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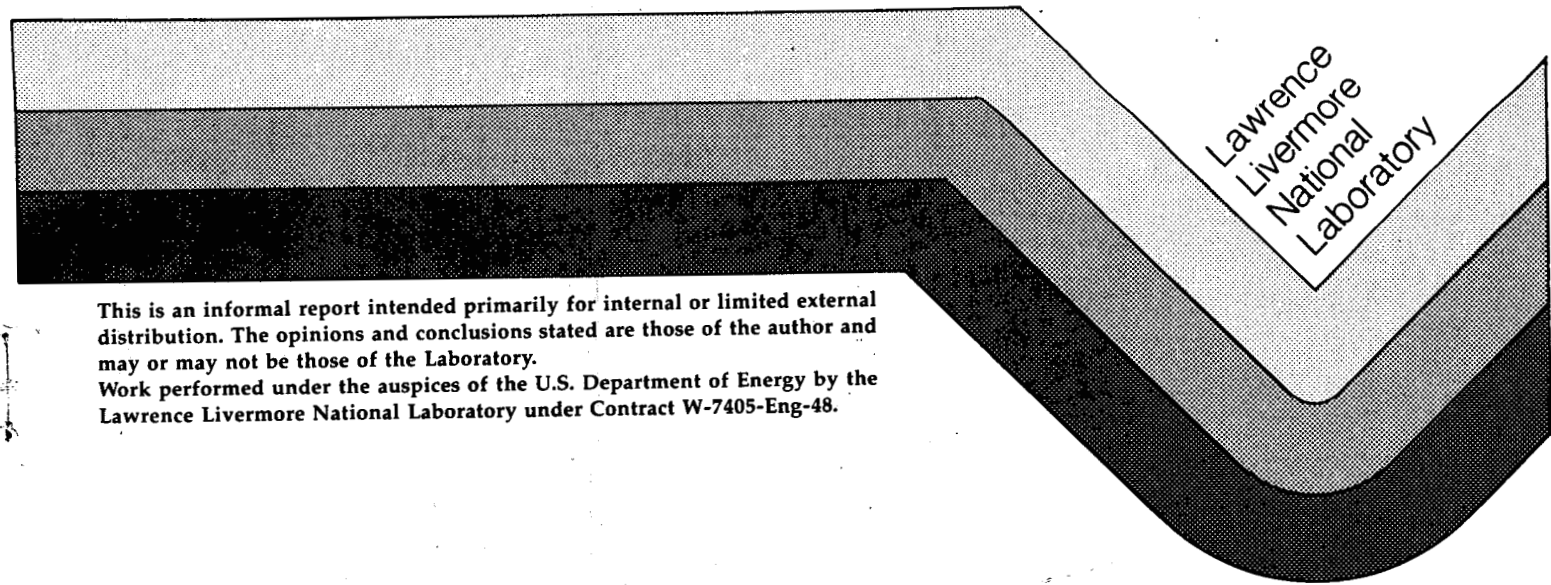
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Potential Corrosion and Degradation Mechanisms
of Zircaloy Cladding on Spent Nuclear Fuel
in a Tuff Repository

A. J. Rothman

September 1984



Lawrence
Livermore
National
Laboratory

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Potential Corrosion and Degradation Mechanisms
of Zircaloy Cladding on Spent Nuclear Fuel
in a Tuff Repository

A. J. Rothman

ABSTRACT

A literature review and analysis were made of corrosion and degradation processes applicable to Zircaloy cladding on spent nuclear fuel in a tuff repository. In particular, lifetime sought for the Zircaloy is 10,000 years. Among the potential failure mechanisms examined were: oxidation by steam, air, and water, including the effects of ions whose presence is anticipated in the water; mechanical overload; stress (creep) rupture; stress-corrosion cracking (SCC); and delayed failure due to hydride cracking.

The conclusion is that failure due to oxidation is not credible, although a few experiments are suggested to confirm the effect of aqueous fluoride on the Zircaloy cladding. Mechanical overload is not a problem, and failure from stress-rupture does not appear likely based on a modified Larson-Miller analysis. Analysis shows that delayed hydride cracking is not anticipated for the bulk of spent fuel pins. However, for a minority of pins under high stress, there is some uncertainty in the analysis as a result of: (1) uncertainty about crack depths in spent fuel claddings and (2) the effect of slow cooling on the formation of radially oriented hydride precipitates. Experimental resolution is called for. Finally, insufficient information is currently available on stress-corrosion cracking. While evidence is presented that SCC failure is not likely to occur, it is difficult to demonstrate this conclusively because the process is not clearly understood and data are limited. Further experimental work on SCC susceptibility is especially needed.

INTRODUCTION

Lawrence Livermore National Laboratory (LLNL) is responsible for high-level nuclear waste package development as part of the Nevada Nuclear Waste Storage Investigations (NNWSI) Project. This project is part of the Department of Energy's Civilian Radioactive Waste Management (CRWM) Program, and is investigating the suitability of tuffaceous rocks at Yucca Mountain, Nevada Test Site (NTS), for high-level radioactive waste disposal. The waste package task at LLNL is developing multibarriered packages for safe, permanent disposal in a repository such as the one being considered at Yucca Mountain. This report summarizes the long-term potential for Zircaloy cladding of spent fuel to provide an additional barrier to radionuclide release.

Regulatory requirements placed on repositories for high-level nuclear waste specify that no more than one part in 10^5 of the 1000-year inventory of radionuclides may be released from the engineered barrier each year for a period of 10,000 years. For unprocessed spent fuel, one way of potentially meeting this criterion is to use the Zircaloy clad already present on the spent fuel. Zircaloy is known to be very corrosion-resistant. If almost all the claddings can be shown to maintain their integrity during most of 10,000 years, then the specification may be met, even allowing for the few that "leak."

In this report, we will concern ourselves only with determining whether the vast majority (approaching 99%) of claddings will not fail during 10,000 years. To accomplish this, we will consider the possible failure modes and mechanisms, and evaluate each one in turn. Work will be done elsewhere to determine the effect of failed cladding on the rate of escape of radionuclides from the engineered barrier.

Among the researchers who have considered various potential failure modes in wet and dry storage for times up to 100 years (so-called extended storage) are Johnson and Gilbert (1983), Johnson et al. (1983), Johnson (1977), Blackburn et al. (1978), and Zima (1979). Johnson and Gilbert (1983) included a useful summary table of degradation modes.

BASELINES AND ASSUMPTIONS

For the purposes of this report, the following is assumed:

o Spent fuel rods from pressurized water reactors (PWRs) and boiling water reactors (BWRs) consist of UO_2 pellets clad with Zircaloy-2 or Zircaloy-4 (Table 1). Diameters and cladding thicknesses are detailed elsewhere (Woodley, 1983; Johnson et al., 1983). For the present purposes, the following representative dimensions are assumed:

	Cladding thickness (μm)	Fuel Rod O.D. (mm)	Nominal diametral gap (μm)
BWR	800 - 900	12 - 14	230 - 300*
PWR	600 - 700	10 - 11	170 - 200*

