POSSIBLE EFFECTS OF UO_2 OXIDATION ON LIGHT WATER REACTOR SPENT FUEL PERFORMANCE IN LONG-TERM GEOLOGIC DISPOSAL

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SUMMARY

Disposal of spent nuclear fuel in a conventionally mined geologic formation is the nearest-term option for permanently isolating radionuclides from the biosphere. Because irradiated uranium dioxide (UO_2) fuel pellets retain 95 to 99 percent of the radionuclides generated during normal light water reactor operation, they may represent a significant barrier to radionuclide release. This document presents a technical assessment of published literature representing the current level of understanding of spent fuel characteristics and conditions that may degrade pellet integrity during a geologic disposal sequence. A significant deterioration mechanism is spent UO_2 oxidation with possible consequences identified as fission gas release, rod diameter increases, cladding breach extension, and release of solid fuel particles containing radionuclides.

Areas requiring further study to support development of a comprehensive spent fuel performance prediction model are highlighted. A program and preliminary schedule to obtain the information needed to develop model correlations are also presented.

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I. INTRODUCTION

National policies announced in 1977 indefinitely deferred reprocessing of spent fuel from commercial light water reactors (LWRs) and designated responsibility to the Department of Energy (DOE) for the safe disposal of spent fuel.⁽¹⁾ The Westinghouse Hanford Company (WHC) as part of its package development and performance evaluation efforts was contracted to develop a fundamental understanding of spent fuel behavior culminating in an analytical model capable of predicting spent fuel performance under all anticipated conditions imposed by transportation, packaging, handling and geologic disposal. This effort is part of the National Waste Terminal Storage (NWTs) Program managed by the Office of Nuclear Waste Isolation (ONWI).

Disposal of highly radioactive materials in conventionally mined geologic formations is the nearest term option for permanently isolating radionuclides from the biosphere.^(2,3) The system preventing radionuclide release during geologic disposal is composed of both natural and man-made barriers. Natural barriers may include such features as a long pathway to the biosphere, stagnant or slowly moving (noncorrosive) groundwaters, and rock having high sorptive properties for radionuclide species.⁽⁴⁾ Engineered barriers are currently conceived as primarily consisting of a metallic container⁽⁴⁾ enclosing spent fuel and helium or other stabilizer. This may be supplemented by using a second enclosing container (over-pack), shaft liners or backfill.⁽⁵⁾ Technical studies at HEDL concentrate on the performance of man-made barriers with particular emphasis on the ability of spent fuel to contain radionuclides during the entire disposal cycle.⁽⁶⁾

Evaluation of available literature indicates that LWR spent fuel pellets retain 95 to 99 percent of the radioisotopes generated during irradiation.⁽⁷⁻¹⁹⁾ Thus, irradiated uranium dioxide fuel pellets may represent a significant barrier to radionuclide release provided that the sintered form can be maintained.^(6,20-30) Conditions that degrade fuel pellet integrity must be understood to predict radionuclide source terms (release rates) for geologic transport models,^(19,23-25) actinide distributions for criticality assessments,⁽²⁰⁾ and effects on overall spent fuel rod/assembly performance.^(21,22)

This document presents a technical assessment of published literature representing the current level of understanding of uranium dioxide behavior under anticipated geologic disposal conditions. Areas requiring further study to support development of a mathematical model of spent fuel performance are highlighted and a schedule for developing model correlations is presented.

II. SPENT FUEL FORM AND PROPERTIES

The reference spent fuel waste form being considered by the CW&SFPP is an irradiated commercial LWR fuel assembly^(4,26) comprising a square array of fuel rods held in position by metallic structural hardware.^(8,27) An irradiated fuel rod consists of a protective metallic sheath (cladding) encasing a column of cracked, uranium dioxide fuel pellets containing fission products,⁽⁶⁻⁸⁾ and a pressurized gas (helium^(8,27) plus fission gases).⁽⁸⁻¹⁸⁾ Some spent fuel rods, estimated to be less than one percent of existing fuel assemblies,⁽²⁸⁾ are expected to have perforated cladding as they enter the disposal cycle; the remainder will be intact.

