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CONVERTING MISCELLANEOUS SNF TO A SINGLE WASTE FORM BY PACKAGING IN DEPLETED URANIUM DIOXIDES

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ABSTRACT

The proposed Yucca Mountain (YM) Repository is designed primarily for disposal of commercial light-water reactor (LWR) spent nuclear fuel (SNF)—uranium dioxide (UO_2) in zirconium alloy tubes. Much information has been gathered on the behavior and performance of this waste form in the proposed repository. However, in the U.S. Department of Energy (DOE) complex, there are also a large number of miscellaneous SNFs and other wastes requiring geological disposal for which there is very little such information. Because the quantities of these materials in individual categories are small, it is not practical to evaluate all of them in detail to understand their behavior and performance in the repository. Therefore, we propose a method for the disposal of these miscellaneous wastes that does not require exhaustive study of each waste form.

We have proposed that many of the miscellaneous SNFs can be packaged in depleted uranium dioxide (DUO_2)—steel cermet waste packages (WPs) with the option of adding DUO_2 fill in the void spaces. In the cermet, the DUO_2 particles are embedded in a steel matrix. The masses of DUO_2 and iron are large in comparison with those of the SNF. By mass action, the local geochemical environment within the WP is controlled by large quantities of DUO_2 and iron relative to the quantities of SNF. Since the behavior of these two major materials is well understood within the repository, the behavior of the proposed WPs becomes more predictable.

The iron and DUO_2 initially create chemically reducing conditions and help control the pH. This helps to preserve some but not all types of miscellaneous SNF. For uranium metal and other SNFs that can be oxidized by water under chemically reducing conditions, the reducing conditions prevent the formation of soluble uranium, neptunium, technetium, and other species. In the longer-term, the oxidizing environment in the repository creates oxidizing conditions within the WP. From this time forward, the evolution of these DUO_2 -dominated miscellaneous SNF WPs will behave in a manner similar to the better understood commercial LWR SNF WPs. In both cases, uranium is controlling the geochemistry.

INTRODUCTION

DOE has ~ 230 types of miscellaneous SNFs and related wastes (sludges, etc.) that require disposal in the proposed YM Repository. The repository WP and repository geology for each of these miscellaneous SNFs must be shown to prevent any significant impacts to human health and the environment. These potential impacts are from the long-lived SNF nuclides, which could be released over very long periods of time. The performance of a repository system depends upon the combined chemical behavior of the SNF and WP in the geochemical conditions of the repository disposal horizon. Because the miscellaneous types of SNF vary widely in chemical composition and the quantities of any particular type are relatively small, the development and implementation of many WP designs could make storage and disposal of these SNF wastes extremely expensive on a per-unit-mass basis.

Therefore, a uniform packaging approach is being investigated to address the long-term disposal of these miscellaneous SNF wastes. Large quantities of steel (iron) and DUO_2 are added to each SNF WP in a sufficient quantity that the overall WP chemistry will be dominated and controlled by these materials. The behavior of this system is examined through the evolution of the WP over time.

WASTE PACKAGES WITH DEPLETED URANIUM DIOXIDE

The proposed steps in the treatment and packaging of miscellaneous SNF are to (1) dry the SNF, (2) place the SNF in a WP made of a DUO₂-steel cermet; and, if required, (3) fill the WP void spaces, including the coolant channels in the SNF, with a DUO₂ sand-like particulate fill. Not all the miscellaneous DOE SNFs would require all of these steps. Cermets [1] consist of DUO₂ particulates embedded in a continuous-steel phase (Fig. 1). They replace the steel components (structural shell and the basket) of (1) WPs and (2) advanced multipurpose casks for storage, transport, and disposal. For all WP applications, the proposed outer WP overpack of a corrosion-resistant metal would remain unchanged. Cermets are a means of making a ductile form of DUO₂ suitable for use as a WP material of construction. The use of DUO₂ particulate fills [2] is an alternative method to add DUO₂ to WPs.

