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CONSIDERATIONS RELEVANT TO THE DRY STORAGE OF LWR FUEL RODS CONTAINING WATER

Hanford Engineering Development Laboratory

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R.E. Woodley

Prepared for the
U.S. Nuclear Regulatory Commission

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ABSTRACT

The performance under dry storage conditions of LWR fuel rods containing water was analyzed to determine if radionuclide containment by the fuel rod cladding would be adversely affected. Fuel rod and storage canister pressurization, as well as cladding and fuel oxidation, were examined using "worst-case" conditions. The results of this study are presented.

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CONSIDERATIONS RELEVANT TO THE DRY STORAGE OF LWR FUEL RODS CONTAINING WATER

I. SUMMARY

The performance under dry storage conditions of LWR fuel rods containing water was analyzed to determine if radionuclide containment by the fuel rod cladding would be adversely affected. Generally, "worst-case" conditions were assumed in the analysis.

If the cladding defect of a fuel rod containing water reseals, the stress-rupture lifetime of the cladding at storage temperatures up to ca. 350°C is not appreciably shortened by pressurization of the rod when the contained water vaporizes. Increased cladding hydriding and the potential for hydride reorientation to a radial direction are not expected to be a problem, but additional information is needed. Pressurization of the storage canister by water introduced with breached fuel rods should be inconsequential. With regard to chemical effects, Zircaloy* oxidation resulting from its thermal or radiolytic reaction with the introduced water should be of minor consequence, as would the thermally-activated oxidation of the urania fuel by water. Extensive water-basin storage experience suggests that fuel oxidation by a radiolytic process (temperature insensitive) involving liquid water would also be negligible; the extent of the radiolytic oxidation of urania by water vapor cannot presently be quantified.

Thus, analyses of the relevant data and experience offer reassurance that fuel and cladding integrity will be maintained in the event that fuel containing water is placed in dry storage. Additional information on cladding hydriding and radiolytic fuel oxidation by water vapor is required, however.

*Zircaloy is a registered trademark of Westinghouse Electric Corp., Specialty Metals Division, Blairsville, PA.

II. INTRODUCTION

The dry storage of spent LWR fuel is being considered for the interim period between its storage in reactor pools and its eventual disposal, either in geologic repositories or by reprocessing. When a fuel rod is intact, the fuel pellets, which contain the majority of the fission products, and the fuel rod cladding serve as primary barriers to the release of actinide and fission-product elements or compounds. Unless they are identified and excluded, a small fraction of the fuel rods entering dry storage will have experienced cladding failure during their reactor residence. In 1970, the percentage of failed rods amounted to about 1%, but this rate of failure is presently reduced to about 0.01% to 0.02% because of various design improvements.[1] Although most cladding breaches are quite small, some of the defected rods may contain water. When placed in dry storage, breached rods which contain water could potentially be degraded, thereby allowing the release of radionuclides into the storage canister.

The present study was undertaken to examine the performance under dry storage conditions of LWR fuel rods containing water and to determine if their presence would be a consideration in radionuclide containment by the fuel rod cladding. This report presents the results of the study.

III. POSSIBLE FUEL ROD DEGRADATION SCENARIOS

Although cladding defects are often microscopic in size, a range of sizes for cladding penetrations can be expected. Consequently, some defects may admit water into the fuel rod while others may not. Defect size will determine the ease with which contained water or steam can be released when the fuel rod is placed in dry storage and its temperature increases. Small defects will hinder relief of the increasing internal pressure and potentially allow greater pressure buildup. Indeed, a small defect could conceivably become totally blocked or "resealed." Mechanisms by which defect blockage might occur include cladding corrosion, in which the corrosion products totally close the defect, thermal expansion of the urania fuel into the defect, and fuel oxidation. If the latter process leads to the formation of U_3O_8 or UO_3, expansion of the fuel into the defect could close it off. On the other hand, it is also possible that expansion of the oxidized fuel will enlarge the defect rather than reseal it,(2) thereby allowing greater access of radionuclides to the storage canister.

The presence of fuel rods containing water in dry storage, whether resealed or not, could lead to certain physical and/or chemical actions resulting in further fuel rod degradation. As a means of bounding possible situations, "worst-case" assumptions regarding the water present and defect resealing are made in these analyses. Thus, when degradation mechanisms involving pressurization are considered, it is assumed that resealing occurs and that sufficient water is present to maintain the maximum internal pressure for any temperature considered. For situations involving chemical interactions, worst cases, both with and without resealing, are possible. The results of all these considerations are thus intended to be conservative. The various situations examined are summarized in Table 1. As amplified in Appendix A, a temperature of 175°C was used as a possible maximum fuel storage temperature in air and 400°C in inert gas. Also, an approximate maximum heating rate of fuel in dry storage was calculated and is given in Appendix B.

TABLE 1

CONDITIONS UTILIZED IN BOUNDING POSSIBLE DEGRADATION DURING DRY STORAGE OF LWR FUEL RODS CONTAINING WATER

Primary Concern	Degradation Mechanism	Conditions
Pressurization	Stress Rupture of Fuel Rod Cladding	Maximum pressure at each temperature; $350°C \leq T \leq 400°C$; fuel rod dimensions to give maximum hoop stress.
	Canister Pressurization	Temperatures: 175°C in air; 377°C in inert gas. Free volume of up to about 1% of fuel rods totally water-filled. Various canister volume conditions.
Chemical Interactions	Thermal Zr/Urania/ Steam Reactions	Temperatures: $175°C \leq T \leq 400°C$. Oxidation of internal cladding surface and UO_2 in a water-filled fuel rod.
	Radiolytic Zr/Urania/ Steam Reactions	Essentially temperature-independent. Oxidation of internal cladding surface and UO_2 in a water-filled fuel rod.

IV. WORST-CASE FUEL ROD DEGRADATION

A. CLADDING STRESS RUPTURE

During dry storage, the pressure within fuel rods containing water will depend upon the conditions under which the breached rods reseal. Two different conditions of possible resealing will be considered:

1) Resealing during reactor operation, with a coolant temperature of about 600°F (315.6°C) and system pressures of about 2200 psi and 1100 psi for PWR's and BWR's respectively.

2) Resealing during pool storage at a temperature of about 110°F (43.3°C) and under an approximate 30-ft head of water (P = 12.9 psi).

Calculations of the internal pressures of resealed fuel rods yielded the results presented in Figures 1 and 2 for PWR and BWR rods, respectively. In all cases, it was assumed that sufficient water entered the rods to maintain the equilibrium water vapor pressure at all temperatures up to the critical temperature, 374.15°C. The total pressure in a fuel rod is then the sum of the equilibrium water vapor pressure and the pressure of the residual helium plus fission gases. Furthermore, the inert gases are assumed to behave ideally over the temperature range of interest, as is the water vapor above its critical temperature. Included in Figures 1 and 2 for comparison are the pressure-temperature relationships for intact fuel rods. In the PWR case, the curve is based on end-of-life pressures of fuel rods with a burnup of 30 GWd/MTU[3] whereas in the BWR case, end-of-life pressures in fuel rods with a burnup of 12 GWd/MTU[4] were employed. Not included in Figure 2 is the case of the BWR fuel rod which reseals during reactor operation. The curve in this instance is almost identical to the curve for the rod which reseals during pool storage, the only difference resulting from the minor amounts of helium present. The pressures in both cases are dominated by the water vapor partial pressure.