A. FRESH SPENT FUEL

Nuclear Fuel is fabricated from high purity uranium dioxide (UO_2) powder, slightly enriched in U^{235} , pressed and sintered to form cylindrical pellets. During reactor operations, the UO_2 fuel undergoes

complex chemical and physical changes due to exposure to neutrons, high temperatures, pressures, and steep thermal gradients.^(8,19) The chemical changes are due to the production and retention of isotopes (hereafter referred to as fission products from nuclear fission, neutron capture, and radioactive decay) within the crystalline structure of the UO_2 fuel pellets. The physical changes result from high pellet center-line temperatures (≈ 1500 K)^(16,18,29) and steep radial thermal gradients (fuel outer surface temperature ≈ 1000 K).^(16,18,29) These thermal conditions are produced by generation of thermal energy from the fissioning process coupled with a low fuel pellet thermal conductivity.^(7,8,30)

The isotopic and elemental composition of a spent fuel pellet changes with time after discharge as a function of as-fabricated composition and irradiation history; e.g., neutron flux, neutron energy spectrum, duration of irradiation segments, intervals between irradiations, etc. Computer codes^(31,32) have been developed to produce (nonvalidated) tables of isotopic inventories in spent fuel assemblies as a function of time after discharge.^(27,33)

In-core thermal conditions^(16,18,29) are expected to have greater influence over the location and chemical states of fission products in intact spent fuel rods than the less extreme thermal conditions anticipated for the UO_2 in dry storage or disposal.⁽⁸⁾ In operating fuel, the extent of fission product relocation or release from the UO_2 matrix is peculiar to the chemical state of each species, the species decay chain, local temperature and oxygen potential.⁽³⁴⁾ Assessments of the chemical state of fission products in uranium oxide⁽¹⁵⁻¹⁸⁾ and mixed uranium-plutonium oxide^(34,35) fuels have been made using fundamental thermodynamic data⁽³⁶⁾ in conjunction with estimates of equilibrium oxygen partial pressures.⁽³⁷⁾ These studies have in common the classification of fission product elements into two main classes; those which form oxides in the UO_2 system and those which do not form oxides. There is

general agreement that the following elements form oxides in the UO_2 matrix: strontium, yttrium, zirconium, niobium, barium, the rare earths, and the actinides. Zirconium and niobium are expected to be in the +4 valence state;⁽¹⁶⁾ strontium and barium in the +2 state; and yttrium, the rare earths and actinides in the +3 or +4 state.⁽¹⁶⁾ These fission product oxides are expected to be found in solid solution with the fuel although separate oxide phases may precipitate at high impurity concentrations (burnup); e.g., at about 4 at.% burnup, a multicomponent oxide $[(\text{Ba}, \text{Sr}, \text{Cs}) (\text{Zr}, \text{Mo}, \text{U}, \text{Pu}) \text{O}_3]$ phase based on barium zirconate (BaZrO_3) may precipitate.⁽³⁸⁾ These fission product elements have little tendency to migrate in the UO_2 matrix and are expected to have fairly uniform concentrations in a radial plane. Fissionable plutonium (a neutron capture-decay product) preferentially forms (and therefore should be located) near the outer surface of the fuel pellet due to resonance absorption of thermal neutrons by uranium-238.⁽¹¹⁾

Elements generally regarded as not forming oxides in UO_2 include: technetium, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, and the noble gases krypton and xenon. These elements can migrate in operating fuel rods depending on temperature, thermal gradients, fuel microstructure, etc., and may precipitate when their concentrations exceed their solubility limit in UO_2 . The gaseous fission products may precipitate as bubbles in the UO_2 matrix and grain boundaries. Again, depending on temperature, etc. these bubbles may migrate to and along fuel grain boundaries to the fuel surface (cracks or interconnected porosity) from which they can escape to the open spaces in the fuel rod.⁽⁷⁻¹⁹⁾ The amount of fission gas generated is approximately 3.5 volumes of gas per volume of UO_2 per 10,000 MWD/MTU;⁽⁹⁾ i.e., LWR spent fuel retains at least ninety percent of the generated gas in bubbles or closed pores and in the fuel matrix under normal operating conditions.