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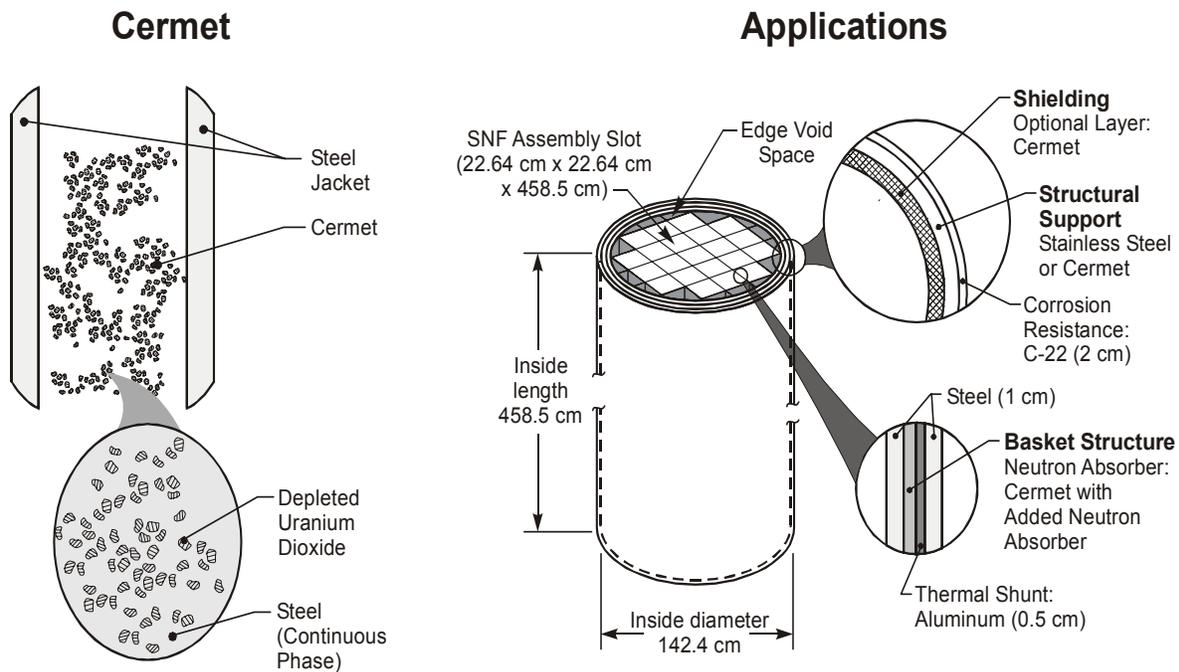


Fig. 1. Cermet Waste Package.

Repository applications of DUO_2 are being investigated for disposal of all types of SNF as (1) a method to improve repository performance, (2) dispose of excess DUO_2 [3], and (3) potentially eliminate one or more other engineered barriers in the repository. The technology, if successful, would be a second-generation repository technology. Like any other facility operated over a period of decades, repository operations will change as more advanced technologies are developed and experience in repository operations is gained. This experience base will provide the necessary scientific and engineering foundation to consider more advanced systems. The use of DUO_2 may be particularly beneficial for miscellaneous SNF because of the variability of these fuels.

PRESERVATION OF SNF

As long as the SNF remains intact, the radionuclides can not be released and migrate. Because radionuclides decay with time, the longer the SNF integrity is preserved, the lower are the radionuclide releases from the repository. As long as the WP remains intact, little SNF degradation occurs. Upon WP failure, the rate of SNF degradation and radionuclide release depends upon the local geochemical environment. The use of DUO_2 -steel cermet WPs and DUO_2 fill maintains geochemical conditions (oxidation potential, pH, and saturation) that slow the degradation of many types of SNF.

Control of Geochemistry of Failed WPs: Oxidation Behavior

SNF UO_2 degrades under oxidizing conditions but does not degrade under chemically reducing conditions (except by the exceedingly slow process of dissolution of U^{+4}). Most radionuclides are trapped in the UO_2 pellets and cannot escape until the SNF UO_2 is oxidized and dissolved in groundwater. The UO_2 must be oxidized to UO_2^{+2} for rapid degradation to occur. Without extensive oxidation, only limited quantities of soluble radionuclides on the grain boundaries of the UO_2 can be leached by groundwater. For repository sites with oxidizing conditions, chemically reducing conditions may be maintained after WP failure by adding materials to the WP that sacrificially remove oxygen from the groundwater before it can react with the UO_2 .