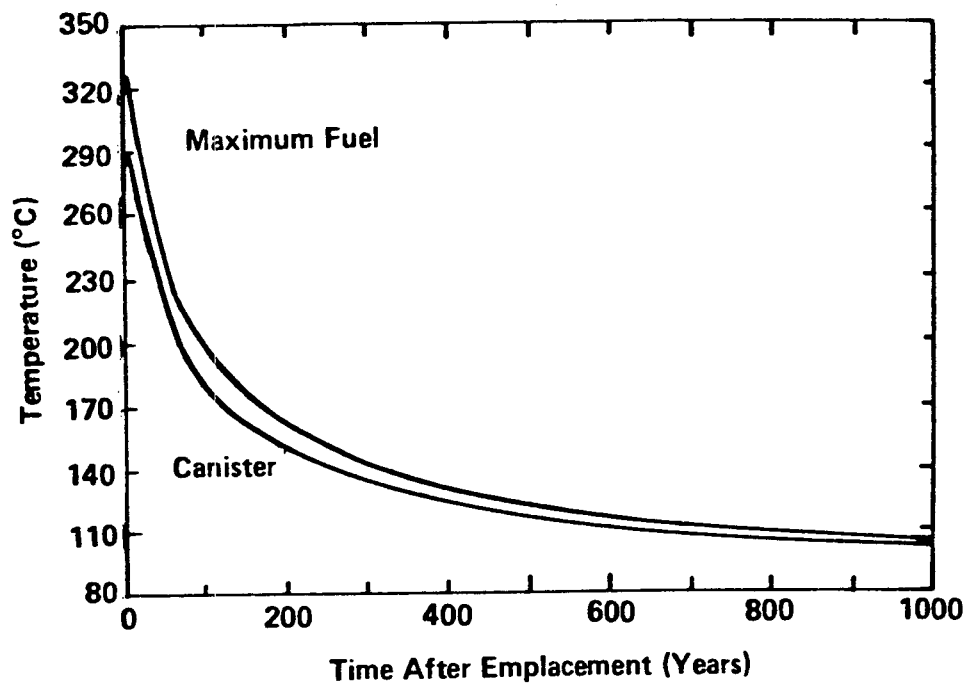
Based on the current interpretation of the literature, the corrosion behavior of Zircaloy-2 and -4 is treated identically. (Zircaloy-4 picks up a smaller fraction of hydrogen during corrosion than does Zircaloy-2, but both have similar corrosion behavior).

o As a typical design case, assume that cladding temperature varies with time as shown in Figure 1 (Hockman, 1984). This plot is based on horizontal emplacement in a repository at 44 kW/acre of a canister containing 10-year-old PWR spent fuel (3.3 kW) with 12 internal fins. Both PWR and BWR canisters will be assumed to have the same thermal history for simplicity.

o Water composition as a function of time as shown in Table 2 (Oversby, 1984).

o After penetration of the canister (assumed at 1000 years, with alternative consideration of 300 years penetration), the surrounding atmosphere will be primarily water vapor and air at 1 atm total pressure. Below 100°C, some liquid water will also be present, in unknown quantities. Water flow rates, however, will be extremely low (virtually stagnant conditions).

*After irradiation, gap may be 25 μm or less.



10 year old waste
44 kW/ acre
3.3 kW/ package
Canister diameter 0.50m
Package length 4.5m
Borehole spacing 52m

Figure 1. Peak Fuel and Canister Temperatures vs Time (44 kW/acre).

o Maximum burnup of spent fuel is $\sim 38,000$ MWd/MTU. Average burnup is $\sim 23,000$ MWd/MTU (Woodley, 1983).

TABLE 1. Composition of Zircaloys^a

Alloying addition (wt %)	Zircaloy 2	Nickel-free Zircaloy-2	Zircaloy 4
Sn	1.50(1.20-1.70) ^b	1.50(1.20-1.70)	1.50(1.20-1.70)
Fe	0.12(0.07-0.20)	0.15(0.12-0.18)	0.20(0.18-0.24)
Cr	0.10(0.05-0.15)	0.10(0.05-0.15)	0.10(0.07-0.13)
Ni	0.05(0.03-0.08)	< 0.007	< 0.007
Total Fe, Cr, Ni	(0.18-0.38)	---	> 0.28
O (ppm)	1000-1400	1000-1400	1000-1400

Element	Maximum impurity levels													
	Al	B	Cd	C	Co	Cu	Hf	H	Mn	N	Si	Ti	W	U
ppm	75	0.5	0.5	270	20	50	200	25	50	80	200	50	100	3.5

^a Adapted from B. Cox, 1976

^b Numbers in parentheses indicate the range of values

It would, of course, be extremely difficult to prove a 10,000-year life of the Zircaloy claddings for effects that are undetectable or almost undetectable at repository temperatures in short-term tests, even 20-year tests. Therefore, the plan is to test at higher temperatures, higher ionic concentrations, etc., to determine whether these show negligible corrosion effects in the times studied, and extrapolate the results to long times under much less rigorous conditions. Of course, it must be demonstrated that mechanisms do not change over the range of testing and extrapolation.

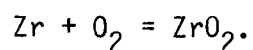
TABLE 2. Experimental Data Indicating Water Chemistry for a
Repository in the Topopah Spring Tuff
(Concentrations in ppm)

Item	Present Comp. J-13, 25°C	Expected High-Temperature Composition Based on J-13 Reacted with Topopah Spring			
		Est			
		50°C	150°C (expt)	90°C (expt)	100°C (interpolated)
Si	27	30	80	40	45
Na	44	38	40	40	40
K	5	7	9	8	8
B	0.12	0.1	0.1	0.12	0.1
Ca	12.5	10	3	8	7
Mg	1.9	1.0	0.1	0.1	0.1
Fe	0.006	.02	0.02	0.01	0.015
Al	0.012	0.30	1.5	0.5	0.6
F	2.3	2.3	2	2	2
Cl	6.8	7	7	7	7
NO ₃	9.2	9	9	10	10
SO ₄	18.8	19	19	19	19
HCO ₃ +CO ₃	134	125	110	115	115
pH	7.6	8	9	8.5	8.5

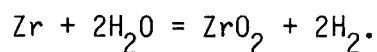
OXIDATION OF ZIRCALOY

General

The oxidation of Zircaloy in air is simply:



In water the reaction is:



Part of the hydrogen may dissolve in and react with the metal, resulting in hydriding of the Zircaloy (discussed later).

Typically, Zircaloy oxidation (in high temperature water, steam, or air) occurs in two stages (Figure 2). In the first stage, the kinetics are "cubic," i.e., with the cube of oxide thickness (weight gain) proportional to time. At some critical thickness, which is a function of temperature and probably other variables, transition to linear growth with time occurs. Thus, the oxide coating becomes less protective. The coating thickness at transition varies, but not markedly (typically 1 to 2 μm thick). This is true for test temperatures of 280°C and above. Below that temperature, times to reach post-transition kinetics would be longer than experiments so far carried out.

Figure 2 and the discussion above are an idealization, although it represents average or macro-behavior of the oxidation process. Bryner (1979) has shown that in high temperature water (360°C), first stage corrosion proceeds by repeated cycles of cube-root kinetics and linear kinetics, corresponding to alternating, dense, columnar-grained layers and narrow, porous layers parallel to the metal. During each cycle, a new protective layer grows at the metal-oxide interface. At a critical thickness, this base layer loses its protectiveness and reverts to the initial rapid rate, beginning a new cycle. The porous layers define the location of the interface at the beginning of each cycle. Since these cycles are out of phase over the metal surface areas, the average corrosion rate still appears as simple cubic kinetics. If the ZrO_2 film were fully intact and unchanged in its behavior toward oxygen diffusion, kinetics would be parabolic. Finally, transition occurs, the oxide film is no longer protective, and linear kinetics follow.