The major differences among various studies revolve around the chemical states of the fission products molybdenum, cesium/rubidium, bromine/iodine, tellurium/selenium, and antimony.⁽³⁴⁾ Recent studies^(15,16,34,37)

indicate that the Mo/MoO₂ couple buffers the fuel's oxygen potential to maintain a near stoichiometric UO₂ composition during irradiation. Cesium/rubidium may form ternary compounds with uranium and oxygen (e.g., Cs₂UO₄, Cs₂U₂O₇) or binary compounds with bromine, iodine, tellurium or selenium.^(15,16)

Physical properties of LWR fuels affected by normal in-reactor thermal conditions, other than fission product relocation and release, include: fuel densification, swelling, restructuring, and grain growth; pellet cracking and fragment relocation; and fuel-cladding chemical interaction. In-reactor fuel densification at temperatures below about 1500 K is virtually complete between 5,000 and 10,000 MWD/MTU after which fuel swelling from fission product accumulation becomes dominant.⁽⁸⁾ Current UO₂ fuel is sintered to about 92-95 percent of its theoretical density (TD=10.96 gm/cm³)⁽²⁷⁾ and will densify to about 96-97 percent TD.⁽¹⁰⁾ Retention of fission products in solid solution in the fuel matrix contributes to fuel swelling at a rate of about one volume per cent per 10,000 MWD/MTU.^(8,10) The combined effects of densification and swelling at about 35,000 MWD/MTU burnup should leave the UO₂ at about 94-95 percent TD. Fuel restructuring and grain growth are usually observed in fuel regions that have experienced temperatures in excess of 1473 K and have an average final grain size of six to ten microns.⁽⁸⁾ It is believed that most pellet cracking occurs during the first few ramps to power⁽⁸⁾ thus leading to the possibility of fragment relocation during subsequent handling.

From thermodynamic considerations, zirconium (zircaloy cladding) should react chemically with the oxygen of the UO₂;⁽²⁹⁾ the chemical reaction rate is apparently limited by the rate of release of oxygen from the UO₂, transport across the fuel-cladding gap and diffusion through the zirconia scale.⁽¹⁶⁾ Elements that have been detected by electron microprobe analysis on the inner surface of zircaloy clad fuel rods include: cesium, uranium, iodine, tellurium, chlorine, manganese, iron, silver, silicon, barium, copper, sodium, and calcium.^(15,16)

The chemical compounds formed by these elements were not identified because of the inherent limitations of electron microprobe analysis.

In summary, freshly discharged, intact fuel rods are expected to contain columns of cracked UO_2 pellets at a density of about 10.4 gm/cm^3 (95% TD). At the designed assembly average burnup of 33 GWD/MTU for pressurized water reactors (PWRs)⁽²⁷⁾ or 28 GWD/MTU for boiling water reactors (BWRs),⁽²⁷⁾ the UO_2 fission product concentrations should be fairly uniform (both radially and axially) at about 4.0 wt% for PWRs and 3.5 wt% for BWRs. Breached spent fuel rods are expected to have lost internal gas pressure and released fission gases. Some water-soluble fission products such as cesium, iodine, chlorine, etc. may be lost while gaining varying amounts of the reactor-purity water⁽²⁸⁾ depending on the nature and extent of the cladding failure.

B. AGED SPENT FUEL

Spent fuel assemblies are currently stored temporarily in monitored water pools prior to entry into a disposal cycle. This practice is expected to continue. A recent survey⁽³⁹⁾ of this type of storage experience found no reported evidence of gross degradation of intact LWR spent fuel rods during pool residence. Methods such as visual inspection or monitoring of pool water for gas or radioactivity release would detect only gross degradation such as cladding failure or fuel pellet disintegration. However, there have been a few instances of cladding failure resulting from mechanical damage during handling.⁽⁴⁰⁾ Another report expects the pool storage environment "to have a small, though not necessarily negligible, potential for degradation of fuel cladding"⁽⁴¹⁾ (i.e., intact fuel rods) because factors conducive to stressed, local attack of the cladding would be more severe under reactor operating conditions with some exceptions.

A comparison of UO_2 pellet temperatures during normal reactor operations (centerline ~ 1500 K, surface ~ 1000 K)^(16,18,29) and water-pool storage (centerline ~ 373 K, surface ~ 323 K)⁽³⁹⁾ indicates that both absolute temperatures and radial thermal gradients are much lower in pool storage. These observations regarding pool-storage environments lead to the expectation that little or no fission product migration will occur in spent UO_2 fuel in intact rods during aging in pool storage. Fission product chemical states should be affected by elemental transmutations resulting from natural radioactive decay.