This strategy was examined using a set of idealized calculations that compared the chemical evolution of: (1) the proposed [4] 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. LWR SNF is used as a stand-in for a variety of miscellaneous SNFs containing oxide fuels to estimate how long chemically reducing conditions may be maintained in the WP. The proposed YM WP consists of an inner package and an exterior 2-cm-thick, corrosion-resistant overpack of C-22. The inner package structurally supports the overpack. In each case, the analysis evaluated the chemical evolution of the inner package, the SNF, and any other additives. The overpack was assumed to remain inert. In each case, it was assumed that after WP failure, YM groundwater (Table I) reacted with the inner package (excluding the external overpack) and its content. Using conditions typical of YM, a generalized representative groundwater composition was selected and oxygen saturation was assumed to be 8.86 mg/L. The groundwater linear flow rate is assumed to be 32.5 mm per year [5]. The degraded WP cross section is assumed to be 21.45 m² (actual cross section is 9.78 m²). The imaginary flow through or over the WP is 6,971,000 L per 10,000 years.

The interactions of the SNF WPs with YM groundwater chemistry were simulated using the HSC Version 4.1 thermodynamic code by Outokumpu Research Oy. Table I summarizes the three WPs and their contents. The 21-PWR assemblies have 41 kmol of UO_2 (11 tonnes) and 25 kmol of zirconium (2.23 tonnes). The YM WP is made of stainless steel and the two cermet WPs are made of carbon steel and DUO_2 . The particulate DUO_2 fills all void spaces in the WP, including the SNF coolant channels. This calculation assumes a 65% volume packing density for a particulate fill. The uranium content of the three packages varies widely.

For these three cases, the model takes 250 steps—each step representing a period of 10,000 years. Then, for each successive step, the model calculates the formation of the predominant compounds in both the solid and aqueous phases by minimizing the Gibbs free energy for a homogeneous mixture of 451 potential compounds. Figure 2 shows the results for the three WPs over 2,500,000 years. For each case, the number of kilomoles of unoxidized UO_2 remaining in the system versus time is shown. The time scale starts after failure of the corrosion-resistant WP overpack. (The model does not include this overpack.) The span of 100 kmol of O_2 represents the amount of oxygen transported to the package by saturated groundwater over 520,000 years.

Table I. Model Parameters

Waste Package Cases				Groundwater Constituents ¹			
Case	YM WP (kmol)	Cermet WP (kmol)	Cermet & Fill WP (kmol)	Species	Conc. (mg/L)	Conc. (kmol/L)	Total per 10,000 y (kmol/10,000 y)
SNF UO ₂	41	41	41	H ₂ O	100E+06	0.056	3.87E+05
Cermet DUO ₂	0	137	137	O ₂ (sat)	8.86E+00	2.77E-07	1.93E+00
Fill DUO ₂	0	0	143	Ca ⁺⁺	58	1.45E-06	1.00E+01
Total U Dioxide	41	178	320	Mg ⁺⁺	4	1.64E-07	1.00E-00
Zirconium (clad)	25	25	25	SiO ₂	50	8.33E-07	5.80E+00
Iron	125	475	475	Na ⁺	184	8.00E-06	5.58E+01
Chromium	28.6	0	0	Al(OH) ₂ ⁺	1	3.71E-08	2.60E-01
Molybdenum	2.07	0	0	HCO ₃ ⁻	400	6.56E-06	4.58E+01
Nickel	21.1	0	0	CO ₃ ⁼	138	2.30E-06	1.61E+01
				H ⁺			1.00E-09

¹Amount of groundwater constituents for YM site's long-term flow (32.5 mm/y) with a package zone-of-influence cross section of 21.45 m² and an oxygen saturation (25EC, 1 atm). In 10,000 years, total water flow is 6.971E+06 L.