To explain this behavior Bryner postulates that initially oxygen diffuses through the oxide film through the easy paths of grain boundaries and sub-grain boundaries in the ZrO_2 film, giving weight gains proportional to the square root of time (normal solid-state diffusion behavior). (I believe that some porosity or "open" grain boundary areas may also contribute to or even dominate this rapid diffusion.) As the film grows, the compressive stress normal to the diffusion direction increases (since the density of

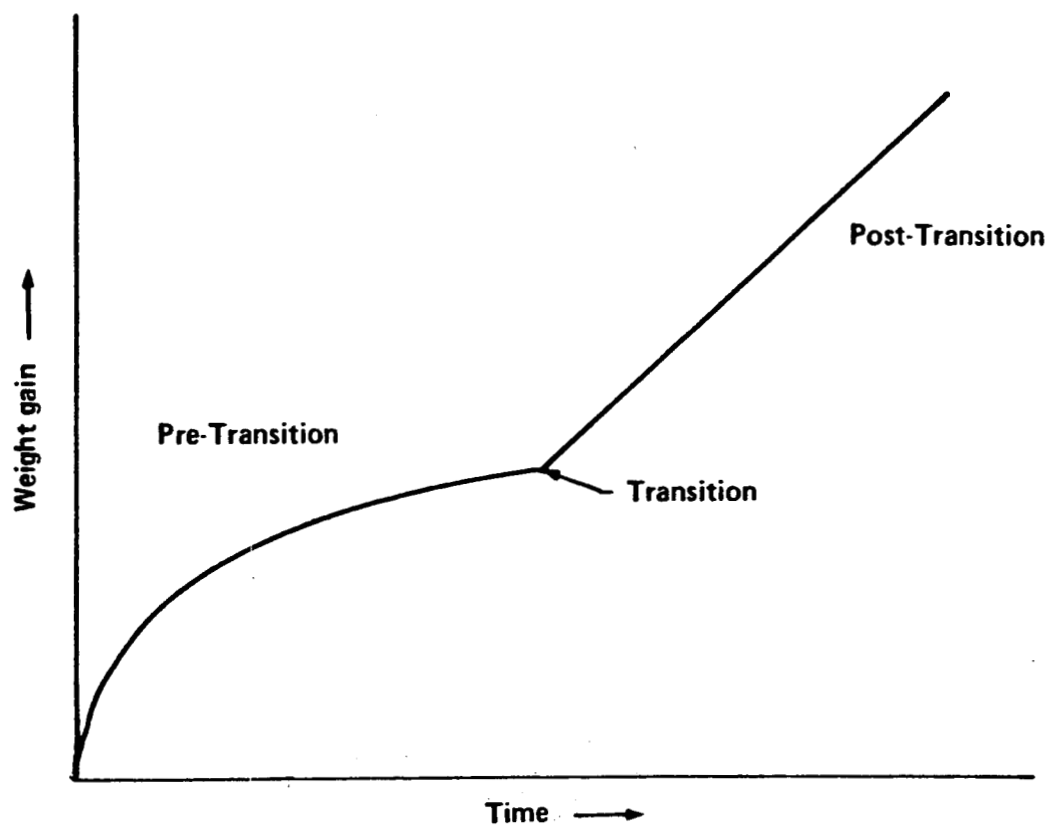


Figure 2. Oxidation of Zircaloy

ZrO₂ is less than that of Zr). In turn the corrosion rate decreases as diffusion paths are constricted by the stress. At some critical value, buckling is assumed to occur, relieving the stress and allowing more rapid diffusion again and a new cycle. Finally, at transition to linear kinetics, the assumption is that openings through the oxide film and at the interface are so large that the film is no longer able to serve as a protective layer. However, details of all stages of oxidation-corrosion have not yet been fully confirmed by experiments.

Other observations are that the oxide film gives diffraction colors for the first few days (at 350°C), becomes black in 10 to 20 days, and finally appears tan, white, or gray well beyond the transition point. In fact, the diffraction color has been used to determine the extent of oxidation (see below). This description implies uniform attack. Under some circumstances (high pressure steam at 475°C and above) or in BWRs, isolated, thick, white oxide lenses ("nodules") appear on Zircaloy fuel rods.

A general comparison by Cox (1976) shows that at the same temperature, pretransition oxidation curves for Zircalloys are virtually identical in a number of environments, including water, a fused salt mixture, and in air for Zircaloy coated with a thin layer of iron oxide (Cox, 1976). These data are for temperatures of 350°C. Few comparative data are available below that temperature.

Both steam and water oxidation appear to fit the same equation in the post-transition region. In addition, Suzuki and Kawasaki (1983) report that the Zircaloy reaction with air fits steam and water post-transition oxidation equations.

Oxidation Calculations

A number of investigators have correlated the oxidation rates of the Zircalloys. Typically, the form is

$$\Delta W^n \text{ (mg/dm}^2\text{)} = Kt \cdot \exp (-E/RT),$$

where ΔW = weight gain/unit surface area,
 K = a constant,
 t = time,
 E = activation energy,
 R = gas constant,
 T = temperature, and
 n = exponent depending on stage of corrosion
 ($n = 3$ pre-transition; $n = 1$ post-transition).

Equations for autoclave studies (exreactor) in degassed, deionized water have been proposed by Hillner (1976), Van der Linde (1965), Dyce (1964), Dalgaard (1976), and Peters (1982), and applied by Garzarolli, et al. (1980). For the most part, these equations included data from about 300 to 400°C. Kass (1969) used the lower temperature corrosion data (to 232°C) in his correlation, which is the same as Hillner's correlation. However, those data apply only to the pretransition regime. Stehle et al. (1975) calculated corrosion under heat flux conditions in a reactor.

These equations are summarized in Garzarolli et al. (1980), and generally include pretransition weight change, post-transition weight change, and time to transition. For the Hillner equations, including Kass's lower temperature data,

$$\begin{aligned} \text{pre-transition } \Delta W^3 &= 6.36 \cdot 10^{11} \exp[-13,636/T] \cdot t, \\ \text{post-transition } \Delta W &= \Delta W_t + 1.12 \cdot 10^8 \exp[-12,529/T] \cdot (t - t_t) \\ \Delta W_t &= 75.3 \exp[-556/T] \\ t_t &= 6.73 \cdot 10^{-7} \exp[11975/T], \end{aligned}$$

where ΔW = weight gain, mg/dm^2 ,
 T = temperature, K,
 t = exposure time, days,
 ΔW_t = weight gain at transition, mg/dm^2 , and
 t_t = time to transition, days.

It is generally recognized that Zircaloy cladding oxidation is in the post-transition stage at the end of its life in a reactor. Therefore we will use only post-transition equations in our calculations.

It should also be noted that experimental tests in air at temperatures of 350°C and above (Suzuki and Kawasaki, 1983) gave post-transition results compatible with those of water and steam using the equations of Van der Linde (1965).

The primary calculation is for the anticipated base case of temperature vs time (Fig. 1). We assume that the canister is penetrated at 1000 years, at which time the fuel temperature is 105°C. The temperature-time curve is divided into arbitrary increments, the oxidation depth is computed for the highest temperature in each increment, and then these depths are added to get the overall depth of oxidation in 10,000 years. The results are somewhat more conservative than integrating the equations over temperature and time. The calculated depth is only 0.006 μm , obviously negligible when compared to the values of cladding thickness.

If, instead, the canister is assumed to be penetrated after 300 years, the calculated peak cladding temperature exposed to water vapor and air is 143°C, and the corresponding calculated oxidation depth is still only 0.03 μm .

A second set of calculations was done for another design configuration (Fig. 3) but one that has an areal power loading that is probably unrealistically high, viz., 82 kW/acre. This case gives a peak temperature of 180°C at 1000 years. The corresponding corrosion depth is 0.5 μm . Canister penetration at 300 years for this areal power loading would give a cladding temperature of 232°C and a calculated corrosion depth of only 10 μm at 10,000 years, still a comfortably low value.

