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EVALUATION OF COVER GAS IMPURITIES
AND THEIR EFFECTS ON THE DRY
STORAGE OF LWR SPENT FUEL

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SUMMARY

In the dry storage of spent nuclear fuel, the fuel cladding must be protected against degradation and gross rupture that would release radioactive contamination in the storage environment. Current designs for the dry storage of light-water reactor (LWR) spent fuel specify the use of an inert gas storage environment to prevent oxidation of cladding or exposed UO_2 fuel. However, even inert cover gases will contain residual reactive impurity gases from various sources.

The purposes of this report are to 1) identify the sources of impurity gases in spent fuel storage casks; 2) identify the expected concentrations and types of reactive impurity gases from these sources over an operating lifetime of 40 years; and 3) determine whether these impurities could significantly degrade cladding or exposed fuel during this period.

Four potential sources of impurity gases in the helium cover gas in operating casks were identified and evaluated:

- residual impurities in the helium cover gas
- air leakage into the cask cavity through the seals between the cask body and primary cover
- residual impurity gases remaining in the cask after evacuation to a finite pressure level
- impurity gases introduced into the cask atmosphere after evacuation and backfill because of outgassing from the structural materials and fuel assemblies.

These sources were evaluated using design information obtained from technical and operating manuals for the TN-24P, Castor-V/21, MC-10, and MSF IV spent fuel storage casks. Impurity contributions from each source were calculated when possible, and gas analysis data from recent cask performance tests were used. Almost no air leakage is expected under normal operating conditions because of the design of the seals and safeguard systems. Contributions from indigenous impurities in the source gas are insignificant ($<0.02 \text{ mol O}_2$) if the cask is backfilled with high-purity (99.995%)

gas. Most of the impurities originate from the remaining two sources, which together are estimated to produce a reactive gas inventory of <0.6 mol each of O_2 (or equivalent oxidizing gases) and H_2 .

Reactive impurity gases could potentially degrade the cladding either by reacting directly with it or by reacting with exposed UO_2 fuel (if cladding breaches are present). Oxidation of exposed UO_2 fuel could cause fuel swelling and cladding rupture. Because the rates of these reactions are strongly temperature dependent, the behavior of the reactive gases and the subsequent effects on the Zircaloy cladding depend largely on two factors: 1) the cladding temperature distribution and its time dependence and 2) the number, size, and location of cladding breaches that could expose UO_2 fuel to oxidation.

Several different bounding cases have been considered, where the reactive gas inventory is either assumed to be completely getterred by the cladding or where all oxygen is assumed to react completely with the exposed fuel. It is concluded that the reactive gas inventory will have no significant effect on the cladding unless all available oxygen reacts with the UO_2 fuel to produce U_3O_8 at one or two cladding breaches. Reaction of 0.6 mol O_2 would produce a fuel volume increase of about 8.5 cm^3 , which would be sufficient to extend cladding breaches if the reaction were localized. Based on Zircaloy oxidation data, the oxygen inventory in a fully loaded pressurized water reactor cask such as the Castor-V/21 will be getterred by the Zircaloy cladding in about 1 year if the peak cladding temperature within the cask is $\geq 300^\circ\text{C}$. Only a negligible decrease in the thickness of the cladding would result.

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INTRODUCTION

In the dry storage of spent nuclear fuel, the fuel cladding must be protected against degradation and gross rupture according to a regulation issued by the U.S. Nuclear Regulatory Commission in Part 72 of 10CFR72, Licensing Requirements for the Storage of Spent Fuel in an Independent Spent Fuel Storage Installation. This regulation is intended to prevent contamination of the storage environment with radioactive fuel materials or with fission products released from ruptured fuel rods.

Current designs for the dry storage of light-water reactor (LWR) spent fuel specify the use of an inert, or nonoxidizing, gas storage environment to prevent oxidation of cladding or exposed UO_2 fuel (Johnson and Gilbert 1983b; Wheeler 1984). Such designs, referred to as inerted dry storage (IDS), assume a nominally pure inert cover gas. In practice, the gas will contain finite concentrations of reactive impurities such as oxygen, water vapor, and hydrogen from various sources. Reactive gases such as oxygen could potentially degrade the cladding either by reacting directly with it (Johnson and Gilbert 1983a) or by reacting with exposed fuel (if cladding breaches are present). Such reactions could cause fuel swelling and cladding rupture.