To satisfy the condition of sufficient water within the fuel rod to maintain the equilibrium vapor pressure up to the critical temperature, a PWR rod would require $\sim$1.6 cm^3 of water within a total void volume of about 22 cm^3. A BWR fuel rod would require $\sim$5.6 cm^3 of water within a total void volume of about 75 cm^3. In either case, if less water were available, then the depicted curves would be followed only up to the point where all of the water is vaporized, after which ideal gas behavior would prevail. Finally, it should be noted that the internal pressure of a resealed fuel rod, as depicted by the curves of Figures 1 and 2, is determined primarily by the reactor or storage system pressure at the time the breached rod reseals and is independent of the internal pressure of the fuel rod when it breaches.

Knowing the variation with temperature of the internal pressure of resealed LWR fuel rods containing water, it is possible to estimate whether the Zircaloy-cladding stress-rupture lifetime will be significantly shortened at temperatures and times within the range of interest. This is accomplished

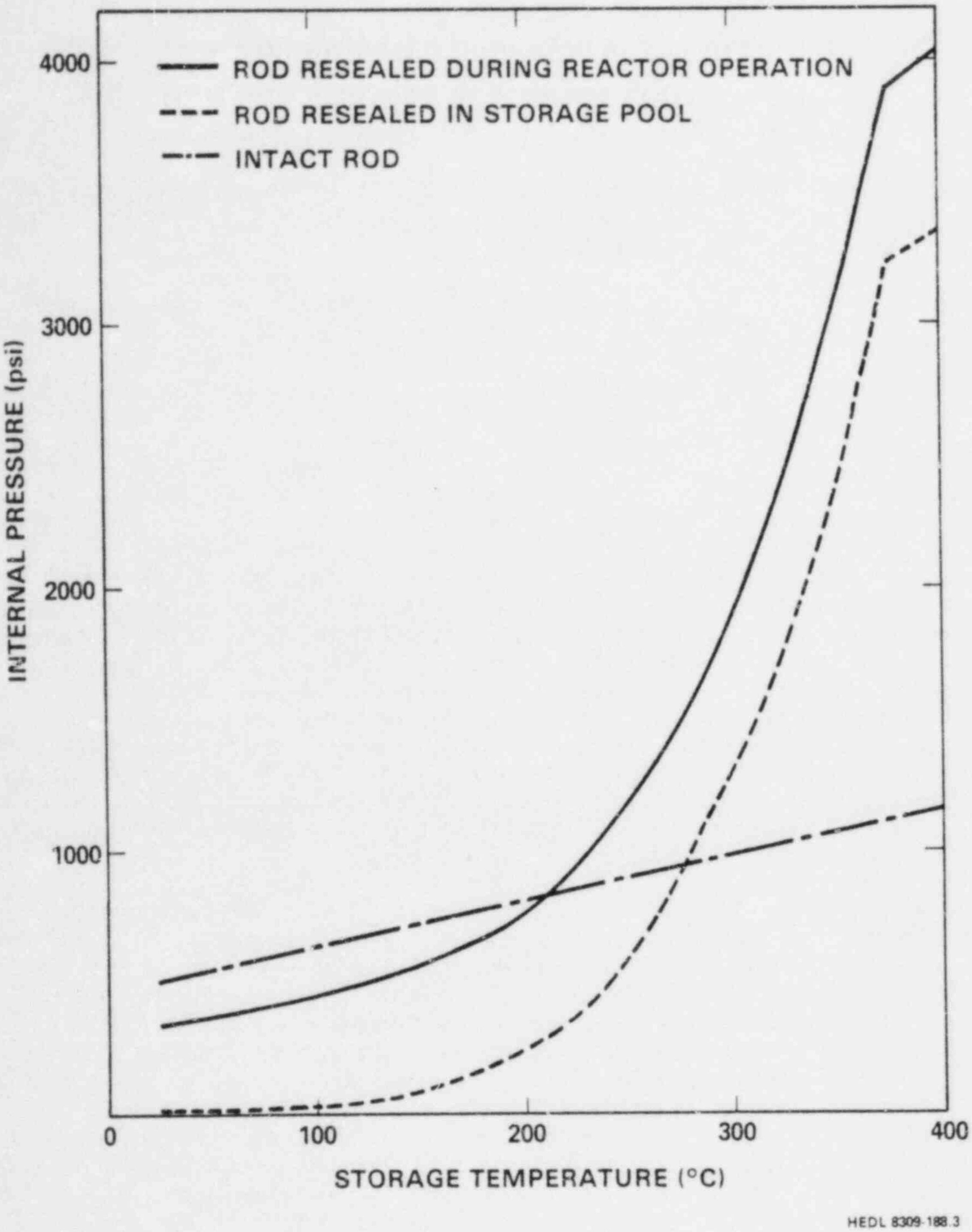

FIGURE 1. Internal Pressure vs Temperature for PWR Fuel Rods Containing Water.