Finally, we have calculated oxidation depths at the 1000-year penetration, making the extremely conservative assumption of a constant temperature of 180°C for 10,000 years, chiefly to obtain comparative results from the equations of each of the investigators. All the results, except those using

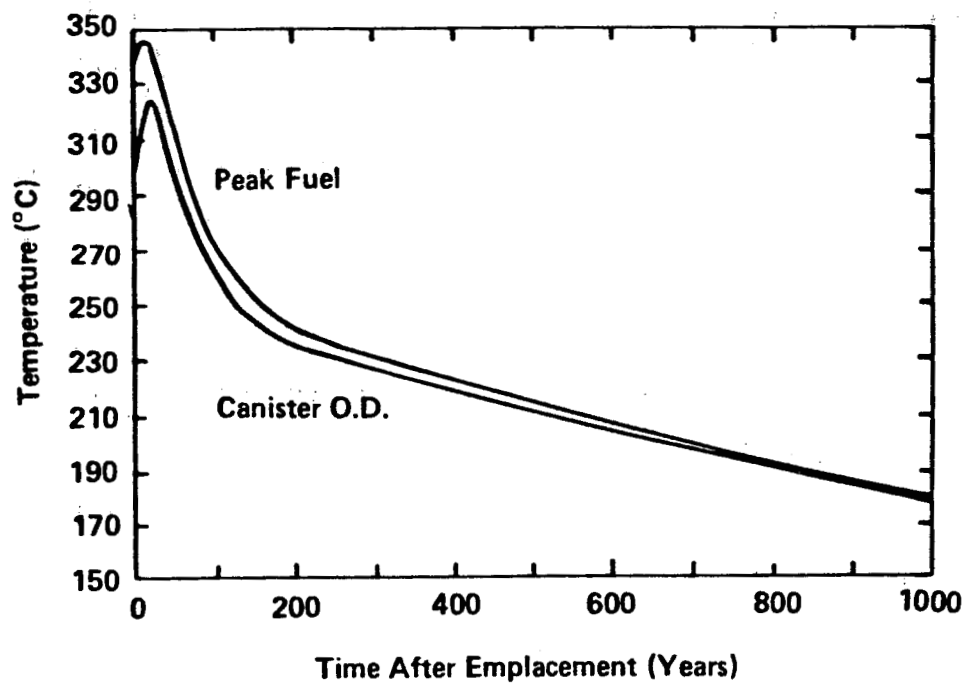
Dalgaard's equations, give smaller oxidation depths than those of Hillner (see Table 3). Also all of them give depths that are a small fraction of the cladding thickness, even for this extreme case of 180°C for 10,000 years.

TABLE 3. Calculated Depth of Oxidation Assuming
Constant Temperature (180°C) for 10,000 years

Reference	Wt gain (mg/dm ²)	Depth of oxidized Zircaloy (μm) ^a
Hillner (1976)	398	17
Dyce (1964)	88	4
Van der Linde (1965)	132	6
Dalgaard (1976)	1200	53
Stehle (1975)[in-reactor]	200	9
Peters (1982)	329	14

^a Values rounded.

At least some confirmation of these extrapolations may be found in work reported by Johnson (1977). He reports work done on exposure of Zircaloy-2 pressure tubes in a pool at ~90°C for 4 and 1.75 years, respectively, in treated Columbia River water. Because the rate of oxidation is so low, it is difficult to measure. Consequently, the investigators estimated oxide film thicknesses by color matching them with anodized films instead of measuring weight changes. Even these measurements are subject to appreciable errors. Columbia River water does, of course, contain dissolved oxygen. The analysis of this water for major ions is shown in Table 4. The estimated oxidation depths calculated using pretransition equations (since calculations show that the times involved are well within the pretransition, or cubic, regime) are 0.0155 and 0.012 μm as compared with the experimental measurements of 0.015 and 0.009 μm at 90°C for the 4-year and 1.75-year exposures, respectively.



10 year old waste
82 kW/ acre
3.05 kW/package
Canister diameter 0.50m
Package Length 4.5m
Borehole Spacing 24m

Figure 3. Peak Fuel and Canister Temperatures vs Time (82 kW/acre)
(Horizontally Emplaced PWR Spent Fuel with
12 Internal Fins)

These close agreements are undoubtedly fortuitous, but the comparisons help to justify the use of the pretransition equations extrapolated to 90°C, and suggest that extrapolation to temperatures near 90°C using the more conservative linear rate law (post-transition equations) is reasonable.

TABLE 4. Composition of Waters at 90°C

	<u>Tuff^a</u>	<u>Columbia River^b</u>
pH	8.5	7.9
HCO ₃ +CO ₃	115	40
Si	40	2
Na	40	3
SO ₄	19	15
NO ₃	10	0.6
Ca	8	15
K	8	0.7
Cl	7	2
F	2	0.15
Mg	0.1	4

Other components < 1 ppm

^a From Table 2

^b Private communication from L. Didicker and T. R. Garland to E. A. Jenne/C.E. Cowan. Pacific Northwest Laboratory, November 12, 1982 (average of two sets of results).

Oxidation depths measured in a comprehensive study (Garzarolli et al., 1982) of more than 700 PWR spent fuel rods were less than 60 µm even for burnups as high as 50 GWd/ton. Values ranged from below 10 to 56 µm, and more than 90% of the rods had oxide thicknesses below 50 µm (2.0 mils). The BWR rods sometimes show nonuniform nodules up to 120 µm thick (Johnson et al., 1983).

Effect of Oxygen

Most of the above-mentioned oxidation studies used de-aerated water, except Suzuki and Kawasaki (1983), who used air. The question arises as to

whether water containing dissolved oxygen shows different corrosion rates than air-free water.

In nuclear reactors, oxygen has been shown to accelerate oxidation of Zircaloy (Bradhurst et al., 1973). For this reason hydrogen is typically added to the circulating PWR coolant water. Out-of-reactor studies have shown conflicting results; some investigators found enhancement of oxidation in the presence of air, others found no enhancement (Shirvington, et al., 1972). Shirvington, who maintained in a letter to J. Nucl. Mater. (1972) that the presence of air increased the oxidation of Zircaloy, later rescinded this conclusion and settled the issue by demonstrating that enhanced oxidation in aerated water occurred only for Zircaloy surfaces that had been pickled in HF/HNO₃ (Shirvington, et al., 1972). In the absence of this artifact, in fact even in the presence of 1 ppm F⁻ and 10 atm O₂, the Zircaloy oxidation rate was no different than for de-aerated, deionized water (Ibid., 1972).

Effect of pH

Cox (1976) points out that the oxidation rates of Zircaloys are independent of pH over the range from 1 to 12 in nitric or sulfuric acid and in ammonium, sodium, or potassium hydroxides. Acidic solutions up to 0.4 M HNO₃ (2.5% NO₃⁻) and H₂SO₄ (4% SO₄⁼) gave no significant difference in oxidation rate compared to that in water (Jenks, 1958 and Cox et al., 1961). This not only indicates that the pH of NTS repository tuff will not enhance corrosion, but also that NO₃⁻, SO₄⁼, Na⁺, and K⁺ ions do not increase the corrosion rate of Zircaloy, even at concentrations three orders of magnitude higher than their concentrations in tuff repository water.

Effects of Ions in Solution

General

Most of the work cited has been done in deionized water. The question arises: is the water that enters a repository at Nevada (above the water table) significantly more corrosive?

To begin with, the Zircaloy will not be in contact with liquid water (and therefore ions in the water) until the temperature drops to 100°C or below. Consequently, if the ions cause enhanced corrosion, it could be compared with the inherently very low corrosion rate in deionized water at 100°C and below.

The water in contact with host rock is presumed to have the composition shown in Table 2. The ions present in significant concentrations are HCO_3^- and $\text{CO}_3^{=}$, Na^+ , $\text{SO}_4^{=}$, Si^{+4} , K^+ , Ca^{++} , $\text{NO}_3^{=}$ and Cl^- . Fluoride ions should also be included, even though the concentration of fluoride is low, since it is important from a corrosion viewpoint.

Evidence for the effect of ions on the corrosion of Zircaloy is limited. The reactor storage tests described above used Columbia River water, which had ionic concentrations comparable to anticipated tuff water in a number of components, but somewhat lower in others, did not show unusual corrosion of Zircaloy-clad tubes at 90°C for several years. The effects of $\text{SO}_4^{=}$, NO_3^- , Na^+ , and K^+ were considered in the section on pH.