The purposes of this report are to 1) identify the sources of impurity gases in spent fuel storage casks, 2) identify the expected concentrations and types of reactive impurity gases from these sources over an operating lifetime of 40 years, and 3) determine whether these impurities could significantly degrade cladding or exposed fuel during this period.

Cladding degradation mechanisms that might occur during IDS have been identified and evaluated by Cunningham et al. (1987). However, that report assumes a completely inert cover gas and therefore does not consider the effects of reactive impurity gases, except for the hydrogen already present in the cladding. Two previous reports (Johnson, Gilbert, and Guenther 1983; Johnson and Gilbert 1983a) examined the possible effects of cover gas impurities on Zircaloy cladding degradation and dismissed the impurity effects as insignificant.

This report re-examines gas impurity effects by 1) including recent gas analysis data obtained from operating spent fuel storage casks, 2) analyzing the various sources of impurity gases in spent fuel storage casks, and 3) evaluating in more detail the effects of residual impurity gases on the integrity of spent fuel.

In this report, effects of reactive impurity gases are evaluated for pressurized-water reactor (PWR) and boiling water reactor (BWR) Zircaloy-clad fuel assemblies in sealed helium-filled storage casks. To provide background for this evaluation, the physical characteristics of metal spent fuel storage casks are briefly described and the procedures used in fuel loading, cask drying, and backfilling are summarized. Cover gas composition data obtained from measurements made during recent performance tests on fully loaded storage casks (Creer et al. 1987; McKinnon et al. 1986; McKinnon et al. 1987) are then presented. These measurements reveal the various types of impurity gases present after short-term cask operation (<1 year) and show that impurity gas concentrations are initially quite low. To predict long-term impurity gas effects over the planned 40-year operating lifetime of the cask, the time behavior of the reactive gas inventory is evaluated by considering four sources of impurity gases. A conservative estimate of the reactive gas inventory is made, and the effects of these gases on cladding degradation are determined. Finally, recommendations concerning cover gas purity and cask operating procedures are given.

CHARACTERISTICS OF SPENT FUEL STORAGE CASKS

In this section, background information is presented on the physical characteristics of several spent fuel storage casks, the thermal environment of the casks, and cask preparation procedures.

PHYSICAL CHARACTERISTICS

The spent fuel storage casks examined for this report are essentially steel pressure vessels designed to contain a maximum of 21 to 24 PWR (or 52 BWR) fuel assemblies, depending on design, and to transfer the spent fuel decay heat to the environment. Design and operating data for the MC-10 (Westinghouse 1985; McKinnon et al. 1987), TN-24P (Transnuclear 1985; Creer et al. 1987), Castor-V/21 (Kingsley 1985; Dziadosz et al. 1986), and MSF IV (McKinnon et al. 1986) casks were surveyed.^(a) The MC-10, TN-24P, and Castor-V/21 casks are designed for PWR fuel. The MSF IV cask can be used to store either BWR or PWR fuel, depending on the basket design; but it contained BWR fuel for the performance tests (McKinnon et al. 1986) that provided the gas impurity data used in this report.

Calculations of the impurity gas inventory in a sealed cask require the total gas volume and pressure and the impurity gas concentrations. The gas volume is approximately equal to the volume of the cask cavity minus the total volume of the fuel assemblies (see Table 1). For the four cask types considered, net gas volumes are $<7 \text{ m}^3$; but calculations of gas impurity levels in this work conservatively assume a net gas volume of 7.0 m^3 . Total gas pressures are also listed in Table 1. These initial pressures were obtained after the helium backfill but before steady-state operating temperatures were reached. The calculations of impurity gas levels given below conservatively assume a total cover gas pressure of 0.15 MPa (1.5 atm) for all casks.

(a) The MSF IV cask was formerly designated REA-2023.