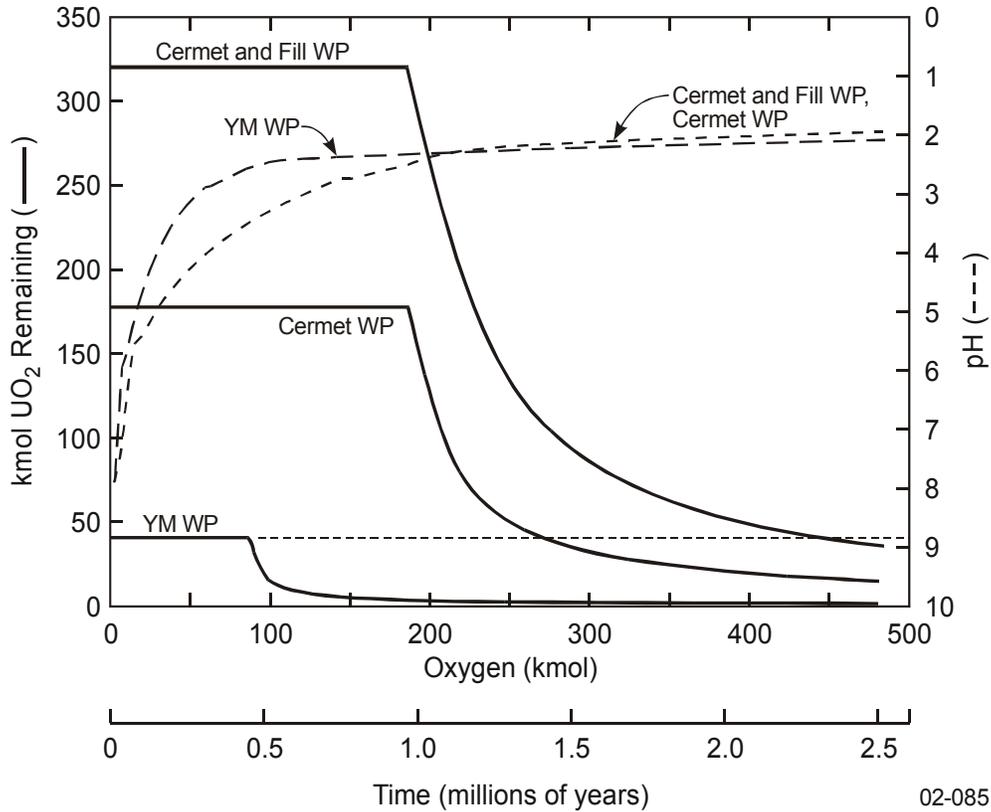


Fig. 2. Oxidation of Uranium Dioxide and Variation of pH in a Waste Package Versus Time.

The oxygen is initially consumed by the less noble metals in the different WPs. Only after the oxidation of the metals is complete is the UO_2 oxidized. The model shows that initial DUO_2 oxidation will occur - 400,000 years after failure of the proposed YM WP and 900,000 years after failure of the cermet WP failure. The cermet WPs have more metal; thus, oxidation of the UO_2 is delayed with that occurring in the existing YM WP. *The steel (iron) in cermet WPs significantly delays the oxidation of (1) any UO_2 in SNF and (2) any SNF cladding that is chemically more noble than steel (iron).* If the cladding is in good condition, fissile materials (containing the fission and actinide products) are protected and radionuclide releases will not occur. However, this analytical model does not account for three phenomena that can significantly alter the performance.

- *Kinetics.* Thermodynamics defines the ultimate equilibrated chemical form. However, chemical kinetics actually controls which materials are oxidized first. The UO_2 oxidizes much more rapidly than stainless steel or zirconium. Consequently, if there are clad defects and SNF UO_2 is exposed to groundwater with oxygen, it will tend to oxidize before the un-reacted stainless steel in the WP. In the cermet WP, experimental evidence shows that the iron has rapid oxidation kinetics. The iron will oxidize first even if some of the SNF UO_2 is exposed to groundwater and thereby prevent the initial oxidation of UO_2 .