Effects of Na, K, Li

Coriou et al. (1962) determined the effects of Li, Na, K, and NH_4 hydroxides on the enhancement of Zircaloy corrosion. Some results are shown in Table 5. It is clear corrosion is not enhanced on coupon surfaces when ion concentrations are orders of magnitude above those in tuff repository waters, even at water temperatures of 360°C. Crevice corrosion for coupons clamped together is not observed for ion concentrations below those listed in the second column. The results also indicate that the cation is responsible for the crevice effects.

A further observation is the marked effect temperature has on corrosion enhancement. For example, for LiOH , the critical concentration for corrosion enhancement increases by a factor of 16 when the temperature decreases from 370 to 330°C. One anticipates that the critical concentration would vastly increase at 100°C and below, and so the effect can be ignored for our repository conditions. In any case Li^+ is not reported in the tuff water and so is probably well below 1 ppm. The ions one would be most concerned about would be Cl^- (7 ppm at 90°C) and F^- (2 ppm).

TABLE 5. Effects of Some Hydroxides on Aqueous Zircaloy Corrosion

<u>Ion</u>	Cation concentration ppm	
	<u>Case 1^a</u>	<u>Case 2^b</u>
NaOH	5000 (0.2 <u>M</u>)	100
KOH	1700 (0.04 <u>M</u>)	19,000 (very slight crevice corrosion)
LiOH	290 (0.04 <u>M</u>)	0.4
NH ₄ OH	10,000 (0.57 <u>M</u>)	10,000+

^a = Very slight or no appreciable enhancement of corrosion compared to deionized water (at 360°C). These results are for single metal coupons.

^b = Crevice corrosion observed only at and above this concentration for metal coupons clamped together, also at 360°C.

Effect of Chloride Ion

Work of Rozenfel'd et al. (1962) showed no adverse effect on corrosion resistance at 1 to 10,000 ppm of chloride ion. Cox (1973) observed stress corrosion cracking (SCC) of Zircaloy-2 in neutral aqueous chloride solutions, but only when the metal was highly stressed (at the yield point) and polarized anodically beyond the film breakdown potential. For solutions containing 5 ppm NaCl (plus 50 ppm Na₂SO₄ to increase conductivity), a potential of 2 V was required to obtain some pitting (not cracking failure). This voltage greatly exceeds any possible galvanic effect between Zircaloy-2 and a stainless steel canister enclosing it. At 50 ppm NaCl and at high stress, an applied potential of 650 mV gave incomplete failure. Even this voltage is beyond any anticipated galvanic effect. When no stress was applied in 50 ppm NaCl, no SCC failure was observed, even at 2 V of applied potential. Similarly, 5 wt % NaCl gave no evidence of cracking when no potential was applied. A further observation is that 50 ppm of SO₄⁼, three times the value in NTS tuff water at 90°C (17 ppm), had no obvious effect on the corrosion. Cox also refers to work reported by Dunham and Kato (1961) and

Thomas and Allio (1965), in which concentrated acidic solutions with iron were required to obtain SCC in Zircaloy-2, but these conditions are not relevant to our repository.

Yau (1983) reports that U-bend specimens of Zr and Zr-704 (zirconium containing 1.5% Sn, and therefore somewhat similar to Zircaloy-2) showed no cracking after immersion in 20% aqueous NaCl at boiling temperature (107°C) for 60 days. Subsequent mechanical testing of the U-bends indicated that they were still ductile. Steel bolts were also used in similar tests to study galvanic effects--in boiling seawater, in 20% NaCl, and in 5% NaCl + 0.5% acetic acid + saturated H₂S (Yau, 1982). No galvanic effect on the Zr and Zr-704 corrosion was found, and a side observation was that the iron in solution from the bolts did not affect the corrosion resistance of the Zr. This last observation also indicates that the corrosion products of the stainless steel canister and steel hole liner would not be expected to enhance Zircaloy corrosion. (The presence of stainless steel in 360°C water in nuclear reactors also shows little or no effect on Zircaloy corrosion.)

Finally, Berry et al. (1963) reports that 0.01 M solutions of LiCl and NH₄Cl (350 ppm Cl⁻ in each case) and LiI and NH₄I (1270 ppm I⁻) showed no accelerated corrosion of Zircaloy-4 after 56 days at 360°C, further confirming that chloride (and also iodide) do not enhance aqueous corrosion of Zircaloy. Therefore, one can conclude that the presence of Cl⁻ in the ground water does not affect Zircaloy corrosion in a tuff repository.

Effect of Fluoride Ion

The effect of fluoride ion on corrosion must also be considered. Early reports by Berry (1963) and Berry et al. (1963) showed that above a threshold concentration of 8500 ppm fluoride in the oxide film (from HF-HNO₃ pickling), spalling of the oxide film and accelerated corrosion of the Zircaloy resulted during subsequent exposure to 360°C water. He observed accelerated corrosion in 300°C water containing 190 ppm fluoride ion, but not in fluoride solutions containing 19 ppm and 1.9 ppm. Rozenfel'd (1962) observed severe corrosion on the Russian equivalent of Zircaloy only in 360°C water containing more than 100 ppm F⁻ (as KF). F. H. Krenz (1962) in Canada

is quoted by Berry as observing enhanced corrosion in 360°C water with as little as 10 ppm F⁻. However, the attack was observed only on the tension side of U-bend (highly stressed) specimens, not on the compression side.

In the various works cited, enhanced corrosion was reported in fluoride-containing solutions, generally at concentrations of 100 ppm or above and in 360°C water. The fluoride concentration in tuff repository water was only 2 ppm, and the temperatures were below 100°C in the liquid phase. One would expect no F⁻ attack under these conditions, because of the much lower concentration, and especially the much lower temperature. Probably some experiments on Zircaloy are called for at and above 100°C (to accelerate potential corrosion effects) and at various concentrations of F⁻, for example, 2, 20, 200, and 1000 ppm (to accelerate any possible effects).

Effect of Gamma Radiation

Based on a number of studies, Cox (1968) states that: "The preponderance of evidence suggests that gamma fluxes do not significantly influence Zircaloy corrosion at reactor temperatures" (300 to 350°C).

These statements refer to reactor-like and early post-reactor conditions. For the repository case when the canister is presumably penetrated (300 to 1000 years) and air and water vapor can reach the Zircaloy, the gamma field has decreased three orders of magnitude from that of 10-year-old waste and even more from that present just before discharge from the reactor.

STRESS-RELATED EFFECTS

Pressures and Stresses in Fuel Pins

Pressures in the fuel pins result both from prepressurization with helium (to avoid cladding collapse from external coolant pressures in the reactor and to improve heat transfer) and from release of fission gases in the fuel pin. Estimates of end-of-life (i.e., reactor life) gas pressures at 25°C in PWR fuel pins are variously given as 1.4 to 2.8 MPa (Locke, 1975); 5.8 MPa (RESAR 3S, 1975); and by Johnson (1977) as 1.7 to 3.8 (typical) and 5.5 MPa

(occasional). Johnson (1977) further refers to 8.3 MPa pressure as "rare." In fact, some fuel pins in the Maine Yankee Reactor reached this pressure. However, they were not prepressurized with helium, and were fueled with UO_2 that was not fully dense. During operation, the fuel densified and shrank away from the cladding, thus raising the fuel temperature and releasing a much higher fraction of its fission gases to the void space ($\sim 20\%$). Higher temperatures and probably smaller void volumes were also caused by not prepressurizing with helium. This resulted in lower gas thermal conductivity in the pin after fission gas release. Both of these factors gave rise to higher end-of-life gas pressures in the fuel pins. The Yankee reactor fuel rods constitute well under 1% (likely much less than 0.1%) of all spent fuel anticipated at present.

Blackburn et al. (1978) estimated a maximum end-of-life pressure as 7.72 MPa. However, they based this value on a regulatory criterion for internal pressure (not to exceed coolant pressure) rather than on any experimental or empirical measurement. We have chosen to use a pressure of 5.5 MPa at 25°C as the upper limit for 99+% of PWR spent-fuel pins.