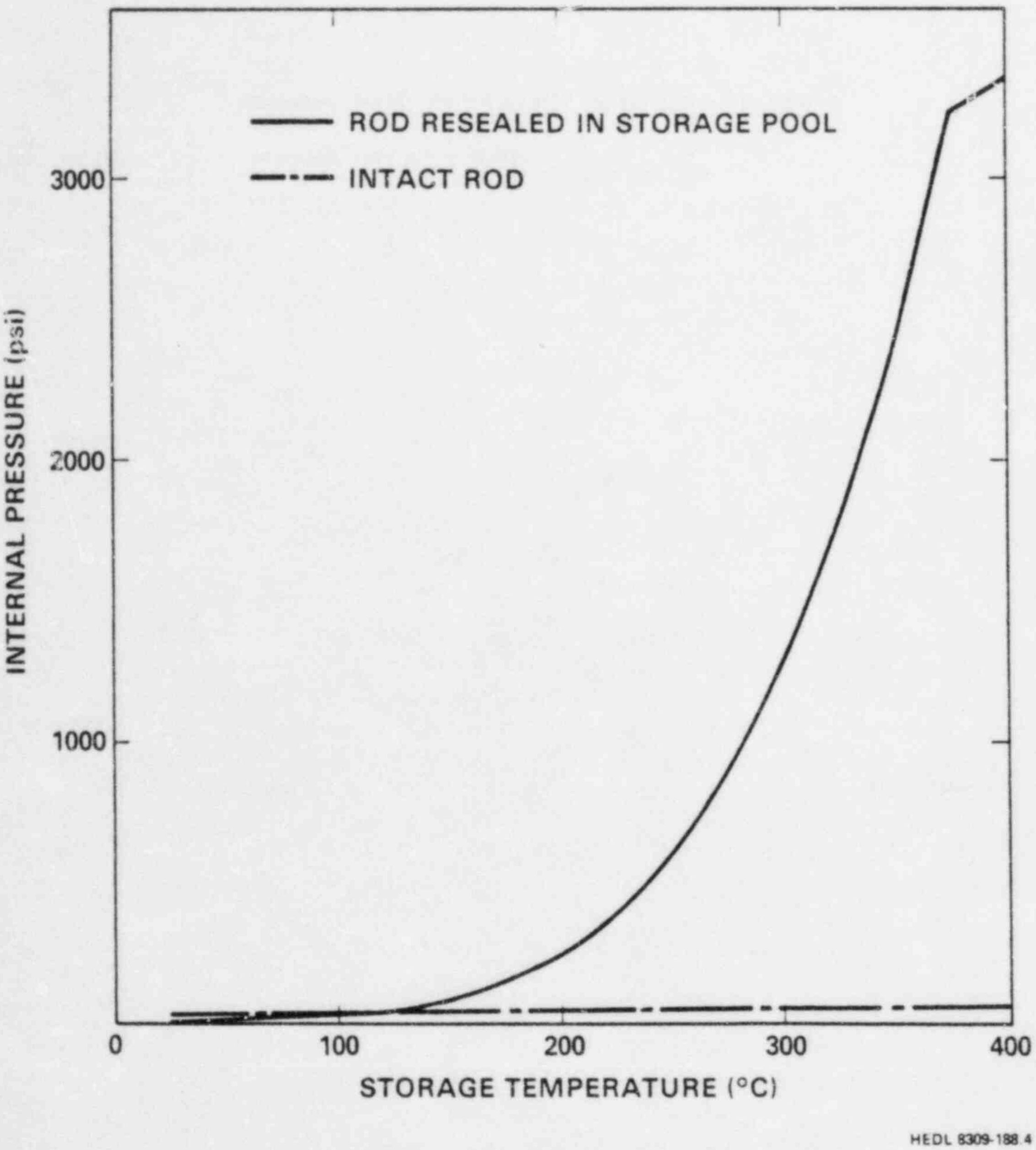

FIGURE 2. Internal Pressure vs Temperature for BWR Fuel Rods Containing Water.

for non-isothermal conditions by determining the damage fraction as a function of lifetime for a variety of starting rod temperatures and the temperature decay given in Appendix A.

The damage fraction (D) is given by the equation

$$D = \int_0^{t_f} \frac{dt(T)}{t_d(T)} \tag{1}$$

where t_f is the cladding lifetime, $t(T)$ is the time at a particular temperature and $t_d(T)$ is the isothermal lifetime. When D = 1, the cladding will have accumulated sufficient damage to breach. The isothermal lifetime (t_d) can be related to the cladding hoop stress by the use of the Larson-Miller parameter (P_{LM}). Thus,

$$P_{LM} = T(20 + \log t_d) \tag{2}$$

and

$$\log \sigma_H = a + bx + cx^2 + dx^3 \tag{3}$$

where T is the temperature in Rankine, t_d is the lifetime in hours, σ_H is the hoop stress in psi, and $x = P_{LM} \times 10^{-4}$.

In order that the lifetimes are directly comparable to those calculated by Blackburn et al.,[5] the coefficients (a = 7.1914, b = -3.39085, c = 1.65427 and d = -0.284513) for unirradiated cold-worked Zircaloy were used in Eq. 3. It should be noted, though, that radiation hardening, oxidation, and hydriding, all of which might occur in the cladding, can affect these coefficients. Their effects will be discussed in subsequent paragraphs.

The hoop stress, σ_H, on the cladding is given by

$$\sigma_H = \frac{r_o^2 + r_i^2}{r_o^2 - r_i^2} (P_i - P_o) - P_o \tag{4}$$

where:

r_o = fuel rod outer radius
r_i = fuel rod inner radius
P_i = fuel rod internal pressure
P_o = external pressure = canister pressure

For the present calculations, cladding dimensions that yield the maximum hoop stress were used and, again following Blackburn's[5] lead, a conservatism factor of 1.5 was included in the hoop stress. Equation (4) then reduces to

$$\sigma_H = 1.5[8.327(P_i - P_o) - P_o] \tag{5}$$

Using the maximum internal pressures at any given temperature from Figures 1 and 2 and assuming the canister pressure, P_o, is always 1 atm., hoop stresses were calculated using Eq. (5) and then used in Eqs. (1), (2) and (3) to determine the lifetime as a function of starting storage temperature. These rupture times are plotted against the storage (cladding) temperature in Figure 3.

Even though these calculations employ properties for unirradiated cladding, they nevertheless provide useful estimates of the storage behavior of resealed LWR fuel rods containing water, especially when compared to lifetime estimates for unbreached rods. They suggest that, for initial storage temperatures less than ca. 350°C, fuel rods containing water are not expected to breach by stress rupture.

Reactor service results in radiation hardening and reduced ductility of Zircaloy cladding. However, Blackburn et al.[5] suggest that, in spite of the reduced ductility, failure times may not be markedly affected, because radiation hardening can lower the creep rate. Einziger et al.[6] indicate that the use of stress-rupture properties for unirradiated Zircaloy is probably satisfactory if storage temperatures exceed ca. 370°C, where radiation hardening is rapidly annealed. By testing intact, irradiated PWR fuel rods at temperatures from 482°C to 571°C, the latter investigators also determined that calculated failure times were substantially exceeded because of the reduced stress caused by cladding creep. In the case of resealed fuel rods containing sufficient water, the internal pressure, and hence the stress, would be maintained in spite of cladding creep. If the amount of water were insufficient to maintain its equilibrium vapor pressure, then cladding creep would, of course, reduce the stress.

The presence of water in Zircaloy-clad fuel rods has resulted in failures due to hydriding of the Zircaloy.[1] Although the oxide film on the cladding inner surface is normally impermeable to H_2,[7] the film may not always be continuous and may be defected during thermal expansion or when cladding creep occurs. Breaks in the oxide film may be repaired by oxidation but breaches perhaps could also act as H_2 sinks. In any event, the potential exists for significant H_2 concentrations in the Zircaloy cladding.