Most of the DUO_2 is expected to oxidize before the SNF UO_2 . The most rapid oxidation kinetics are associated with oxidation of the steel in the cermet which releases the DUO_2 particulates. Multiple factors favor the oxidation of DUO_2 over the SNF UO_2 . Whatever the direction of groundwater, it first contacts the DUO_2 particulates. Thus, the oxygen can first react with these particulates. The DUO_2 particulates have high surface areas compared with SNF UO_2 , which allows more rapid oxidation of the former. The SNF UO_2 is protected by cladding with slow oxidation kinetics. Last, it is experimentally observed that oxidation of SNF UO_2 is much slower [6] than oxidation of unirradiated UO_2 due to the presence of rare earth fission products and actinides that slow oxidation kinetics. If one assumes full oxidation of the DUO_2 before the SNF UO_2 , the cermet WP (Fig. 2) delays SNF UO_2 oxidation until 1.4 million years after WP failure. For the cermet WP with DUO_2 fill, SNF UO_2 oxidation is delayed until 2.3 million years after WP failure.

- *Fluid flow.* The oxidation 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 [2]. This expansion slows the flow of groundwater through the WP by filling the void spaces. This further slows the oxidation of the WP, DUO_2 , and SNF. It also slows the migration of radionuclides in groundwater from the WP. However, fluid flow paths through the WP debris will bypass some fraction of the DUO_2 and reduce the period of time until the SNF UO_2 is oxidized.

Experimental evidence [2] provides some support to the above mechanisms. The interiors of natural uranium ore deposits with UO_2 in environments similar to the proposed YM repository have remained intact for long periods of time because the uranium on the exterior acted as a sacrificial material. Similar effects have been observed for piles of iron objects that have been buried for several thousands of years. The impact on groundwater flow depends upon the metal oxidizing before the SNF UO_2 does and upon the ratio of DUO_2 to SNF UO_2 (since this is a surface-to-volume effect). The benefits are strongly dependent upon a large WP with significant quantities of reduced materials.

- *Gaseous oxygen.* The 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. The above calculations did not include air source of oxygen. The atmospheric exchange of air with the geology is not well understood. Furthermore, the steel in tunnel liners, rail tracks, and other features will consume large quantities of oxygen after repository closure. However, if air is present in the repository drifts, oxygen can be transported to the inside of a degraded WP by oxygen diffusion through capillary water, oxygen diffusion through the gas-phase pore spaces, and air transport via barometric pumping through the gas phase. All of these processes are slowed or stopped by the oxidation products that fill the void spaces within the degraded WP. Studies [7] are underway to better understand and quantify these phenomena.

Control of Geochemistry of Failed WPs: pH Effects

The use of a cermet WP or WP with fill has an additional benefit. Both slow the rate of change in the pH (acidity) within the WP (Fig. 2), which is important for slowing degradation of many types of SNF. For example, the corrosion rates of aluminum and several other SNF cladding materials are strongly dependent upon the pH. If the pH is controlled within a specific range, the corrosion rates become very slow. Aluminum forms a protective oxide layer under neutral pH conditions. However, this protective oxide layer is soluble and disappears at higher- or lower-pH conditions. Figure 3 shows the solubility [8] of this corrosion layer [$\text{Al}(\text{OH})_3$] as a function of pH. Only in the pH range of -6 to 10 is the solubility of this protective layer low. Outside of this range, the oxide is highly soluble, quickly dissolves, and thus does not protect the aluminum. Chemical pH buffering by a cermet WP can significantly delay SNF degradation.