Of the total number of spent fuel rods entering pool-storage, less than one percent are expected to have lost cladding integrity during irradiation.⁽²⁸⁾ Those rods with reactor-induced cladding breaches may expose the UO_2 pellets to oxygen-saturated pool water capable of leaching radionuclides and oxidizing the UO_2 to a higher uranium oxide (e.g., U_4O_9 , UO_3). A leaching study⁽⁴²⁾ of irradiated fuel indicates that the following elements will be selectively dissolved by deionized, oxygen-saturated water: cesium, antimony, strontium, yttrium, plutonium, and curium (in decreasing order of relative leachability). Storage experience with breached fuel rods^(39,40) indicates that the rate of UO_2 pellet degradation is low, with the extent of degradation dependent on the type of cladding defect (i.e., pinhole, small crack, split or broken) present.⁽⁴¹⁾ There is one report of a small increase in rod diameter at a breach site after nine years of pool storage.⁽³⁹⁾

The condition of spent fuel after water-pool storage has yet to be systematically investigated and documented. An effort to characterize spent fuel condition on entry into the disposal cycle is being undertaken.^(43,44)

III. ASSUMPTIONS CONCERNING DISPOSAL

The most readily implemented means for long-term isolation of radionuclides is currently considered to be emplacement of waste packages in a conventionally mined geologic repository.^(2,3) Current concepts for waste packages containing spent fuel consist of an airtight container enclosing one or more unmodified spent fuel assemblies, hardware to hold the assemblies in place, and a void space occupied by an inert gas or other stabilizer.^(4,26) This package will be placed in a shaft drilled into a conventionally mined, deep, geologically stable formation such as salt, basalt, granite, or tuff.⁽³⁾ The shaft may or may not be lined; the package may or may not be overpacked.^(4,5,26)

Disposal cycle environments which may affect spent fuel rod integrity range from inert gas through air of varying humidities to water containing dissolved gases and other chemicals. The chemical reactivities of species in these environments are affected by radiation (ionization) and heat (temperature) generated within the spent fuel from radioisotope decay. Temperatures are anticipated to range from 323 K to 679 K,⁽⁸⁾ the currently recommended maximum allowable temperature for mechanical overload.

The anticipated phases of a spent fuel disposal cycle and associated environments include:

- Handling (and storage) at temporary sites such as reactor storage basins, where the external environment may be air (or oxygenated water);^(39-41,45)
- Transportation, with a probable atmosphere of humid air inside the shipping cask;
- Packaging operations, lag storage, package emplacement, or retrieval; where the atmosphere will be either air, an inert gas,⁽²⁶⁾ or a

currently unidentified stabilizer material surrounding the fuel rods/assembly; and

- Package disposal-mode residence in geologic media, where a breached package opens the system to allow (free) circulation of air, moisture or ground water.⁽⁴⁾

IV. MODES OF UO₂ DETERIORATION

Uranium dioxide pellet deterioration is an important consideration in evaluating radionuclide retention by discarded nuclear fuel because LWR-irradiated UO₂ pellets contain more than 95 percent of the radionuclides (fission products and actinides) evolved during the energy-productive life of commercial nuclear fuel (see Section II). Deterioration of cracked UO₂ fuel pellets⁽⁸⁾ in spent fuel rods in the absence of a cladding breach is expected to be minimal because:

- (a) External mechanical loads are borne mainly by the cladding;
- (b) Current LWR fuel rod designs include plenum springs⁽²⁷⁾ to hold the fuel in place and absorb most shock, thus minimizing further pellet fragmentation and physical relocation due to mechanical disruptions;
- (c) The internal environment of an intact spent fuel rod is benign to the UO₂; i.e., the chemically active fission products are already reacted and contained within the UO₂ structure,^(15-20,34,37) fission gas release is expected to be minimal,^(11,46) and volatile fission product compounds (e.g. CsI, CsBr) are expected to affect the cladding rather than the fuel (source);^(15,17,41) and
- (d) The fluorite crystal structure of UO₂ is very resistant to self-radiation damage, experiencing average lattice strains of about 0.16% at temperatures below 673 K,⁽⁷⁾ and therefore UO₂ is not

expected to become amorphous under any radiation field likely to exist during disposal.