Zircaloy cladding is normally manufactured with a texture which promotes circumferential precipitation of dissolved hydrogen during cooling, as when Zircaloy-clad fuel rods are cooled to 50 to 80°C upon removal from a reactor to pool storage. Fuel rod cladding typically contains from 40 to 100 ppm H_2. When the fuel is then transferred from pool storage to a dry storage canister, its temperature may approach 380°C, depending upon its age, packing density, and the heat rejection capability of the canister. In the unlikely event that a fuel rod containing water reseals and remains sealed

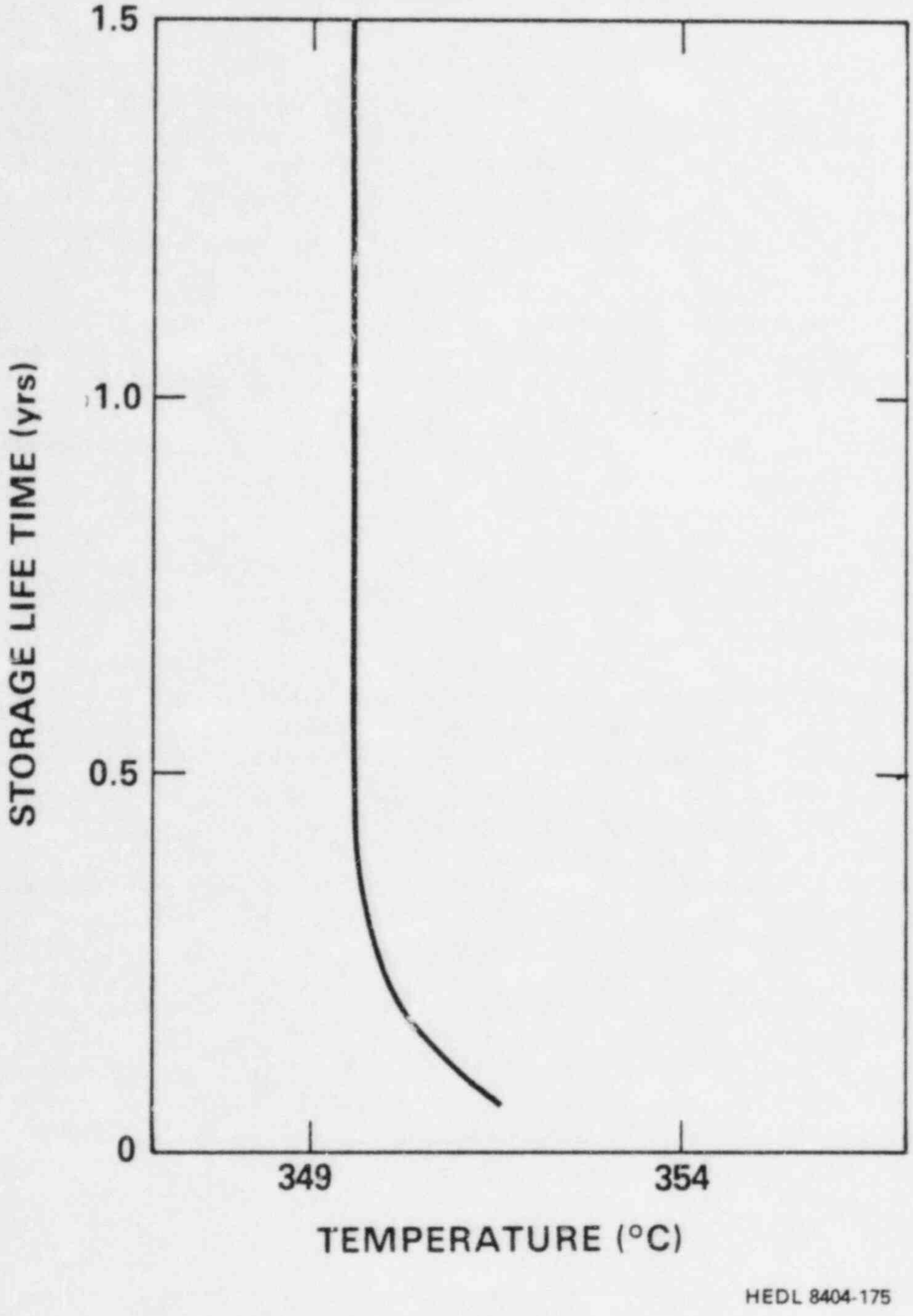

FIGURE 3. Time of Rupture vs Temperature for LWR Fuel Rods Containing Water.

as its temperature rises, precipitated hydrides will redissolve and the cladding will undergo a hoop stress resulting from the internal steam pressure (Figures 1 and 2). With the subsequent reduction in decay heat, the fuel rod temperature will again decrease and the dissolved H_2 reprecipitate. Now, however, precipitation will occur while the cladding is under stress, a far different situation than cooldown in-reactor, where the internal pressure of the fuel rod is balanced by the coolant pressure and little stress is exerted on the cladding.

The direction of hydride orientation will depend upon the magnitude of the hoop stress and texture of the cladding. While a stress threshold for hydride reorientation has not been defined, stresses in the range of 10,000 psi to 30,000 psi generally initiate reorientation,(6) although other factors including the fabrication history, hydrogen concentration, and the temperature and its rate of fall may influence the reorientation stress level. Resealed fuel rods containing water could exhibit hoop stresses in the range where hydride reorientation commences. If the hydrides are circumferentially oriented, they will exert little influence on the mechanical properties of the cladding, possibly even improving them somewhat. However, if hydrides in excess of 40 ppm reorient to a radial direction, perpendicular to the circumferential hoop stress, degradation of the cladding mechanical properties could follow, and thus lower life expectancy. Unfortunately, with our limited knowledge of the stress required for hydride reorientation under dry storage conditions, it is not possible to determine if this effect will occur. In any event, less than 0.01% of the fuel rods placed in storage are expected to be breached, and only a negligible fraction of these rods are expected to contain water, be resealed, and remain resealed during dry storage heat-up. Hydriding is not expected to have a significant effect on fuel rods in which the cladding defect remains open and offers internal pressure relief, the most probable condition of defected fuel rods.

B. CANISTER PRESSURIZATION

Apart from any other effects of cladding rupture on LWR fuel rods containing water, in the event of rupture, there will always be the release of water and possibly H_2 resulting from the Zircaloy-water reaction into the canister volume. For this reason, it is of interest to determine the magnitude of the maximum or bounding canister pressurization, which depends on several factors, including the canister design, the fuel, the number of fuel rods containing water, etc. The canister design selected for this calculation was that described by Eggers,(8) the REA 2023 PWR and BWR dry storage casks. The canisters will contain either 24 PWR fuel assemblies or 52 BWR fuel assemblies and their dimensions are consequently somewhat different. In the absence of any fuel assemblies, the free volume of the PWR canister amounts to 9.35×10^6 cm^3, whereas that for the BWR canister is 8.49×10^6 cm^3.