TABLE 1. Cask Volumes and Initial Gas Pressures

<u>Cask Type</u>	<u>Fuel Type</u>	<u>Cask Cavity Volume, m³</u>	<u>Fuel Assembly Volume, m³</u>	<u>Initial Gas Pressure, MPa (atm) at 300K</u>
MC-10	PWR	9.8	2.2	0.152 (1.5)
TN-24P	PWR	6.9	2.2	~0.10 (~1)
Castor-V/21	PWR	7.6	1.9	0.06 (0.6)
MSF IV	BWR	8.5	1.8	~0.10 (~1)

THERMAL ENVIRONMENT

The reaction rates between impurity gases and materials within the cask depend strongly on reactant temperatures. The axial and radial temperature profiles within a cask depend on many factors, including cask design, cask orientation, backfill gas characteristics (Creer et al. 1987; McKinnon et al. 1986), and fuel burnup and age (Levy et al. 1987). Cask design and backfill gas characteristics determine heat transfer rates to the environment; burnup, age, and quantity of fuel determine the decay heat power generated within the cask. The decay heat power and hence fuel temperature decrease rapidly during the first 7 years after removal from the reactor; they decrease more slowly thereafter (Levy et al. 1987). This behavior must be considered in calculating reaction rates and quantities of reaction products.

In their report, Johnson and Gilbert (1983b) recommended a maximum initial cladding temperature limit of 380°C for dry storage. This limit was the allowable peak cladding temperature used for the Castor-V/21 (Dziadosz et al. 1986) and TN-24P (Creer et al. 1987) cask performance tests, although actual peak temperatures were lower. Average cladding temperatures with helium or nitrogen cover gases were typically much lower than 380°C, even with total cask heat loadings of 28 kW (Dziadosz et al. 1986).

CASK PREPARATION PROCEDURES

The residual gas inventory in a cask depends in part on the procedures followed in loading the cask with fuel, removing water, drying the inside of the cask, and backfilling the cask with inert gas. At a reactor site, spent fuel assemblies are normally loaded into the cask underwater (Kingsley 1985; Transnuclear 1985; Westinghouse 1985). However, in the cask performance

tests from which the gas purity data (described below) were obtained, only the MSF IV cask was loaded underwater; the others were loaded in dry air.

In underwater loading, the primary cover is bolted on after loading; and water is removed from the cask by draining or purging with pressurized helium. After most of the water is removed in this way, vacuum drying and helium backfill procedures are implemented. These procedures, as described in the operating manuals cited above, vary considerably with manufacturer. After the water is removed, radioactive decay heat causes the internal components to heat up, and residual water is vaporized and removed by the vacuum system. The combination of low pressure and elevated temperature should remove all liquid water. Vacuum pumping is continued until the cavity pressure decreases to about 2×10^{-4} MPa (2×10^{-3} atm) and remains at that level for 10 to 30 min. At this point, the cask is backfilled with helium to a pressure of 0.06 to 0.15 MPa (0.6 to 1.5 atm; see Table 1).

GAS COMPOSITION DATA FROM CASK PERFORMANCE TESTS

Performance tests conducted on spent fuel storage casks (Creer et al. 1987; McKinnon et al. 1986; McKinnon et al. 1987), during which cover gas samples were withdrawn and analyzed, provide a realistic picture of the impurity content of the cover gas in sealed casks during initial operation. These measurements are used as a baseline in the following analysis. In the performance tests, the casks were fully loaded with spent fuel and were back-filled with helium or nitrogen cover gases. As mentioned above, only the MSF IV cask was loaded underwater, while the others were loaded in dry air. However, the MSF IV cask contained no more water vapor than the other casks, indicating that the vacuum drying process is very effective. Further procedural details are available in the performance test reports referenced in Table 2.

Results of cover gas composition analyses for the TN-24P, MC-10, and MSF IV casks are summarized in Table 2. Gas composition data were also available for the Castor-V/21 PWR spent fuel storage cask (Dziodosz et al. 1986); however, those samples were contaminated with air because of either faulty valves on the sample bottles or faulty fittings on the cask. Those data are not considered in this report. The compositions listed in Table 2 are the maximum gas concentrations from the data presented in each reference; samples contaminated by air leakage were not included.

Noninert impurities present in the helium cover gas include O_2 , H_2 , CO_2 , CO , and H_2O . The H_2O concentrations represent water vapor and do not include H_2O adsorbed on the vessel walls (Creer et al. 1987). Each of the above impurities is present at concentrations ≤ 0.1 vol%, and the total impurity gas concentration is $\leq 0.2\%$.

TABLE 2. Typical Cover Gas Composition in Operating Casks^(a)

Cask Type	Reference	Concentration, vol%							
		He	N ₂	O ₂	Ar	CO ₂	CO	H ₂ O	H ₂
TN-24P	(b)	>99.8	<0.06	<0.02	<0.01	<0.01	<0.01	~0.10	<0.01
MC-10	(c)	>99.8	<0.10	<0.02	<0.01	<0.01	0.01	>0.01	<0.04
MSF IV	(d)	>99.7	<0.25	<0.06	<0.01	<0.01	<0.01	0.04	--

(a) Based on cask performance test data.