Significant UO_2 fuel pellet deterioration is expected to commence with the exposure of the UO_2 to high temperature oxidizing⁽⁴⁷⁾ environments; e.g., cladding breach formation in a chemically-active environment. Cladding breaches that release internal rod gases allow contact between fuel, fission products, and external chemical species. The point in the disposal cycle at which the cladding loses its integrity will influence subsequent radionuclide movement from the spent fuel rod due to (1) changing time-temperature relationships anticipated for each phase of the cycle, (2) the relative chemical reactivities between internal rod constituents and external species, and (3) possible physical relocation of fuel fragments caused by mechanical disruptions.

Possible consequences of oxidative fuel deterioration include: fission gas release,⁽⁴⁷⁾ spent fuel rod diameter increases,⁽²¹⁾ cladding breach extension,⁽²¹⁾ and release of solid fuel particles⁽⁴⁷⁾ containing radionuclides (i.e., actinide redistribution). These consequences are strongly dependent on the preferred locations for oxidation, the oxidation rate, temperature, and identity of the reaction product (e.g., U_3O_8).

Research on UO_2 oxidation rates, mechanisms, and reaction product identification prior to 1960 has been thoroughly summarized by Aronson.⁽⁵⁰⁾ The rate of oxidation of unirradiated UO_2 powder depends upon temperature, reactant concentrations and purities (fission products may be considered impurities in spent fuel), and the surface area available for reaction. Oxidation of a sintered (fuel) body will initially proceed at exposed surfaces and grain boundaries (unexposed surfaces) before the bulk of the matrix is affected.^(48,49) Spent fuel oxidation rates and threshold temperatures may also be affected by the energy deposited in the lattice as strain⁽⁷⁾ (from ionized or displaced species) caused by the associated radiations: alpha and neutron particles, and beta and gamma rays.

The temperature at which UO_2 oxidation occurs not only influences the oxidation rate but also affects the chemical composition and crystallographic form of the reaction product. Laboratory studies⁽⁵⁰⁻⁵⁴⁾ indicate that between 140 and 323 K, oxidation is solely a surface reaction affecting a depth of 1 to 4 nm (1 nm if the final product is UO_3 ; 4 nm if the product is U_4O_9)⁽⁵²⁾ depending on the available surface area.⁽⁵¹⁾ There is evidence that the oxidized surface layer which forms on UO_2 at 298 K is amorphous UO_3 .⁽⁵²⁻⁵⁴⁾

Matrix (bulk) oxidation of UO_2 occurs above about 333 K.^(50,52,55,56) There is general agreement that thermally activated oxidation of the dioxide to U_3O_8 occurs in two stages.^(50,52,55-62) The first stage follows a diffusion-controlled rate law between about 333 K and 523 K^(50,52,55,56,59) and is complete at or near an oxygen-to-uranium (O/U) ratio of 2.33 (U_3O_7). The second stage is a nucleation and growth type oxidation of UO_2 to $\text{UO}_2^{2.67}$ (i.e., U_3O_7 to U_3O_8) which occurs above 523 K.^(21,48-51,60-62) Reports identifying the temperature at which U_3O_8 initially appears vary from a low of 513 K⁽⁶³⁾ to a high of 713 K,⁽⁶⁴⁾ depending on the specific surface area of the samples,⁽⁶⁴⁾ the rate of temperature increase,⁽⁵⁰⁾ etc. It has been suggested that a slow formation rate for U_3O_7 tends to prolong the induction period preceeding the formation of U_3O_8 .⁽⁶⁵⁾

The identity of the oxidation product has been emphasized in the preceding discussion because there are significant differences in the physical properties; e.g. volume occupied or retention of crystalline form in a radiation field. A large density difference (Table 1) will significantly affect overall spent fuel performance in oxidizing environments. Formation of low density U_3O_8 or UO_3 from oxidation of high density UO_2 or U_3O_7 results in an increase in the volume occupied. If the reaction takes place on unconstrained surfaces, spallation of the product occurs upon reaching a limiting thickness or loss of crystallinity (i.e., the product becomes amorphous).⁽⁷⁾ A volume increase at fuel body grain boundaries would effectively pulverize that body into grain-sized fragments, allowing fission product and actinide redistribution and increasing the surface area available for further oxidation. A fuel

