of Spent Fuel and Release of Nuclides Within a Defective Canister," *Nucl. Technol.* **137** (3), 228 (2002).
4. B. Miller and N. Chapman, "Postcards from the Past: Archaeological and Industrial Analogs for Deep Repository Materials," *Radwaste* (January 1995), p. 32.
5. O. Landstroem and E. Tullborg, *Interactions of U, Th, REE, Ra, Cs, and Sr with Clay Minerals, Fe-oxyhydride and Calcite: Examples of Geochemical Processes in Natural Systems From the Aespoe Hard Rock Laboratory*, SKB Technical Report (Studsvik Eco & Safety AB, Studsvik, Sweden, 1995).

6. J. Patoczka, R. Johnson, and J. Scheri, "Trace Heavy Metals Removal with Ferric Chloride," Industrial Waste Technical Conference, Nashville, Tennessee, March 1-4, 1998.
7. J. H. Kessler, G. C. Roberts, L. R. Dole, and M. T. Morgan, "Formulation and Durability of Tailored Cementitious Hosts Applied to TRU Waste Generated at the Rocky Flats Plant," in *Scientific Basis for Nuclear Waste Management VI*, edited by D. G. Brookins (North Holland, New York, 1983) pp. 611-618.
8. E. W. McDaniel, T. M. Gilliam, L. R. Dole, and G. A. West, *Weldon Springs Raffinate Pits 1, 2, 3, & 4: Preliminary Grout Development Studies for In Situ Waste Immobilization*, ORNL/TM-9264 (Oak Ridge National Laboratory, Oak Ridge, Tennessee, April 1987).
9. C. W. Forsberg and L. R. Dole, "Depleted Uranium Dioxide Waste Package for Spent Nuclear Fuel," in *Scientific Basis for Nuclear Waste Management XXV*, Edited by B. P. McGrail and G. A. Cragolino (Mat. Res. Soc., Proc. 713, Warrendale, PA, 2002). pp. 143-150.
10. S. W. Benson, *The Foundations of Chemical Kinetics* (McGraw Hill, New York, 1960), p.185.