(b) Creer et al. 1987.

(c) McKinnon et al. 1986.

(d) McKinnon et al. 1987.

SOURCES OF IMPURITY GASES IN OPERATING CASKS

The gas impurity data given in Table 2 indicate the impurity concentrations present during initial cask operations. The purpose of this section is to determine whether the impurity gas inventory will increase significantly with time because of air in-leakage or other factors. Various sources of impurity gases in a spent fuel storage cask were evaluated, as determined from cask performance test reports (Creer et al. 1987; Dziadosz et al. 1986; McKinnon et al. 1986, 1987) and from technical operating manuals (Westinghouse 1985; Kingsley 1985; Transnuclear 1985). This analysis assumed normal cask operating conditions according to the licensed design and operating procedures and did not consider impurities introduced by abnormal events or equipment failures.

Four principal sources of impurity gases in the helium cover gas in operating casks have been identified. First, residual impurity gases remain in the cask after evacuation to a finite pressure level. Second, the helium backfill gas contains residual impurity gases, the concentrations of which depend on the purity of the source gas and on the amount of impurities introduced during gas transfer operations. Third, air leakage into the cask cavity through the seal between the cask body and the primary cover is a possibility. Finally, impurity gases are introduced into the cask atmosphere after evacuation and backfill because of outgassing from the structural materials and fuel assemblies.

The quantities and types of impurity gases arising from each of these sources, and their time dependence, are evaluated below. Total impurity levels are then estimated. The quantity of gas from each source, in moles, is determined from the ideal gas law. For reference, the quantity of gas contained in a 1.0-m^3 volume at a pressure of 1 atm (0.1013 MPa) at 300K is 40.6 mol.

RESIDUAL IMPURITIES DUE TO IMPERFECT PUMPOUT OF CASK CAVITY

The cask operating manuals examined for this report (Kingsley 1985; Transnuclear 1985; Westinghouse 1985) define a minimum pressure that must be achieved during evacuation of the loaded storage casks after the vacuum

drying operation and before the final helium backfill. This pressure varies from 4×10^{-4} MPa (0.004 atm) for the MC-10 cask to about 1×10^{-4} MPa (0.001 atm) for the TN-24P cask. Conservatively choosing the higher pressure of 4×10^{-4} MPa, the residual gas remaining in the 7-m^3 cask volume amounts to about 1.2 mol. However, reactive gases will comprise only a fraction of this residual gas, especially if the cask was purged with inert gas or was evacuated and backfilled more than once. This was verified by the gas composition measurements obtained during cask performance testing (Table 2), which showed that the actual reactive gas concentrations were below 0.2 vol%, corresponding to ~ 0.6 mol reactive gas in the 7-m^3 cask volume.

RESIDUAL IMPURITIES IN HELIUM BACKFILL GAS

Of the cask operating manuals cited above, only the Castor-V/21 manual (Kingsley 1985) specified the use of certified high-purity helium (99.995%) for the final backfill. Generally, the backfill gas is welding-grade helium (purity of 99.995% but uncertified). If helium gas of this purity level is used for backfilling and if care is taken to prevent gas contamination during backfilling as recommended by Creer et al. (1987) and McKinnon et al. (1987), then the impurity level indigenous to the helium is 0.005 vol% (50 ppm by volume). Using the ideal gas law at 300K and 0.152 MPa (1.5 atm) pressure, 0.005 vol% impurities in a 7-m^3 cask volume represents only 0.0213 mol of impurity gas. However, the reactive gas concentration is < 0.0213 mol because reactive gases comprise only a fraction of the impurities (Air Products 1987).

AIR LEAKAGE THROUGH SEAL GASKETS

The storage casks cited in Table 1 are thick-walled metal pressure (vacuum) vessels that are impermeable to gases at ambient temperatures. Under normal operating conditions, the only pathways for air leakage into the storage casks are the seals between the primary lid and the cask body. The casks also contain several small ports for drainage, pumpout, and instrumentation. However, these ports are sealed leak-tight after use; for example, the MSF IV cask ports are sealed with a series of pipe plugs (McKinnon et al. 1986).