Nothing is said in Reference 8 regarding the presence of dividers in the canisters to maintain the positions of the fuel assemblies. Thus, for the present calculations of canister pressurization, four different canister volume conditions were employed: 1) a canister with no dividers; 2) a canister with dividers which take up half of the available space between the fuel assemblies; 3) a canister with dividers which take up all of the available space between the fuel assemblies; and 4) a canister as in 3) but with an added stabilizer with 10% void volume. Different numbers of fuel rods in the canisters were assumed to contain water. The free volume of those fuel rods containing water was assumed to be totally filled with water, such that a PWR rod contains $\sim$1.25 mol of H_2O and a BWR rod $\sim$4.25 mol of H_2O. Two temperatures, which were assumed constant throughout the canister volume, were used: 1) a temperature of 175°C for the case of an air-containing canister; and 2) a temperature of 377°C, which assures that all of the water released into the canister will exist as vapor. If H_2 is present, it will exert the same pressure at 377°C as the water it replaces. At 175°C, vaporization of all of the water is possible in all but two cases, and the presence of H_2 will increase the pressure slightly in those instances. The two cases involve the maximum number of fuel rods releasing their water into the minimum available free volume. In the PWR case, the calculated pressure only slightly exceeds (0.6 psi) the equilibrium water vapor pressure at 175°C. In the BWR case, the equilibrium water vapor pressure is exceeded by about 69 psi. Here, an equivalent quantity of H_2 would make up the pressure difference, giving a canister pressure of about 198 psi. In any event, as may be seen in Tables 2 and 3, not even in the most improbable cases, where $\sim$1% of the fuel rods contained in the canister are water-filled and release their water into the canister, does the canister pressure approach 300 psi.

The hoop stress on the canister resulting from this internal pressurization can be calculated by employing Eq. (4) and the dimensions of the REA 2023 storage casks.[8] For this calculation, only the canister proper was considered. The surrounding neutron shield was ignored. The hoop stresses corresponding to the highest pressures given in Table 2 amount to 874 psi for the PWR canister and 1322 psi for the BWR canister. Neither of these stresses would be expected to have an adverse effect on the storage canister.

C. THERMAL $Zr/UO_2/H_2O$ REACTIONS

The presence of water and/or steam in a resealed fuel rod, or in the storage canister after the rod breaches, can lead to its reaction with the Zircaloy cladding, the fuel, or the canister material. Potential reactions with the fuel rod components are of particular interest here, and reactions with the canister will not be considered.

The relative affinities of urania and Zircaloy for the oxygen atom in the water molecule are determined by their oxygen potentials or the free energy of formation of their oxides relative to water, as depicted in Figure 4. Zirconium oxide (ZrO_2) is much more stable with respect to reduction than water, and hence Zircaloy is readily oxidized by steam, yielding free hydrogen as a by-product, viz.

TABLE 2

CANISTER PRESSURIZATION AT 377°C

Canister Volume Conditions:	PWR	BWR
1. Canister with no dividers	7.28×10^6 cm^3	6.80×10^6 cm^3
2. Dividers use half available space	4.93×10^6 cm^3	4.90×10^6 cm^3
3. Dividers use all available space	2.59×10^6 cm^3	2.90×10^6 cm^3
4. Same as 3 plus stabilizer with 10% voids	2.59×10^5 cm^3	2.90×10^5 cm^3

Number of Fuel Rods Containing Water	Canister Pressure (psi)			
	1	2	3	4
1 PWR Rod	0.135	0.199	0.378	3.78
5 PWR Rods	0.673	0.994	1.89	18.9
50 PWR Rods	6.73	9.94	18.9	189
1 BWR Rod	0.490	0.680	1.15	11.5
3 BWR Rods	1.47	2.04	3.45	34.5
25 BWR Rods	12.25	17.0	28.7	287

TABLE 3

CANISTER PRESSURIZATION AT 175°C
(Canister Volume Conditions: See Table 2)

Number of Fuel Rods Containing Water	Canister Pressure (psi)			
	1	2	3	4
1 PWR Rod	0.093	0.137	0.261	2.61
5 PWR Rods	0.464	0.685	1.30	13.0
50 PWR Rods	4.64	6.85	13.0	129.4
1 BWR Rod	0.338	0.469	0.792	7.92
3 BWR Rods	1.01	1.41	2.38	23.8
25 BWR Rods	8.44	11.7	19.8	129.4

$$Zr + 2H_2O = ZrO_2 + 2H_2$$

Urania (UO_2), on the other hand, exhibits a very limited affinity for the oxygen in water and any oxidation that might occur would be insignificant, as indicated in Figure 4. Consequently, steam will react almost selectively with the Zircaloy at a rate determined by the temperature and the available surface area.

The oxidation of Zircaloy by steam results initially in the formation of a tightly adherent oxide film and proceeds by an approximately cubic rate law. After the oxide film has attained a thickness of from 2 μm to 3 μm, further oxidation is expected to follow linear kinetics.(9) At the completion of a normal reactor residence, the oxide film on Zircaloy cladding will always be in the post-transition range and subsequent oxidation is expected to follow the linear rate law.(10) Hillner compiled available rate data and arrived at the following equation giving the post-transition weight gain rate:(9)

$$\text{Rate } (mg/dm^2/day) = 1.12 \times 10^8 \exp(-12{,}529/T) \qquad (6)$$

For a PWR fuel rod, with its ~22.5 cm^3 void volume totally filled with water, there would be about 1.25 mol H_2O available to oxidize the cladding. Assuming total reaction over the internal surface of the rod, the average depth of reaction would be about 3 mil and H_2 equivalent to 5100 ppm would be generated. Approximately 10% of the hydrogen may find its way into the cladding. If the water had access to the canister interior and hence to the other fuel rods, the average reaction depth would be even more microscopic. The approximate rates at which oxidation would occur at various temperatures were calculated using Eq. (6) and are given in Table 4. Also included in Table 4 are the times required for complete reaction of the 1.25 mol H_2O at constant temperature. Considering that the oxidation depth is only 3 mil, or about 12% of the cladding thickness, when only the interior surface of a single fuel rod is oxidized by the maximum amount of water that could be present in a single rod, it would appear that cladding oxidation by steam is of minor consequence, particularly when one realizes that the oxidation rate will continually decrease with the rapidly falling temperatures. Under the circumstances, it is extremely unlikely that the reaction would attain completion, i.e., that 1.25 mol H_2O would totally react, at least by means of the thermally-activated oxidation reaction under consideration.