TABLE 1
DENSITIES OF SOME URANIUM OXIDES(7)

<u>Chemical Formula</u>	<u>O/U Ratio</u>	<u>Density gm/cm³</u>	<u>Crystal Structure</u>
UO ₂	2.00 $\pm$.02	10.96	Cubic (Fluorite)
U ₄ O ₉	2.25 $\pm$.06	11.16	Cubic (2 phases)
U ₃ O ₇	2.33 $\pm$.03	11.4	Tetragonal (3 phases)
U ₃ O ₈	2.67 $\pm$.05	8.35	Orthorhombic (Amorphous under radiation)
UO ₃	3.0 + ?	7.30	Amorphous

volume increase inside a spent fuel rod exerts stresses on the cladding breach⁽²¹⁾ over the entire length of the fuel column. It is also known that the U_3O_8 is very susceptible to loss of crystalline structure due to radiation damage⁽⁷⁾ thereby enhancing the possibility for its suspension in intrusive waters.

Calculations were performed to determine the maximum extent of fuel oxidation in a 4.88m-long, cylindrical canister (inner diameter = 432mm) containing either one PWR or three BWR spent fuel assemblies with breached rods.⁽²⁶⁾ Assumptions involved in these calculations included: a package void volume filled with helium to one atmosphere at room temperature, an oxygen impurity content in the helium equal to 0.1% by volume, an absence of water, theoretically dense UO_2 fuel, and the absence of other chemical reactions competing for the free oxygen. The results indicated that up to 21 grams of UO_2 in the PWR package or 20 grams of UO_2 in the BWR package could be converted to U_3O_8 . Taking the upper limit of radionuclide impurity concentration as 4 wt% yields a release of 0.8 gm of radionuclides for this amount of oxidative deterioration in an unbreached package.

Formation of a high density oxidation product such as U_3O_7 or U_4O_9 does not result in a significant change in surface area⁽⁵⁰⁾ (or volume) and therefore is not expected to lead to appreciable release of fission gases that might reside on grain boundaries. For the same reason, none of the other deleterious consequences of fuel oxidation are expected to accompany the formation of U_3O_7 (i.e., at temperatures below 523 K).

Reactant concentrations and purities will also influence spent fuel oxidation rates, but there is no agreement regarding the effect of solid-solution fission products (impurities) on the oxidation rate for pure UO_2 . One study indicates that the rate is unaffected⁽²¹⁾ while three studies^(49,57,60) report a decrease in the oxidation rate. The presence of fission products presumably affects the diffusion of oxygen through the solid, leading to an increase in the activation energy for diffusion-controlled oxidation.^(49,60) Since, a fuel rod breach exposes only a small portion of the geometric surface

of one or two fuel pellets to an oxidant, knowledge of how the UO_2 oxidation rate is affected by the presence of fission products, may be important for predicting whether a cladding breach is enlarged by fuel expansion during oxidation⁽²¹⁾ or plugged by the expanding fuel.⁽⁵⁸⁾

Other variables in the low temperature oxidation of unirradiated UO_2 which have been investigated are the effects of oxygen pressure and water vapor. Thermally activated oxidation of UO_2 to U_3O_8 requires the presence of free oxygen, whether it be gaseous oxygen in air or helium or oxygen dissolved in water; it is not thermodynamically possible to form U_3O_8 from UO_2 by a purely thermal process involving only water vapor or liquid water, within the range of temperatures likely to prevail in a geologic repository [up to a maximum cladding temperature of 653 K⁽⁸⁾].

The rate at which UO_2 is oxidized at a given temperature is independent of the partial pressure of oxygen in the surrounding atmosphere, except at very low partial pressures where the fuel surface is not fully saturated with oxygen.^(51,62) The pressure below which the oxidation rate of UO_2 powder is pressure dependent is about 10 torr at 473 K.⁽⁵⁰⁾