The exact method of sealing the cask cavity varies with manufacturer. In all cask designs, the main seal between the cask storage cavity and the environment is a steel primary cover containing two concentric O-ring gaskets. For all casks except the MSF IV, at least one O-ring (the inner one) is metallic. The primary cover is then capped with a sealed secondary protective lid. The secondary lid of the MSF IV cask is seal-welded to the cask body (McKinnon et al. 1986); therefore, no gas leakage into the storage cavity is expected. In the other designs, the helium leak rate of each primary cover gasket must be verified to be $<1 \times 10^{-6} \text{ cm}^3/\text{s}$. This leak rate corresponds to a volume of only 0.0013 m^3 (0.06 mol) over 40 years. However, consideration of the cask seal design indicates that air leakage into the storage cavity is inhibited by the pressure differential across the primary gaskets. In the TN-24P (Transnuclear 1985) and the Castor-V/21 (Kingsley 1985) casks, the interlid or intergasket space is pressurized with inert gas or nitrogen, and this space contains pressure sensors to detect pressure changes due to gasket leakage. Therefore, air leakage is not considered to be a significant source of impurity gases.

GAS IMPURITIES DUE TO DESORPTION AND OUTGASSING

The terms "desorption" and "outgassing" refer to the emission of gases from surfaces or open pores or cavities containing a gas or volatile liquid. Of concern are air and water adsorbed on surfaces within the loaded cask or trapped in pores, crevices, etc., that would gradually contaminate the back-fill gas. Outgassing rates depend on many factors, including component design, gas species and concentration, temperature, time, ambient pressure, surface quality, surface composition, and total surface area. In a complex assembly such as a loaded storage cask, outgassing rates are difficult to predict. However, consideration of the metal cask and fuel assembly design suggests the absence of pores and cavities. Most outgassing and desorption should occur during the initial vacuum drying process, where low pressure and elevated temperature greatly accelerate the outgassing process. The data listed in Table 2 probably include most of the impurities released by outgassing over the operating lifetime of the cask.

TOTAL IMPURITY LEVELS

The above analysis indicates that nearly all of the impurity inventory in the cask is introduced at loading. This inventory results mainly from residual gases that are not completely removed during vacuum drying and from outgassing. Impurities indigenous to the compressed helium are negligible. No significant air leakage into the cask is expected under normal operating conditions; therefore, the impurity inventory is not expected to increase with time.

Because nearly all of the reactive gas inventory is introduced at loading, the reactive gas concentrations in Table 2 will be used as a basis for calculating potential cladding degradation. The concentrations of each gas that is theoretically available for reaction are summarized in Table 3. These values were chosen by selecting the maximum concentration of each gas from the data of Table 2. The theoretical molar concentrations of O_2 and H_2 available from each gas are also listed in Table 3. Calculations of molar concentrations assume a cover gas pressure of 0.15 MPa (1.5 atm) at 300K.

TABLE 3. Impurity Gas Concentrations Theoretically Available for Reaction

<u>Gas Species</u>	<u>Concentration, vol%</u>	<u>O_2 Concentration, mol/m³</u>	<u>H_2 Concentration, mol/m³</u>
O_2	0.06	0.037	0
CO_2	0.01	0.006	0
CO	0.01	0.003	0
H_2O	0.10	0.031	0.061
H_2	0.04	0	0.024

RELEVANT CLADDING DEGRADATION MECHANISMS

Zircaloy cladding degradation mechanisms and degradation rates depend on the types and concentrations of reactive gases in the cover gas, the cladding temperature, and the physical and mechanical state of the cladding. The cladding can potentially be weakened or damaged by direct reaction with the gases listed in Table 3 or by oxidation and swelling of UO_2 fuel that is exposed at cladding breaches (Einziger and Strain 1986; Einziger and Cook 1985). Cladding degradation mechanisms relevant to IDS in a nominally pure inert cover gas have been reviewed in detail by Cunningham et al. (1987). Only those mechanisms pertaining to the interaction of Zircaloy cladding or UO_2 fuel with the reactive gases present in the cask will be considered in the following sections.