D. RADIOLYTIC $Zr/UO_2/H_2O$ REACTIONS

In the presence of the intense radiation field (~10^5 rad/hr) existing within the canister volume, water vapor will undergo a radiolytic reaction, the primary products of which are H_2 and H_2O_2.(11) As indicated in Figure 4, H_2O_2 is unstable with respect to both Zircaloy and urania and either material could therefore be oxidized by H_2O_2. These reactions apparently have not been studied, but would yield ZrO_2 and a higher oxide of uranium, respectively. The rate of either reaction would depend on the temperature, the

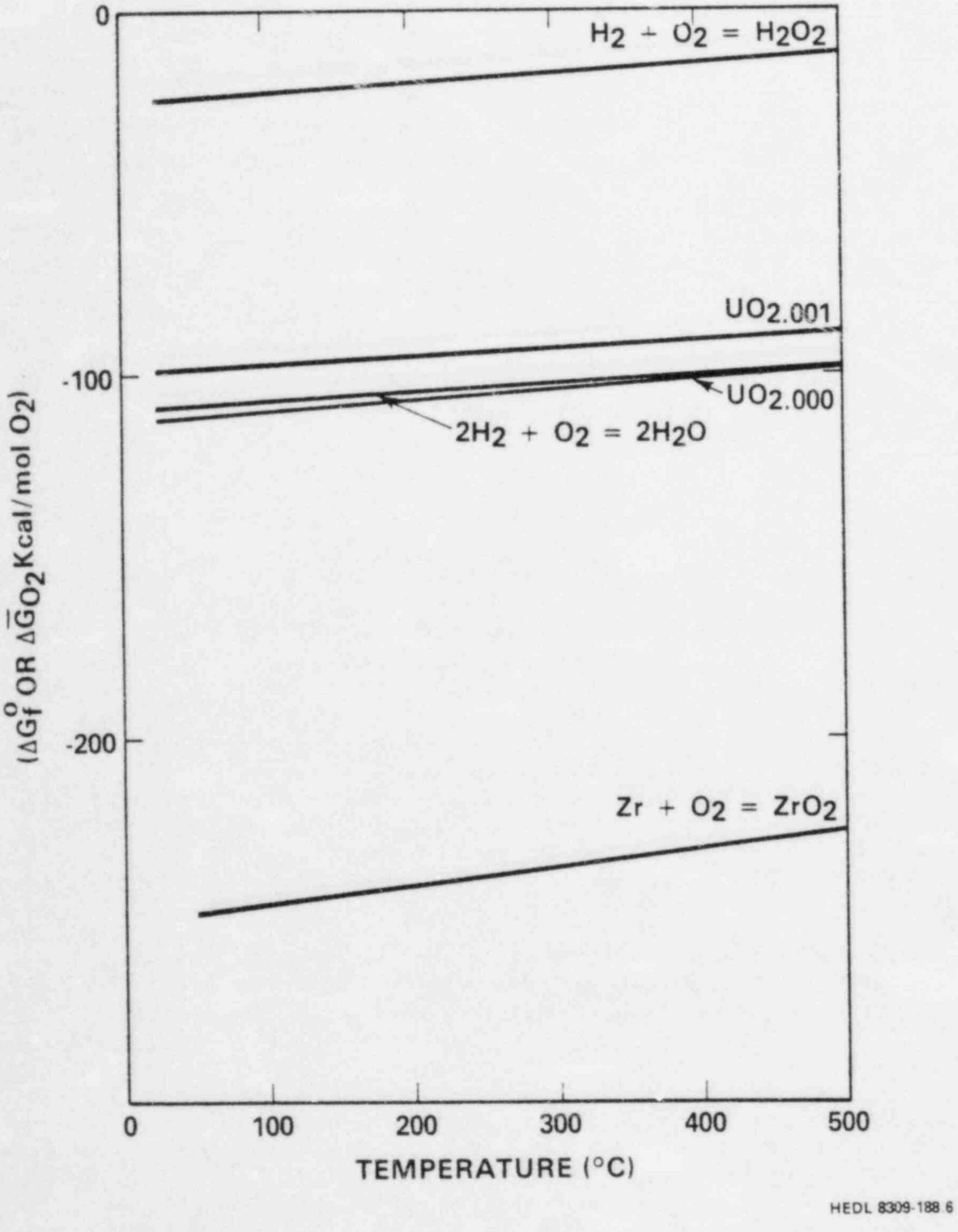

FIGURE 4. Free Energies of Formation and Oxygen Potentials Pertinent to the UO_2 - Zr - H_2O System.

TABLE 4

OXIDATION OF ZIRCALOY BY STEAM

Temperature (°C)	Weight Gain Rate* (mg/hr)	Time to Completion** (year)
175	3.85×10^{-5}	5.93×10^{4}
300	1.71×10^{-2}	134
350	9.90×10^{-2}	23.1
380	2.49×10^{-1}	9.2
400	4.41×10^{-1}	5.2

*For a Zircaloy surface area = 1.15×10^3 cm^2.
**At constant temperature. Total weight gain = 20 g.

surface area available, and the concentration of H_2O_2, the latter quantity depending upon the dose rate within the canister volume and the amount of steam present. Although the rates of the reactions of Zircaloy and UO_2 with H_2O_2 cannot be quantified, the reactions will probably occur and water present in the storage canister may eventually react either by the thermal or a radiolytic process.

Other mechanisms for the radiolytic oxidation of Zircaloy and urania by water are possible. Atoms and free radicals produced by the radiolysis of water could react directly with the fuel rod components without forming the H_2O_2 intermediate. A process of this nature would be essentially independent of temperature. While a radiolytic reaction between UO_2 and H_2O vapor is known to occur,(12) its mechanism and its rate under dry storage conditions are unknown.

Extensive experience with water-basin storage of spent fuel has not revealed a problem with fuel oxidation and defect enlargement by liquid water at radiation intensities not greatly different than those expected for dry storage. Apparently, under these conditions, the oxidation of UO_2 by liquid water by a radiolytic process is of little consequence.

As indicated previously, the internal surface of a PWR fuel rod could be oxidized to a depth of about 3 mil by 1.25 mol H_2O, whether the process were thermal or radiolytic. If this same quantity of water were able to react with UO_2 by means of a process involving the radiolytic formation of H_2O_2, the amount of UO_2 affected would depend upon the reaction product. If U_3O_8 were formed, about 506 g or 20% of the UO_2 in the fuel rod would be oxidized, increasing the volume of the affected fuel by about 36%. If the reaction product were UO_3, then about 338 g or 13% of the UO_2 in the fuel rod would be oxidized, increasing its volume by about 59%. A cladding defect would be significantly enlarged by the expansion occurring in either of these processes. Until additional information on the UO_2-H_2O_2 reaction becomes available, its effect on fuel rods containing water must remain unknown. However, it is highly improbable that the quantity of water present will even approach 1.25 mol, and it thus seems likely that fuel oxidation, should it occur, will not cause severe defect enlargement.

It should also be noted that both the thermal and radiolytic reactions of water with fuel rod components yield H_2 which, as was discussed in Section IV.A, can affect the mechanical properties of the Zircaloy cladding in an adverse manne , leading to embrittlement and possible handling problems.

V. CONCLUSIONS

The extent to which LWR fuel rods containing water could pressurize if defect resealing occurs depends upon several factors. The following conclusions regarding pressurization of LWR fuel rods were reached using conservative, "worst-case" assumptions.

1) Calculations indicate that the cladding of resealed fuel rods containing water will not fail in 100 years from internal pressurization at temperatures below 350°C. For intact fuel rods, the corresponding temperature for stress rupture failure by internal pressurization given by Blackburn(5) is 380°C.

2) More information is needed on possible hydriding during storage of the cladding on a resealed fuel rod containing water. Hydrogen formed by chemical or radiolytic reactions, absorbed by the cladding, and then precipitated possibly in a radial orientation could adversely affect the mechanical properties of the Zircaloy cladding.