Similarly, internal pressures for BWRs are 1.4 to 2.0 MPa (Johnson, 1977) and 1.83 MPa (Blackburn et al., 1978, calculated from data in GESSAR-251, 1975). Blackburn et al. (1978) also cites a value of 3.8 MPa as a maximum pressure for BWR pins, but this, too, is based on the external pressure instead of measured values. We will use 2.0 MPa, i.e., the highest of the cited pressures (other than the 3.8 MPa, because it is not a measured one).

These pressures at 25°C (5.5 MPa and 2.0 MPa) for PWR and BWR give values of 11.0 MPa (1620 psi) and 4.0 MPa (590 psi), respectively, at 325°C , the maximum fuel temperatures anticipated in the repository. Calculations for BWR spent fuel pins show much lower stresses than those for PWRs. Consequently, we will concentrate on PWR spent fuel in our subsequent evaluations.

An alternative way of determining end-of-life pressure is to add the estimated fission gas release to the initial helium pressure. Using Combustion Engineering Calvert Cliffs rods as a typical case and the parameters shown in Table 6 (Lanning, 1983), we obtain a total pressure of

1670 psi, after correcting for the increased void volume due to differential expansion between the Zircaloy and the UO_2 . The corrections were made using GAPCON code (Lanning, 1983).

Helium buildup generated from actinide decay must also be considered. This contribution to pressure is small in the first 100 years, but becomes increasingly important from 1000 to 10,000 years. Consequently, we have taken it into account in Table 6. To calculate internal gas pressures, one adds the pressures of the fill gas, the fission gas (mainly Kr and Xe) released to the pin (assumed release is 20%), and helium generated from actinide decay. The assumption of 20% release of fission product gases is also very conservative. Releases of 10 to 20% have been observed only in some Maine Yankee fuel pins, which, as mentioned above, constitute well under 1% of all fuel pins. For the vast majority of pins, the release is 3% or less. The fission gas contribution to total fuel pressure is one-fourth if release is 20%. For 3% release, therefore, the total pin pressure is reduced by almost one-fourth, adding another margin of safety. Finally, we calculate pressure decrease with temperature, and the void volume change with temperature.

Competing factors are pressure increases due to helium buildup and pressure decreases due to cooling. These factors more or less offset one another. Note the conservative assumption of total release of the helium to the void volume. In practice probably some helium would be retained in the fuel pellets.

Data from which the above were calculated were in a letter communication from Don Lanning, Pacific Northwest Laboratory, Dec. 21, 1983, and are based on Calvert Cliffs Rod 5 (Combustion Engineering) and ORIGEN2 computer code calculations for helium production for a 36-MWd/kg U burnup.

The relevant issue here is that the previously listed conservative pressure of 1690 psi calculated at 325°C may be used for the 10,000-year period, and remains conservative. The hoop stresses calculated from these pressures and the worst-case fuel pin sizes listed in the baseline assumptions (page 2 above) are respectively 95 MPa (14,000 psi) and 34 MPa (5000 psi) for PWR and BWR fuel pins at 325°C and end of reactor life. These values are considered conservative. The vast majority will have much lower stresses.

TABLE 6. Pressure vs Time in Fuel Rods
(Based on Calvert Cliffs Combustion Engineering Fuel Rod #5)

<u>Time (Years)^a</u>	<u>T(°C)</u>	<u>Moles He Generated per MTU^b</u>	<u>Total Pressure (psi)</u>
0	322	0.35	1690
10	310	0.51	1670
100	194	1.69	1500
1000	105	7.35	1500
10,000	30	19.35	1530

Assumed Parameters

Pre-irradiation void volume	= 41 cm ³
Fuel weight per rod	= 2317 gU
Enrichment	= 3.2%
Fill gas pressure	= 500 psi (20°C)
Fission gas release to void	= 20%
Helium released to void	= 100%
End of life void volume ^c	= 41 - 0.3 x BU (MWd/kg U) = 30 cm ³ for 36 MWd/kg U
Fission gas production rate	= 31 cm ³ (1 atm. 0°C) per MWd (ANS Standard)

^a Time after emplacement in repository. Waste assumed to be 10 years old.

^b Based on ORIGEN2 Calculations [Lanning (1983)].

^c From Lanning (1983), based on data fits from Calvert Cliffs rods.

Temperature Limit for Mechanical Overload

An analysis comparing design stress with both yield strength and ultimate strength shows that a conservative upper limit for Zircaloy is 396°C for PWR spent fuel and > 427°C for BWR spent fuel (Blackburn et al., 1978), even

with the higher pin pressures they assumed compared to those chosen in this report. Typical service stress levels in the cladding are well below the design value. In PWR cladding, for example, the ratio of design to average stress is 2, and since the temperature selection is based on one-half the ultimate strength, the safety margin is a factor of four. For the rare cases in which a flaw is halfway through the cladding wall, the safety margin is two. At 325°C, an additional 20% margin is available.

Stress (Creep) Rupture

Another potential failure mechanism due to hoop stresses in the Zircaloy clad is stress- or creep-rupture. In this discussion, creep-rupture and stress-rupture (used by Blackburn et al., 1978) will be used interchangeably. To determine whether this is a problem, we selected and modified Blackburn's approach to deal with decreasing temperature with time anticipated in the repository environment.

Blackburn combined the data base for Zircaloy-2 and -4 since the creep-rupture behavior of these alloys was not distinguishable. Based on Locke's paper (1975), he points out that annealed material is typical of BWR cladding, whereas cold-worked and stress-relieved material is typical of PWR cladding. Unfortunately, few creep failure data on irradiated materials are available, and so he assumed that unirradiated properties could be used to represent post-irradiation failure. Quoting Blackburn et al. (1978), "Although substantial irradiation hardening and reduced ductility in short-term tests is known to result from reactor service, it is possible that time-to-rupture in creep tests is not markedly affected since irradiation hardening can lower the creep rate and result in little change in failure times in spite of reduced ductility. Zirconium alloys do not appear to be susceptible to helium embrittlement-type effects as are the stainless steels; therefore, the large irradiation-induced reductions in rupture life of stainless steels may not be typical of Zircaloy fuel cladding."

More specifically, Carpenter and Watters (1974) showed that the hardness of neutron-irradiated Zircaloy-2 decreased after heating for 1 hour above 300°C, indicating annealing (i.e., length recovery after growth in reactor

irradiation). Other work done by R. B. Adamson (1977) and modeled by C. C. Dollins (1979) showed substantial annealing. For Zircaloy exposed to 12 hours at 350°C, 42% of the growth was recovered (by shrinkage).

Einzigler and Kohli (1984) imply that the work cited above showed annealing because the irradiations were done either at room temperature, or well below the subsequent annealing temperatures. Einzigler and Kohli (1984) describe tests of five spent fuel pins pressurized to 9.5 MPa at 23°C that showed negligible annealing at 323°C for 2000 hours. Corresponding hoop stress at 323°C was ~152 MPa. Absence of annealing was determined by hardness measurements, which contrasts with similar measurements made on claddings tested at 482 and 571°C (Einzigler et al., 1982) that showed large drops in hardness. One could argue that the time for these 323°C tests was only 2% of the approximately 10 years during which cladding temperatures are at 305 to 325°C, based on Figure 1, and so very low rates of annealing might not be detected within the error of hardness measurements. Also note that the authors did observe a 0.16% strain after testing, which would correspond to an 8% drop in the hoop stress. Extrapolating these results to multi-year time frames could give appreciable reductions in hoop stresses. Also, these investigators used an isothermal analysis, and temperatures drop steadily and considerably as the spent fuel decays. Nevertheless, this work raises questions about the use of stress-rupture data on unirradiated Zircaloy to predict behavior of irradiated Zircaloy (Blackburn et al., 1978).