INTERACTION WITH ZIRCALOY

Reaction of Zircaloy with the gases listed in Table 3 has been discussed previously by Johnson and Gilbert (1983a; 1983b). Nitrogen, present as an impurity in the helium cover gas, is considered to be inert because it does not react readily with Zircaloy at temperatures of concern. Thermodynamically, CO and CO_2 are capable of oxidizing zirconium and UO_2 (Kubaschewski and Alcock 1979) and are reported to oxidize Zircaloy at about the same rate as O_2 (Johnson and Gilbert 1983a). Water vapor can potentially dissociate and oxidize Zircaloy, especially under conditions where radiolysis can occur (Gilbert, Knox, and White 1985).

Oxygen reacts with Zircaloy to form ZrO_2 scale according to the following reaction:

This reaction reduces cladding thickness and increases cladding stress. However, as noted by Johnson and Gilbert (1983b), LWR spent fuel cladding contains an average of $\sim 25 \mu\text{m}$ of ZrO_2 in addition to a "crud" layer composed of metal oxides (Hazelton 1987). Available O_2 must diffuse through these layers to react with the cladding.

Hydrogen can be absorbed by Zircaloy, forming hydride precipitates after the solubility limit is exceeded. At sufficiently high precipitate concentrations, cladding failure can occur by several mechanisms. These degradation mechanisms have been reviewed by Cunningham et al. (1987). Johnson and Gilbert (1983b) noted that LWR Zircaloy cladding absorbs up to 20 to 150 ppm hydrogen by weight during reactor operation; therefore, hydrogen picked up during storage must add significantly to this inventory to have a marked effect on cladding integrity.

INTERACTION WITH UO₂ FUEL

Interaction of various reactive gases with UO₂ fuel has been discussed by Wheeler (1987); Johnson, Gilbert, and Guenther (1983); and Gilbert, Knox, and White (1985). If UO₂ fuel is exposed to the cask environment through cladding breaches, it can react with available oxygen to form U₃O₈ (Campbell et al. 1987; Gilbert, Knox, and White 1986; Einziger and Strain 1986) according to the following reaction:

This reaction is undesirable for two reasons. First, the specific volume of U₃O₈ is greater than that of UO₂; thus, U₃O₈ formation causes fuel swelling that can enlarge the cladding breach and expose additional quantities of UO₂ to the storage environment. Secondly, the reaction product is granular or powdery and is easily dispersed (Klingensmith 1980).

The oxidation rate of UO₂ depends strongly on temperature (Campbell et al. 1987). Water vapor apparently does not dissociate and oxidize UO₂, even when strong gamma fields and radiolysis products are present. In tests performed in moist nitrogen (31°C dew point), Gilbert, Knox, and White (1986) demonstrated by weight gain measurements that spent UO₂ fuel did not transform to higher oxides at 380°C after 46 days of exposure. These results also showed that radiolytic nitrogen oxides either did not form at 380°C or did not react with and oxidize the UO₂. Carbon dioxide can apparently dissociate slowly and oxidize UO₂ (Johnson, Gilbert, and Guenther 1983).

EVALUATION OF REACTIVE GAS EFFECTS

The discussion in the previous section indicates that all of the gases listed in Table 3 can potentially react with Zircaloy cladding, while only O_2 , CO_2 , and CO are expected to react with exposed UO_2 fuel. With the exception of hydrogen absorption by the Zircaloy, the dominant reactions involve oxidation according to Equations (1) and (2). At least some of the available oxygen will react with the Zircaloy. However, UO_2 fuel will be oxidized only if one or more cladding breach of sufficient size is present and is located in a region where the fuel temperature is high enough to produce a significant reaction rate. Then the Zircaloy and the fuel will compete for oxygen. It is beyond the scope of this document, and may be impossible, to uniquely determine the fate of the reactive gases within a sealed cask because of statistical variations from case to case. Therefore, only some bounding cases will be considered here.

ZIRCALOY DEGRADATION

From Table 3, about 0.54 mol of O_2 is potentially available to react with the Zircaloy in a 7-m^3 cask volume if O_2 from all sources is considered. If the available 0.54 mol of O_2 reacts uniformly with the BWR Zircaloy cladding in the MSF IV cask, for example, then 0.54 mol (~50 g) of Zircaloy will be consumed according to Equation (1). This would reduce the cladding thickness by a negligible $0.018\text{ }\mu\text{m}$. Even if all of the O_2 reacts with only the hottest 1% of the cladding, the subsequent $1.8\text{-}\mu\text{m}$ loss represents <1% of the cladding thickness. The reaction product would be even thinner on the PWR cladding in the other casks because the total cladding surface area for PWR fuel assemblies is greater than that for BWR assemblies (see Table 4).