Because moisture may enter an intact spent fuel package on an intact assembly or within a breached fuel rod subjected to previous storage underwater, any effect which water may have on the thermal reaction between UO_2 and free oxygen may eventually affect overall spent fuel performance. It has been suggested that the blockage of reaction sites on the UO_2 surface by absorbed water effectively prevents the oxidation of UO_2 at room temperature.⁽⁵³⁾ On the other hand, over an extended period of time (15 years) at room temperature, moisture in combination with oxygen reacted with UO_2 to form $\text{UO}_3 \cdot 2\text{H}_2\text{O}$.⁽⁵⁴⁾ Confinement of the reaction to the UO_2 surface may preclude fuel pellet disintegration even though UO_3 has a lower density than UO_2 . Other studies indicate that water vapor may enhance the rate of unirradiated UO_2 oxidation,^(50,52) although a recent study reported that it probably has no effect.⁽²¹⁾ While it appears likely that, within the temperature range anticipated for disposal, water will have little if any effect

on the thermally-activated oxidation of UO_2 , the true role of moisture in influencing the rate of fuel oxidation must be understood in order to predict long-term effects on spent fuel performance and to decide what effort should be exerted to exclude water from spent fuel packages.

Two areas in which little pertinent data have been located are the rate of fission gas release during spent fuel oxidation⁽⁴⁷⁾ and the effect of radiation on the oxidation of UO_2 even though it is known that gamma radiation can decompose water to form oxygen atoms and ions, hydrogen peroxide, and other aggressive oxidants.⁽⁶⁶⁾ In-reactor studies^(67,68) indicate that a low UO_2 oxidation rate prevails in a dynamic system having very low concentrations of free oxygen. No experimental data appear to be available on the radiolytic reaction between UO_2 and free oxygen. Here the oxidation rate would undoubtedly be higher, but the rate as well as any influence on the effective threshold temperature for U_3O_8 formation would have to be determined empirically. An investigation of the oxidation of UO_2 under the action of gamma radiation has been performed,⁽⁶⁹⁾ but little or no information has been made available on the results obtained.

Another area which has received little attention is the simultaneous oxidation of fuel and zircaloy at low temperatures. One study of artificially breached spent fuel rods (of Candu design) reported rod swelling at the defect, defect enlargement, and secondary swelled regions some distance from the original defect.⁽²¹⁾ This study utilized temperatures in excess of 523 K and a continually replenished oxygen supply.

Finally, the thermodynamic stability of the phases formed on UO_2 oxidation should be considered for application to the geologic time scale. For samples in the composition range UO_2 and $\text{UO}_{2.25}$, annealing (for an unreported time) in the absence of oxygen at temperatures of 473 K and above causes disproportionation of the oxidized structures into UO_{2+x} and U_4O_9 .⁽⁵⁰⁾ (The "x" in UO_{2+x} denotes the amount of oxygen dissolved in that phase and increases with temperature.) There is very little published information regarding the

physico-chemical properties of U_4O_9 . Two published articles that were located disagree on the lower temperature limit at which U_4O_9 oxidizes to U_3O_7 : just below 433 K⁽⁵²⁾ or above 473 K.⁽⁵¹⁾ It is difficult to speculate on the effect of U_3O_7 disproportionation on overall spent fuel ability to retain radionuclides even though this solid-state reaction has a high probability of occurring in intact packages containing rods breached prior to packaging.

The thermodynamic stability of the tetragonal phases (α -, β -, γ - U_3O_7) in the composition range above $UO_{2.25}$ has not been definitely established within the range of temperatures anticipated for geologic disposal. (One study⁽⁵²⁾ reports that annealing samples with a composition above $UO_{2.25}$ at temperatures above 773 K produces a mixture of U_4O_9 and U_3O_8 ; again, the time required for the disproportionation was not reported. Annealing mixtures of U_4O_9 and U_3O_8 between 338 K and 748 K does not produce U_3O_7 ;⁽⁵²⁾ (i.e., the disproportionation is irreversible). The thermodynamic stability of the tetragonal phases in the composition range above $UO_{2.25}$ has not been definitely established⁽⁵⁰⁾ at temperatures below 773 K.

V. TEST ACTIVITIES

Although UO_2 oxidation has been extensively investigated, the majority of reported experimental data deal with pure, unirradiated powder behavior while spent LWR fuel is expected to be in the form of contaminated sintered pellet fragments that generate radiation (alpha, gamma and some neutrons) within their crystalline structure. Consideration of disposal conditions in conjunction with this literature survey has identified the following areas as requiring further investigation:

- The oxidation of spent UO_2 fuel pellets in zircaloy cladding,
- The effect of fuel oxidation on overall rod behavior,
- Fission gas release from spent fuel without simultaneous oxidation, and

- The effect of U_3O_7 disproportionation.