3) Only minor pressurization of the storage canister by water introduced from breached fuel rods appears possible and should not pose a problem. However, canister designs and loadings can vary and each situation should be analyzed separately.

Whether fuel rods containing water reseal or not, the presence of water in the storage canister could lead to chemical reactions with the Zircaloy cladding and/or the urania fuel. Consideration of possible chemical effects has led to the following conclusions.

1) Because storage temperatures diminish with time, the thermal oxidation of Zircaloy cladding by steam occurs at a rapidly decreasing rate. The radiolytic reaction may proceed more rapidly, but in either case, the depth of reaction is of minor consequence for any quantity of water reasonably assumed to be present in the storage canister because of the substantial Zircaloy surface area available to the oxidant.

2) Theoretically, water entering a fuel rod could react with UO_2 by a radiolytic process to produce a lower density oxide, such as U_3O_8, resulting in cladding deformation and defect enlargement. Based on extensive experience with water-basin storage of spent fuel, it is unlikely that fuel oxidation by a purely radiolytic (temperature-insensitive) reaction involving liquid water will create significant problems. While the radiolytic oxidation of UO_2 by water vapor is known to occur, its rate cannot presently be quantified, but, for quantities of water likely to be present, the reaction would not cause severe defect enlargement.

Thus, analyses of the relevant data and experience offer reassurance that fuel and cladding integrity will be maintained should fuel containing water be placed in dry storage. Additional information is needed on cladding hydriding and the radiolytic oxidation of urania by water vapor.

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A P P E N D I X A

DRY STORAGE TEMPERATURE CONSIDERATIONS

APPENDIX A

DRY STORAGE TEMPERATURE CONSIDERATIONS

Based on stress-rupture considerations for PWR fuel assemblies, Blackburn et al.,[A1] recommended a maximum cladding temperature of 380°C for spent fuel storage in an inert atmosphere, with the qualification that the maximum temperature could be reduced if stress corrosion cracking were operative. Subsequent experimental measurements by Einziger et al.,[A2] using well-characterized PWR fuel rods, indicated that significant creep strain of the Zircaloy cladding reduced the internal pressure of the fuel rods. Consequently, a conservative maximum storage temperature of 400°C, again based on stress-rupture considerations, was indicated for a 1000-year cladding lifetime. It should be noted, however, that, in the presence of sufficient internal water, a fixed internal pressure would be maintained at a given temperature, even though the fuel rod dimensions were enlarged by creep. Nevertheless, for the purposes of this report, a maximum storage temperature of 400°C was assumed for spent fuel stored in an inert atmosphere. For storage in canisters containing an air atmosphere, the maximum allowable temperature assumed was 175°C.[A3] Both temperatures were employed in the analysis of canister pressurization.

Because the decay heat of the spent fuel continually decreases with time, once the immediate storage facility temperatures rise to essentially that of the fuel, the cladding temperature will decrease. If it is assumed that the temperature difference between the cladding and the surrounding heat sink is proportional to the decay heat,[A1] then the variation in the cladding temperature over the first 50 years of dry storage, commencing with an assumed maximum of 400°C for a five-year-old typical LWR fuel, would occur approximately as pictured in Figure A.1.

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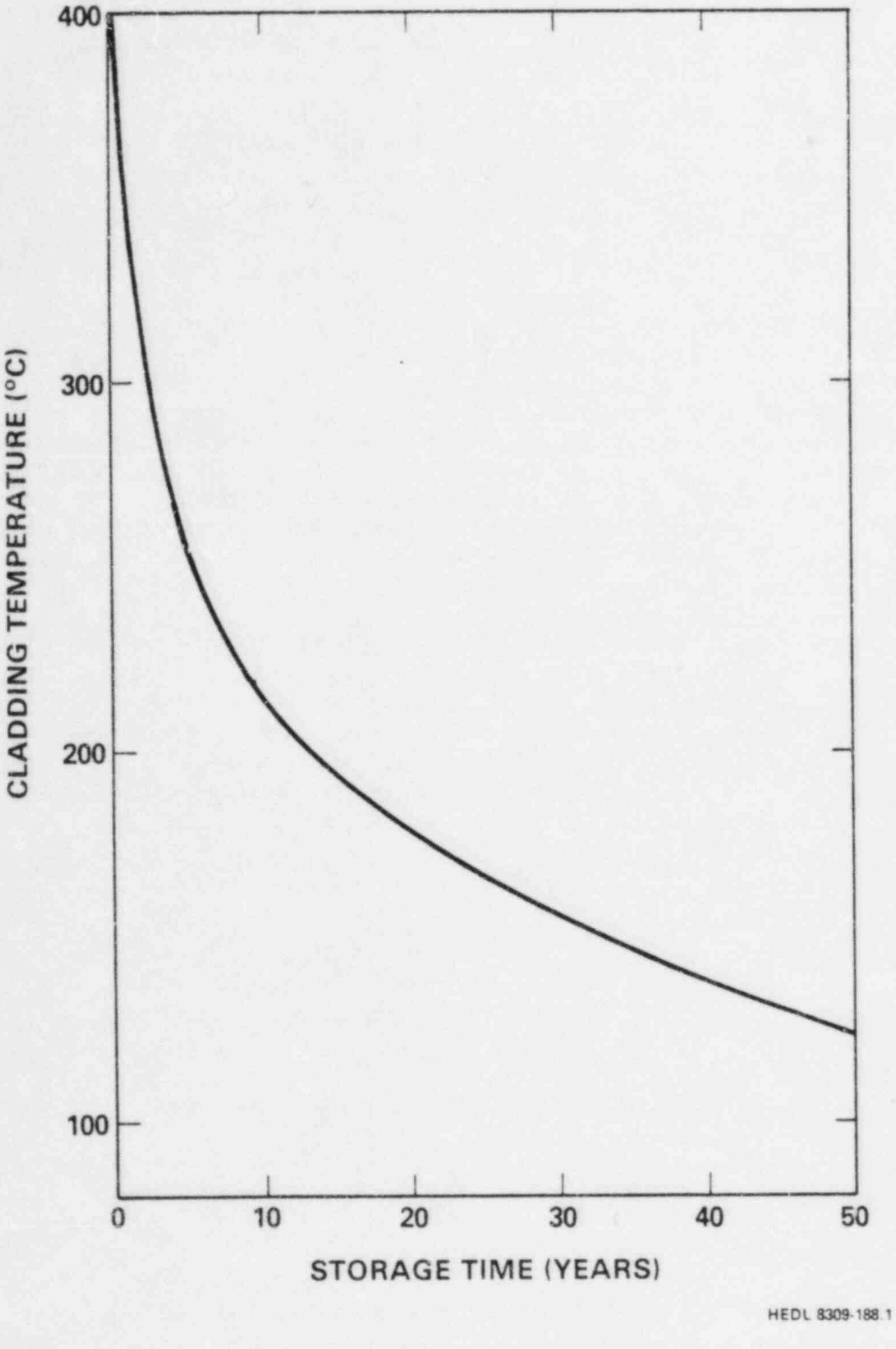

FIGURE A.1. Cladding Temperature vs Storage Times for Five-Year Old LWR Fuel.