TABLE 4. Zircaloy-Clad Surface Area in Fully Loaded Storage Casks

<u>Cask Type</u>	<u>Fuel Type</u>	<u>Surface Area, m^2</u>
MC-10	PWR	704
TN-24P	PWR	704
Castor-V/21	PWR	616
MSF IV	BWR	488

Although the Zircaloy cladding is thermodynamically capable of reacting with the inventory of oxidizing gases, the oxidation kinetics are slowed by the relatively low cladding temperatures in storage and by the pre-existing oxide scale on the spent fuel cladding. The rate of oxygen consumption by the cladding can be estimated from low-temperature Zircaloy oxidation data, which has been reviewed by Hillner (1977). From these data, Hillner developed empirical equations to describe oxide formation rates in saturated steam. Because spent fuel cladding contains an existing oxide scale that is typically $>5 \mu\text{m}$ thick, its oxidation rate is described by linear post-transition kinetics. From about 260 to 400°C (533 to 673K), the weight gain in units of mg/dm^2 is given by the following equation:

$$\Delta W = 1.12 \times 10^8 \exp(-12,529/T) \times t \quad (3)$$

where t is time in days and T is absolute temperature (Kelvin). This equation does not account for diffusion through the crud layer, which may reduce the oxidation rate of spent fuel cladding.

From Equation (3), the weight gain after 1 year at 260°C is $2.5 \text{ mg}/\text{dm}^2$ ($0.25 \text{ g}/\text{m}^2$), which corresponds to the consumption of about 0.002 mol of O_2/m^2 of cladding. Therefore, the entire 0.54 mol O_2 inventory would be consumed in 1 year by $\sim 270 \text{ m}^2$ of cladding at 260°C. This area represents somewhat more than one-third of the cladding surface area in a fully loaded PWR cask, and one-half of that in a BWR cask (Table 4).

Examination of the cladding temperature profiles measured during the cask performance tests on fully loaded casks indicates that roughly half of the cladding in the helium-filled Castor-V/21 cask was hotter than 260°C (Dziadosz et al. 1986), but none of the cladding in the helium-filled TN-24P cask (Creer et al. 1987) reached this temperature. If there is no competition for oxygen by exposed UO_2 fuel, then the rate of oxygen consumption by the cladding will depend largely on the various factors that determine cladding temperature distribution and temperature history (Levy et al. 1987). In a hot cask, where much of the cladding is initially above 300°C, it is probable that the entire oxygen inventory will be consumed by the cladding during

the first year of storage. However, in a cask where most of the fuel cladding is initially cooler than 200°C, little of the oxygen may be gettered even in 10 years.

Effects of hydrogen on the Zircaloy cladding can be evaluated by assuming that the 0.6 mol (1.2 g) H₂ inventory (Table 3) in a 7-m³ cask is completely absorbed by the Zircaloy. The total mass of Zircaloy cladding in the 52 BWR fuel assemblies within the fully loaded MSF IV cask is about 2680 kg (5900 lb). If the 1.2-g H₂ inventory was uniformly absorbed, the hydrogen concentration in the cladding would increase by only 0.45 ppm. This amount is significantly less than the hydrogen concentration picked up during in-reactor operation, which ranges up to 150 ppm by weight (Johnson and Gilbert 1983b); therefore, the effects would be negligible.

UO₂ FUEL OXIDATION

A worst-case event is the reaction of the entire oxygen inventory with UO₂ fuel at a single breach site. For this to occur, the Zircaloy cladding and other materials within the cask must getter almost none of the oxygen or the oxygen must be consumed by the UO₂ fuel at the breach site at a much faster rate than at competing sites. Furthermore, the single cladding breach must be sufficiently large and must not become plugged by reaction products. This worst-case event is extremely unlikely because cladding penetrations, in addition to being rare, are also very small (<1 mm²). Even for a 1-mm² breach, the exposed fuel area is initially almost 10⁹ times smaller than the Zircaloy cladding area; hence, the UO₂ oxidation rate will probably not be competitive with the Zircaloy oxidation rate.