Finally, Johnson et al. (1983) quote creep-rupture data by Yaggee et al. (1979, 1980) on irradiated Zircaloy. These are high-temperature, short-term measurements, but the data fit reasonably well with Blackburn's Larson-Miller parameter plot, at least for the cold-worked, stress-relieved Zircaloy (PWRs). This helps to justify Blackburn's use of unirradiated data on Zircaloy.

Blackburn correlates the data using Larson-Miller (1952) calculations, viz.

$$P = T (20 + \log \tau)$$

where P = Larson-Miller parameter,
 T = Temperature (°R),
 τ = time to failure (hours).

P is a function of hoop stress. He plots both biaxial and uniaxial stresses vs P, and defines the minimum stress-rupture correlation as the lower 95%/95% tolerance on the data fit, i.e., there is a 95% confidence that the correlation is the lower bound of 95% of the population. Indeed, examination of his P vs stress curve shows that all experimental points fall on or above the curve.

Using his values for the Larson-Miller parameter P as a function of stress, α , one calculates $P = 30,000$ for a conservative stress of 14,000 psi (for PWR pins). Rearranging the Larson-Miller equation and converting T to degrees K and t to years, one obtains

$$\log \tau = 16667/T - 23.9425.$$

Time to failure is then calculated stepwise for temperature-time increments. The temperature at the beginning of the increment is used (conservative). (A more accurate calculation could be done allowing continuous temperature with time and integrating the result. Much longer times to failure would result.)

The life fraction rule first suggested by Robinson (1938) and utilized by Bocek (1979) for life predictions of structures during ramp loading conditions is

$$\frac{\Delta t_1}{\tau_1} + \frac{\Delta t_2}{\tau_2} + \dots + \frac{\Delta t_n}{\tau_n} = 1 \quad .$$

One calculates τ_i for each temperature (time) increment. Then the ratio of that time increment to time to failure for the corresponding temperature is determined, and the results are added. In effect, this procedure assumes these fractions are additive to produce ultimate fracture. If the sum so obtained is less than one, creep failure should not occur.

Temperatures were taken from Fig. 1 data and the stepwise calculation was made by calculating τ for the highest temperature in the increment. The

result for $\sum \Delta/\tau = 0.001$, i.e., 10,000 years, is only 0.1% of the Larson-Miller failure lifetime. Even if a stress of 20,000 psi is used, the sum is 0.007.

A second calculation was done at 20,000 psi using the unlikely but very conservative temperature-time history in Figure 3. In that case the life fraction is still only 20% of the Larson-Miller failure time.

Similar calculations for BWR fuel pins, assuming annealed Zircaloy cladding and the highest value of hoop stress from the previous section of this report (extremely conservative), one obtains a Larson-Miller parameter greater than 32,000. Without further calculation, it is clear that this value will give even longer lives than those for PWRs.

Except for the uncertainty of using unirradiated creep data and the life fraction approach, the calculations are very conservative:

1. The highest stress used (20,000 psi or 140 MPa) is conservative, representing the extremes determined to date. Typical values are half of this or less.
2. Uniaxial stress-rupture data were used instead of biaxial data to calculate P. Biaxial data are more appropriate for hoop stress in the pressurized pins. Stresses to failure using biaxial data are about 30% higher than those for uniaxial data.
3. Minimum stress to failure was used. As mentioned, the data points were all above this value, except for a few points that fell on the curve.
4. The stepwise calculation exaggerated the clad temperatures, and so added further conservatism to the calculation.
5. BWR spent-fuel claddings would have even longer lives than those calculated for PWRs.

6. The later paper by Johnson, Gilbert, and Guenther (1983) gives maximum internal pressures in the PWR and BWR pins of 2000 and 450 psi, giving corresponding maximum hoop stresses of 16,000 (PWR) and 3800 psi (BWR). These are lower than the values used in the calculations above, and also add conservatism.
7. Design cladding stresses are higher than expected stresses in service.

Einzigler and coworkers (1982) did a post-irradiation study of 14 PWR rods that had been irradiated for two or three reactor cycles in the Turkey Point Unit 3 reactor. They exposed the rods to high temperatures (482 to 571°C) in air or helium for up to one year to accelerate the effect of longer times in dry storage at lower temperatures. Both nondestructive and destructive tests were made on the rods. Among other observations, there was no evidence for SCC or hydriding as active cladding failure mechanisms, although they point out that the (stress) conditions are not in a regime where SCC would be expected to occur during the time under test, i.e., less than 20,000 psi, which Yaggee et al. (1979, 1980) stated as the threshold stress for SCC.

In this work they observed stress-rupture life orders of magnitude longer than would be predicted by Blackburn's analysis (1978). A prediction based on Blackburn's analysis would give a 98% probability of breaching during the test time at temperature, but no failure occurred. They attributed this extended life to creep strain in the Zircaloy cladding, which reduced the pressure inside the rods, and consequently reduced the hoop stresses. They conclude that the cladding could survive 1000 years at 400°C with a 95% confidence level without stress rupture limiting the life, while the calculations we used above would predict only 1.2 years at 400°C. Similarly, below 300°C creep strain is very low (Woodford, 1979), and so the stress is not expected to change over the life of the rod.

It is important to note that Einzigler quoted results for isothermal conditions, while in practice the temperatures are constantly decreasing. Thus, 325°C is the peak cladding temperature in the repository. At this temperature, stress relaxation is expected to occur. The claddings are at temperatures between 325 and 300°C for only 20 years. For the remaining

thousands of years the claddings are well below 300°C, the creep rate is reduced to very low values, and so creep rupture is not likely during this period.

Finally, note that the Larson-Miller constant used (20) in four cases out of five predicts rupture times that are conservative compared with the experimental values (Furillo et al., 1977). The fifth case predicted a life that is three times too long. However, these tests were for a specific class of alloys (precipitation- and oxide-dispersion-strengthened superalloys). These authors obtained very good agreement (within 10%) for all five test cases using a more detailed equation but one similar to that of Larson-Miller, and appropriate constants for individual cases (loc. cit.).

As mentioned earlier, Einziger et al. (op. cit.) stated that the use of 20 for the Larson-Miller constant gave extremely conservative results compared to their experimental observations. E. R. Gilbert (1984) pointed out, however, that Einziger apparently overestimated stress in the claddings, since as creep strain occurred, pressures in the pressurized pins decreased as did the hoop stress.

Potential for Failure Due to Extension of Cladding Flaws

A subcritical flaw may grow and cause penetration by several possible mechanisms:

1. The flaw may extend through the cladding until the stress exceeds fracture toughness, leading to rapid failure.
2. The flaw may extend through the cladding more slowly and cause penetration.

Blackburn et al. (1978) plotted curves showing that the minimum expected fracture toughness for Zircaloy-2 and -4 is 25,000 psi-in.^{1/2} at 25°C, 30,000 at 100°C, and probably even higher at higher temperatures, based on the data of Walker and Kass (1974). This is for hydrided, unirradiated material. The lower limit for fracture toughness of all irradiated, unhydrided Zircaloys is even higher, viz. 29,000 psi-in.^{1/2} at 25°C and 32,000 at 100°C. It is important to note that all fracture toughness data points were above the

curves mentioned. On this basis, mechanism (1) may be rejected as a plausible failure mechanism. Mechanism (2), above, may occur by hydrogen-induced delayed cracking or stress-corrosion cracking, to be discussed below.

Hydriding failures from the interior of a cladding have been observed in early operations (Locke, 1975) and were traced to residual water vapor in the fuel. Since then fuel elements have been vacuum dewatered, so a minority of unfailed spent fuel is subject to hydride failure from the interior. External hydriding is discussed elsewhere in this report.

Pellet-Clad Interaction (PCI)

PCI is a term that was first applied to physical interaction between pellet and clad, i.e., solid expansion of the fuel itself against the cladding, producing stresses in the cladding. Subsequently, the potential role of fission products reacting chemically with the cladding was recognized. It is now accepted that PCI is a joint effect of fission product attack on the cladding under conditions of sufficiently high wall stresses in the Zircaloy. Under these stresses, small cracks are chemically attacked by fission products, especially at the root of the crack where localized stress concentration is high. Most investigators attribute the attack to iodine, although there is controversy on this point (see below).