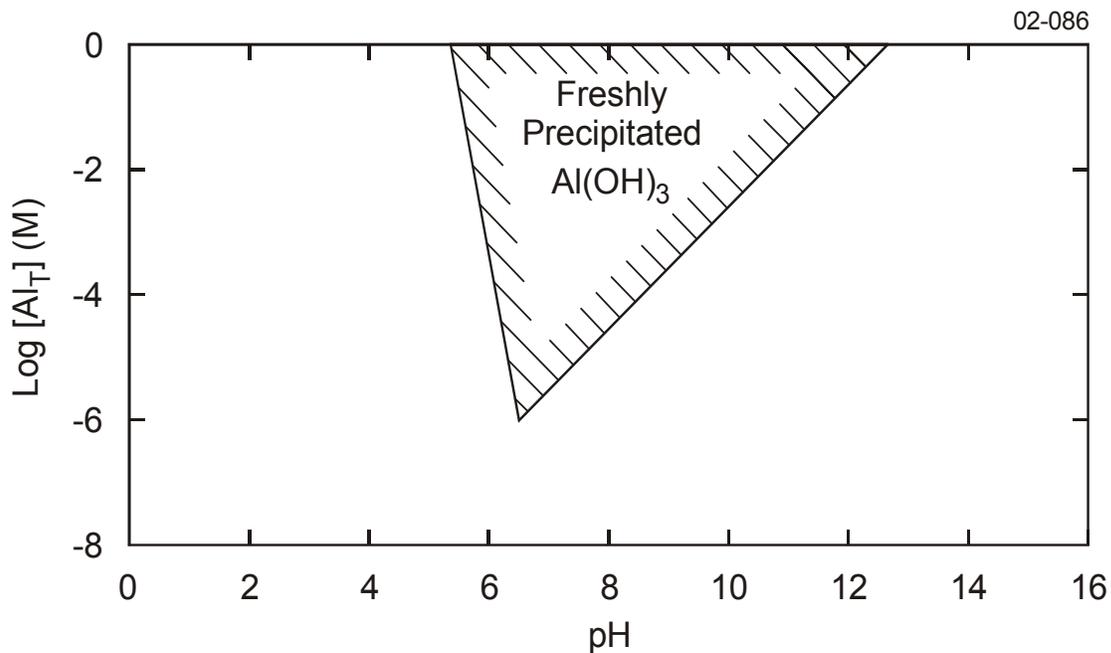


Fig. 3. Solubility of Protective Oxide Coating on Aluminum Versus pH.

DEGRADATION OF SNF

SNF Degradation Under Reducing Conditions

Miscellaneous SNFs made of uranium metals and certain other uranium forms can be oxidized by water. Consequently, reducing agents in the WP can not prevent their degradation. However, the addition of iron and DUO_2 provides several benefits. The oxidation of uranium metals by water produces insoluble oxides that trap many radionuclides. The higher volume (lower density) of the oxides tends to fill void spaces and reduce groundwater flow. In contrast, fully oxidized uranium (UO_2^{+2}) is somewhat soluble in water. Maintaining reducing conditions delays further oxidation of the uranium with the release of additional radionuclides. Reducing conditions

also maintain neptunium and technicium in their insoluble forms. These two nuclides are among the isotopes that control repository performance. If DUO_2 particulate fill is used, its mass reduces the chemical reactivity of the uranium metal or other species. Last, the long-term evolution of the degraded WP as conditions become oxidizing follows the same pathway as WPs with DUO_2 or LWR SNF (see below). The evolution under reducing conditions is not well understood and significant experimental work is required.

For repositories with oxidizing geochemistry, the use of cermets and fills creates a reducing–oxidizing radionuclide trap that may persist for very long periods of times. Some radionuclides are insoluble under oxidizing conditions (e.g., selenium), and others are insoluble under chemically reducing conditions (e.g., neptunium and technicium). A WP that maintains chemically reducing conditions for long periods of time traps those radionuclides that are insoluble under reducing conditions. Radionuclides that are soluble under reducing conditions can escape the WP if exposed to groundwater. However, some of those soluble radionuclides are insoluble under oxidizing conditions. Once this groundwater again becomes oxidizing, these radionuclides precipitate. In effect, a WP with reducing conditions within an oxidizing geochemical environment traps radionuclides that are soluble under oxidizing or reducing conditions.

Degradation Under Oxidizing Conditions

The longer-term (oxygen saturation) degradation of a cermet WP with miscellaneous SNFs will be similar to a WP with LWR SNF. In effect, the addition of DUO_2 by mass action makes all WPs look very similar. This also implies the following.