The objective of these proposed investigations is to correlate spent fuel deterioration with its consequences on radionuclide release and cladding stress state/breach extension. The correlations are needed for incorporation into the comprehensive spent fuel performance prediction model for geologic disposal (Figure 1).

A. OXIDATION RATES

Irradiated UO_2 oxidation rates and threshold temperatures in the presence of zircaloy cladding and fission products must be established to allow radionuclide release rates to be predicted. The effects of moisture and radiation on the oxidation process should be investigated to determine their significance with respect to spent fuel condition and radionuclide distributions at the time of package loss of integrity and prior to the onset of leaching. Fuel oxidation rates should also be correlated with the rate of fuel pulverization and volume change.

Oxidation rates should be determined in experimental systems where the following variables can be precisely and independently fixed: temperature (298-653 K), oxygen pressure ($0-2.67 \times 10^4$ Pa), moisture content (0 humidity to saturation at temperature), fuel surface area (maximum of 5×10^2 mm²/g of UO_2), zircaloy surface area ($0-10^3$ mm²), and gamma radiation (0 to maximum capacity of HEDL cobalt gamma facility). The spent UO_2 used in these tests should be obtained from freshly sectioned spent fuel rods and disproportionation tests (see Figure 1 and Section V.D. following).

B. ROD BEHAVIOR

Correlation between the rate of fuel swelling due to oxidation and rod effects, such as diameter changes or cladding breach enlargement, should be established to predict an expected "incubation time" between the onset of fuel oxidation and measurable loss of radionuclide containment ability. Rod

Figure 1. Test Activity Relationships

sections and full length spent fuel rods with artificial or natural cladding breaches should be tested under selected spent fuel pellet oxidation conditions so that known rates of fuel volume increase can be correlated with rod diameter changes, cladding stresses, cladding breach enlargement or blockage and pulverized fuel particle release. Cladding breach configuration (directly exposed surface area) will replace gamma radiation as a test parameter in the defected rod section tests. The full length spent fuel rods will use selected breach configurations and oxidizing conditions to investigate the effects of thermal gradients and possible oxidant entrainment in the internally connected spaces of the fuel rod (e.g., fuel-cladding gap or fuel pellet cracks) which could lead to rod swelling and secondary breaching in regions physically removed from the original breach site.

C. FISSION GAS RELEASE

While the rate of fission gas release resulting from spent fuel oxidation would be measured in Test Activity V.A herein it should also be investigated as a function of mild thermal transients to determine the validity of the assumption that temperature excursions encountered in the disposal cycle do not affect fuel body capability to act as an engineered barrier to radionuclide release while cladding integrity remains intact. Test variables should include: rate of temperature increase (1-20 K/hr), maximum temperature achieved (500-700 K), and inert gas pressure (10^5 to 8.3×10^9 Pa). Test material should be obtained from freshly sectioned spent fuel rods and disproportionation tests (to simulate rods breached prior to packaging).

D. DISPROPORTIONATION (METASTABLE PHASES)

The effects and rates of metastable oxide disproportionation must be established to predict oxidized fuel behavior in rods breached prior to packaging during the initial isolation period when packages retain their integrity, oxidant pressures are low to nonexistent, and thermal conditions are most severe. These investigations are needed to determine whether phase

separation of metastable uranium oxides is an important degradation mechanism (i.e., does disproportionation release radionuclides or affect oxidation rates subsequent to package loss of ability to contain radionuclides?).

Test variables would include: uranium oxide composition ($\text{UO}_{2.16}$ to $\text{UO}_{2.40}$), temperature (298-653 K), inert gas pressure ($5\text{--}20 \times 10^4$ Pa), and time (1-12 months). Partially oxidized spent fuel used in these tests should be obtained from oxidation rate measurements or rod behavior tests (Test Activities A and B). Disproportionated material should be subjected to oxidation and fission gas release rate measurements (Sections V.A. and C and Figure 1).

In the event that a package internal stabilizer other than helium is selected for use in commercial disposal operations, compatibility tests between the UO_2 fuel and stabilizer material should augment the previously described test activities.

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