A P P E N D I X B

FUEL HEATING RATES IN DRY STORAGE

APPENDIX B

FUEL HEATING RATES IN DRY STORAGE

A very conservative estimate of the heating rate can be obtained by dividing the decay heat of a fuel assembly by its heat capacity. For example, for a PWR 15 x 15 fuel assembly five years after discharge, the decay heat is estimated to be about 750 watts. The fuel assembly contains 518.4 kg of UO_2 and 133.3 kg of metallic components, about 82.5% Zircaloy-4.[B-1] Making the conservative assumption that all the metallic components are Zircaloy and using specific heats for UO_2 and Zircaloy from Figure B.1,[B2,B3] the heating rate at 200°C is

$$\frac{dT}{dt} = \frac{750 \times 860.42}{(518.4 \times 0.0660 + 133.3 \times 0.0732)10^3} = 14.7°C/hour$$

Implicit in this calculation is the assumption that the system is adiabatic, i.e., that all of the decay heat is absorbed by the fuel assembly itself and none is lost to the surroundings. This is obviously a "worst case" condition because some of the heat will be lost to the surroundings, particularly the massive canister enclosing the fuel assemblies. Consequently, the heating rates will actually be appreciably less than the values estimated in this manner. The calculation was repeated for fuel of different ages and at various temperatures within the range of interest. A range of temperatures was employed because the specific heats of urania and Zircaloy increase, and consequently, the heating rates decrease, with increasing temperature. The results of these calculations may be found in Table B.1. In spite of the very conservative assumptions employed, it is apparent that the heating rates are insufficient to cause a rapid pressure buildup.

TABLE B.1

CALCULATED HEATING RATES FOR A 15 x 15 PWR FUEL ASSEMBLY WITH 28,400 MWd/MT BURNUP

Decay Time (years)	Estimated Decay Heat (kW)	Heating Rate (°C/hr)		
		T = 25°C	T = 200°C	T = 400°C
2.5	2.00	44.9	39.1	36.6
5	0.75	16.8	14.7	13.7
10	0.50	11.2	9.8	9.2
50	0.20	4.5	3.9	3.7

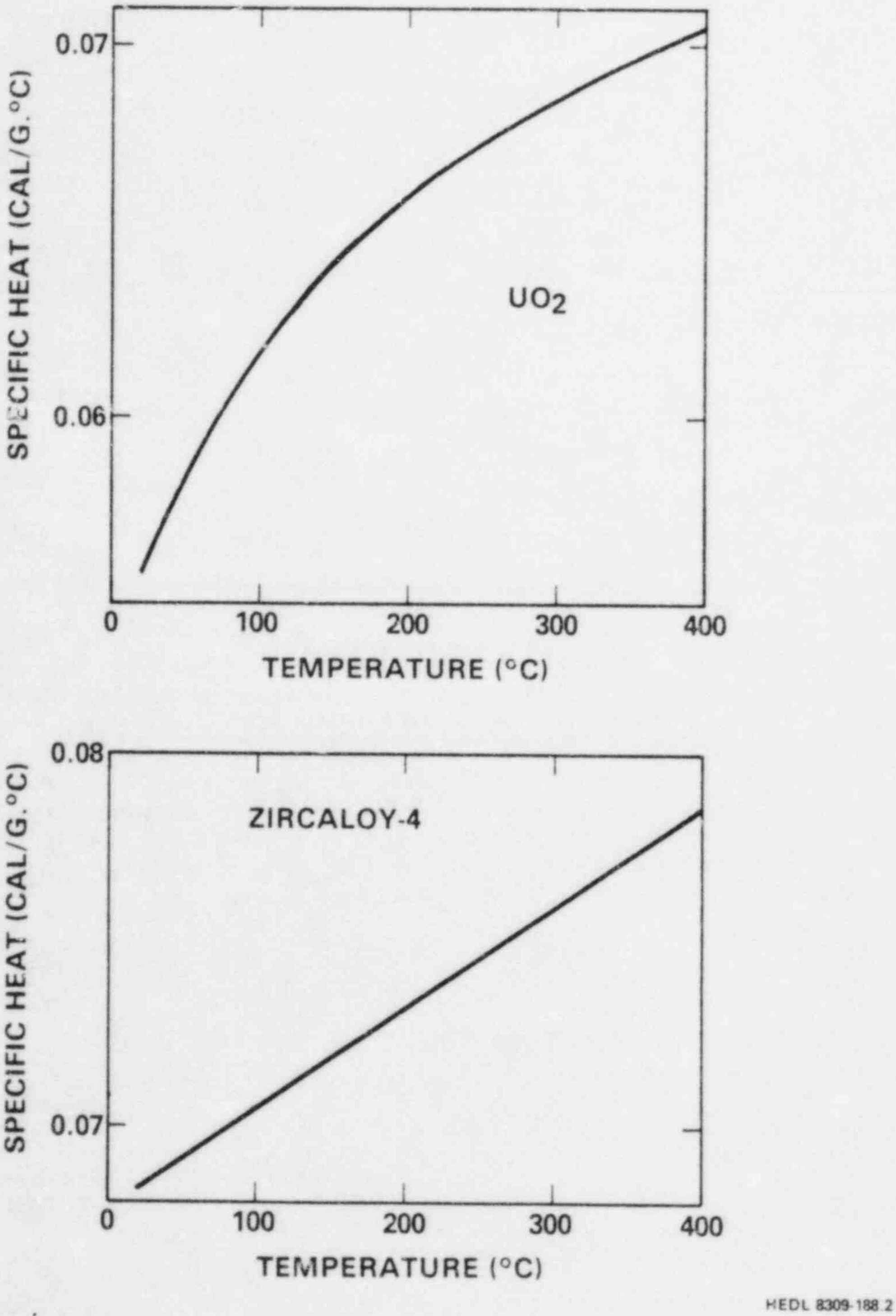

FIGURE B.1. Specific Heats of LWR Fuel Rod Components.

If one makes some reasonable assumptions about the nature of the storage canister and includes the canister in the adiabatic system, the heating rate calculated above, 14.7°C/hour, is reduced to only 4°C to 5°C/hour. Thus, the fuel rod temperature will increase slowly to the allowed maximum value, and the subsequent behavior of a resealed fuel rod will depend only on how well its cladding, and particularly the original defect, endure the internal pressures corresponding to the thermal history and to the maximum temperatures experienced during dry storage.

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The performance under dry storage conditions of LWR fuel rods containing water was analyzed to determine if radionuclide containment by the fuel rod cladding would be adversely affected. Fuel rod and storage canister pressurization as well as cladding and fuel oxidation were examined using "worst case" conditions. The results of this study are presented.

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