- *Criticality.* The potential for nuclear criticality can be minimized by addition of DU to the WP. As the WP and SNF degrade, the DU is expected to mix with the SNF-enriched uranium through dissolution, ion exchange, and co-precipitation of the different uranium isotopes in the WP. The average WP uranium enrichment will be lowered sufficiently that nuclear criticality can no longer occur [2].
- *Sorption.* Recent SNF leaching experiments show that certain long-lived radionuclides (e.g., neptunium) are retained by hydrated uranium oxides [9-11], such as those created by oxidation of DUO_2 . Hydrated iron oxides (hydroxides) will also retain a variety of radionuclides by several mechanisms, including scavenger precipitation using iron hydroxides. In addition, the various degradation products will filter various radioactive colloids (small particulates) from the groundwater. These specific radionuclides are those that control repository performance [5]. Because sorption is directly dependent upon total mass, the large quantities of DU and iron create the potential for sorption to be a significant mechanism in the retardation of selected radionuclides.

CONCLUSIONS

The disposal of miscellaneous SNFs presents a challenge because of their widely varying properties. It is proposed to construct WPs for these miscellaneous SNFs with large excesses of DUO_2 and iron. By mass action, all such WPs begin to show similar behavior in the repository environment. The chemical characteristics of the iron and DUO_2 will (1) help maintain the integrity of many DOE SNFs by controlling or buffering the oxidation potential and pH of the YM groundwater and (2) delay the further degradation of insoluble uranium species formed by the reaction of uranium metal SNFs with water. The DUO_2 assures that the longer-term behavior of the WP under oxidizing conditions is similar to that of an LWR WP. Significant additional work will be required to fully understand and demonstrate this approach to miscellaneous SNF management.

REFERENCES

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

1. Forsberg, C. W., and Haire, M. J., "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. Forsberg, C. W., "Effect of Depleted-Uranium-Dioxide Particulate Fill on Spent-Nuclear-Fuel Waste Packages," *Nucl. Technol.*, **131**, 337–353 (September 2000).
3. Leeds, E. J., "Comments on DUF₆ Materials Use Roadmap," Dated September 1, 2000, Letter to the U.S. Department of Energy from the U.S. Nuclear Regulatory Commission, ML003762080, NRC Public Reading Room, Bethesda, Maryland (October 18, 2000).
4. U.S. Department of Energy Office of Civilian Radioactive Waste Management, *Yucca Mountain Science and Engineering Report*, DOE/RW-0539, Washington, D.C. (May 2001).
5. U.S. Department of Energy, "Total System Performance Assessment—Viability Assessment Analysis Technical Basis Document," B00000000-01717-4301-00006, Rev. 01 (1998).
6. Poinssot, et al., "Expected Evolution of Spent Nuclear Fuel in Long Term Dry Storage and Geological Disposal: Major Outcomes of the French R&D Program PRECCI," *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).
7. Forsberg, C. W. and Dole, L. R., "Maintaining Chemically Reducing Waste Package Conditions," 2002 Materials Research Society Meeting; Symposium II: Scientific Basis for Nuclear Waste Management XXVI, December 2–6, 2002 (in preparation).
8. Morgan, J. J., "Applications and Limitations of Chemical Thermodynamics in Natural Water Systems," in *Equilibrium Concepts in Natural Water Systems*, R. F. Gould, Editor, American Chemical Society, Washington, D.C. (1967).
9. Rechar, R., "Dissolved Concentration Component of Waste Form Model in TSPA-SR," in *2001 International High-Level Radioactive Waste Management Conference, Las Vegas, Nevada, April 29–May 3, 2001*, American Nuclear Society, La Grange Park, Illinois (May 2001).
10. Finch, R. J., "Precipitation of Crystalline NpO₂ During Oxidative Corrosion of Neptunium-Bearing Uranium Oxides," *Scientific Basis for Nuclear Waste Management XXV*, Materials Research Society, Warrendale, Pennsylvania (2001).
11. Finch, R. J., et al. "Neptunium Incorporation into Uranium(VI) Compounds Formed During Aqueous Corrosion of Neptunium-Bearing Uranium Oxides," *Scientific Basis for Nuclear Waste Management XXV*, Materials Research Society, Warrendale, Pennsylvania (2001).

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