Nevertheless, in a 7-m³ cask, about 0.32 mol of O₂ is available for UO₂ oxidation from the O₂, CO₂, and CO impurity gases (Table 3). The UO₂ is assumed to transform to U₃O₈ according to Equation (2). If the available 0.32 mol of O₂ reacts completely with the UO₂ fuel, then 0.96 mol (259 g or 24 cm³) of UO₂ is transformed, producing 0.32 mol (270 g or 32.5 cm³) of U₃O₈. This transformation represents a fuel volume increase of 8.5 cm³, which could cause cladding fracture if the transformed volume were sufficiently localized.

CONCLUSIONS AND RECOMMENDATIONS

Under normal operating conditions as defined in the technical and operations manuals for the casks considered here (Kingsley 1985; Transnuclear 1985; Westinghouse 1985), less than 0.6 mol each of O_2 and H_2 is expected to be available for cladding degradation reactions over the 40-year storage lifetime. Nearly all of the reactive gas inventory is introduced during initial fuel loading and is not expected to increase with time because air leakage into the cask will be negligible under normal operating conditions.

The reactive gas inventory is not expected to cause significant cladding degradation unless the entire inventory reacts with UO_2 fuel at one or two cladding breach sites, which is very unlikely. Some or all of the oxidizing gases will be gettered by the Zircaloy cladding, depending mainly on the cladding temperature distribution throughout the cask. Reaction of the entire oxygen inventory with the cladding would cause only a negligible reduction in cladding thickness, even if oxidation is confined to the hottest 1% of the cladding. Likewise, reaction of the entire hydrogen inventory with the Zircaloy cladding would not significantly increase the cladding hydrogen concentration above pre-existing levels. These conclusions are in agreement with the analysis of Johnson and Gilbert (1983a) on the effects of residual reactive gases on cladding in dry storage.

Localized cladding rupture could occur if the entire oxygen inventory reacted with UO_2 fuel to form the less-dense U_3O_8 at one or two breach sites. The small amount of oxygen present has a larger impact in this case because the fuel oxidation reaction is confined to relatively small regions. This conclusion relates only to the theoretical possibility, but not to the probability, of an oxygen- UO_2 reaction producing a fuel volume increase sufficient to rupture the cladding. The latter depends on many factors such as the number, size, and location of the cladding defects and on the amount of oxygen available that is not gettered by other materials within the cask. Because of the low initial O_2 concentration in the cover gas, the small area of fuel likely to be exposed at a cladding breach, and the subsequent reduction in oxygen concentration as the oxidation reaction proceeds, the rate of U_3O_8 formation may be extremely slow if the situation occurs at all.

Adhering to the operating procedures given in the technical and operating manuals for each cask should ensure that the reactive gas concentrations in the cover gas do not exceed the levels estimated in this report. Especially important to the conclusions of this report is that care be taken in the preparation and preservation of the gaskets and sealing surfaces to prevent air leakage during cask operation.

The cask performance test reports (Creer et al. 1987; Dziadosz et al. 1986; McKinnon et al. 1987) include recommendations that are intended to assure the purity of, or prevent the contamination of, the cover gas. These recommendations are repeated below:

- The cover gas system used to evacuate and backfill the cask must be designed and operated carefully to prevent contamination of the cover gas with air.
- After loading, the cask should be evacuated and backfilled with inert gas at least two times to reduce the concentration of residual impurity gases, which, as the above analysis indicates, is perhaps the largest contributor to the reactive gas inventory in the sealed cask.

An additional recommendation, based on this analysis, is to establish a cover gas impurity limit. The purity of the cover gas in each cask should be verified by sampling after final backfilling. This sample would reveal any cover gas contamination that occurred because of procedural errors, hardware failures, or contaminated backfill gas. The gases of concern are those that can oxidize exposed UO_2 fuel: O_2 , CO_2 , and CO . A recommended maximum quantity of oxidizing gases is 1 mol per cask for the types of casks evaluated in this report: total gas volume of $\leq 7 \text{ m}^3$ at a pressure of about 0.15 MPa (1.5 atm). This corresponds to a maximum allowable oxidizing gas concentration of about 0.25 vol%. This concentration is about three times greater than the concentration of oxidizing gases found in the gas samples in the cask performance tests; therefore, it should not be difficult to obtain in practice. Based on the present analysis, an oxidizing gas concentration of 0.25 vol% is much too low to degrade the cladding even if all of the gas

reacts with the cladding. It could cause localized cladding rupture only in the very unlikely event that all of the oxidizing gas reacted with the exposed fuel.

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