Stress-Corrosion Cracking (SCC)

The only known cases of failure in nuclear reactors as a result of SCC have occurred in isolated fuel rods, typically during rapid increases in reactor power (ramp-ups). Johnson et al. (1983) and Johnson and Gilbert (1983) report that no known cases have occurred either during actual pool storage or in dry storage investigations. The events are rare, even for fuel assemblies that have resided in a nuclear reactor for 16 to 17 years and have experienced operating conditions for 12 years (Johnson et al., 1983; Hillner, 1980; Mayman 1978).

Metallurgical examinations of irradiated Zircaloy-clad fuel, with few exceptions, show no evidence of fission product attack or SCC initiation (Johnson et al., 1983; Fuhrman et al., 1976).

If SCC occurs only during rapid temperature ramps, it is very unlikely that SCC would occur in the repository. However, if cracks are initiated during reactor operation, their subsequent history must be addressed.

During the first few years after emplacement, the spent fuel will reach temperatures of 325 to 345°C, according to the limits chosen. (Of course this temperature could be reduced by design changes, at some economic penalty.) Total times at temperatures above 300°C are short, and the absence of high fuel temperatures that could cause further release of fission products from the fuel pellets would tend to remove concern about SCC. However, the effect on SCC of moderate to low temperatures during very long times must be addressed. The issue is whether cracks can propagate to failure during the 10,000-year repository storage. Several investigators (for example, Kohli and Holub, 1980; Sejnoha and Wood, 1979; Peehs et al., 1979) have attempted to simulate the attack of fission product iodine with nonradioactive iodine on stressed Zircaloy outside of a reactor. In fact, Peehs et al. (1982) found that unirradiated Zircaloy claddings did not fail when subjected to iodine vapor at 100 and 300°C for test times up to 550 days, even at iodine concentrations ten times higher than the threshold concentration previously determined (Peehs et al., 1979). Other investigators question whether iodine is indeed the culprit, and offer the possibility that other metals, especially cadmium, perhaps in combination with cesium, may be the active reagent (Syrett et al., 1977; Grubb and Morgan, 1979; Shann and Olander, 1983; Kohli and Holub, 1980).

A recent analysis by Miller and Tasooji (1983) used two approaches to determine lifetimes due to SCC failures in spent fuel: a model approach and a "data-centered" approach using fracture mechanics on 2000-hour tests of split ring specimens. The latter approach is said to be applicable only up to about 290°C. In the first approach, the "SCCIG" model is used (Tasooji, Einziger, and Miller, 1982; Miller, Ocken, and Tasooji 1981; Miller, Challenger, et al., 1981; Tasooji, 1982). Unfortunately, there are so many uncertainties in the data input to the model, that the authors themselves question the conclusions. For example, the unknowns are:

1. The chemical environment inside the fuel rod. There are viewpoints that:
 - (a) Enough cesium is present to effectively tie up all the iodine, and so it is not reasonable to attribute SCC attack to free iodine (Olander, 1982).
 - (b) Free iodine can be released from CsI by radiolysis or by reaction with UO_2 in quantities sufficient to cause SCC (Cubiciotti et al., 1976, 1982; Hoffman and Spino, 1981).
 - (c) Cadmium or other elements may cause SCC even if iodine does not (Shann and Olander, 1983).

2. The effect and concentration of "chemical defects," i.e., inhomogeneities. (EPRI-sponsored work is underway to incorporate chemical inhomogeneities in the SCCIG model.)

3. Internal pressures due to fission gas release in the fuel rods. Miller uses an extremely conservative 50% release, a figure four to five times higher than that used by Johnson and Gilbert (1983). Blackburn et al. (1978) cite 20% as the maximum fission gas release in GESSAR-251 (1975) for the highest design power density rod.

There are other uncertainties, such as mechanical flaw size distribution and activation energy for iodine penetration, necessary for extrapolation to long times at lower temperatures compared to shorter-time data taken at 300 to 350°C.

Miller's conclusion is that the "worst-case" limiting (maximum) temperature for SCC in storage of fuel rods (up to 100 years, presumably) is 150°C. The "typical case" equivalent temperature is > 400°C. Clearly, more work needs to be done to get better definition here.

A problem in selecting a conclusion is that the use of "typical" end-of-life fuel rod conditions does not quantify the number of fuel rods that fail during the repository isolation lifetime. On the other hand, the worst-case conditions may well be excessively conservative and incur economic penalties. Miller suggests using a compromise approach having typical conditions and a quantitative estimate of the small fraction of worst-case rods likely to fail. Clearly, this calls for a probabilistic approach. Unfortunately, relatively few data points are currently available.

The second approach in the Miller-Tasooji paper is primarily experimental. In one set of experiments, split-ring specimens were precracked to various depths using a solution of iodine in methanol, then exposed to iodine vapor for up to 2000 hours at various temperatures up to 200°C (J. C. Wood, 1982; Hunt et al., 1981). Other experiments determined the effect of cadmium, cesium, and iodine vapor at up to 300°C (Hunt et al., 1981; Wood, 1974).

The results are reported for conditions that yield failure in 2000 hours and those for which integrity is maintained. Using these data as well as linear elastic fracture mechanics (LEFM) and stress intensity factors, Miller and Tasooji (1983) predicted allowable temperatures for storage lifetimes (100 years).

There is a wide discrepancy in the allowable temperature depending on whether data on small cracks are included with data of large cracks. In the former case, the allowable temperature is 220°C, whereas in the latter case, the allowable temperature is 290°C. Even these data do not necessarily apply to spent fuel since they were obtained for unirradiated Zircaloy. The authors point out that for short cracks (length less than 0.1 of the cladding wall thickness), behavior is affected by global (hoop) stresses and LEFM is not applicable, and in fact results in overly conservative predictions. They get around this by using the SCCIG model to analyze behavior of short cracks. They show that the temperature must be at least 290°C for the short cracks to cause SCC failure in 100 years. Below 290°C only larger incipient cracks can fail in 100 years at the hoop stresses assumed, and LEFM may be used for predictions.

In sum, while some evidence indicates SCC failure of Zircaloy would not occur in the repository, stronger proof is not yet available. At the least, further work is required on shorter term, higher stress conditions at temperature to supplement existing data. Additional tests at lower temperatures, longer times, and higher stresses may also be needed to determine the effect of decreasing temperature. Application of models is still quite primitive. However, work is continuing for dry storage and the waste package program may avail itself of forthcoming data and modeling, especially the work sponsored by EPRI. Even though cladding lifetimes of

10,000 years are sought in a repository, temperatures decrease significantly after 100 years. Since SCC is temperature-dependent, failures are most likely during the first 100 years. Thus, work for dry storage (100 years) generally applies to lifetimes in a repository. Nevertheless, the waste package program may need to initiate or support some SCC work.

Alternate Mode of PCI Failures

Chung and coworkers (1983) showed that PCI-type failures, as evidenced by electron microscopic examination, could be induced in high-burnup spent-fuel Zircaloy cladding without the addition of fission product simulants (e.g., I, Cs, Cd). They attributed the brittle-type fractures to the presence of precipitates of Zr_3O segregated at irradiation-induced defects as follows:

"It appears that a high density of irradiation-induced defects, intrinsic oxygen augmented by corrosion, and local stress fluctuations (due to thermal expansion of the fuel pellets) are conjointly conducive to oxygen segregation and Zr_3O precipitation in high-burnup cladding, which could lead to minimal plastic deformations and PCI failures. TEM microstructural evaluations of Zircaloy cladding from fuel rods that have experienced in-reactor PCI failure are required to further explore the brittle fracture mechanism associated with oxygen segregation and Zr_3O precipitation in regions of localized deformation."

The relevance of this work to the life of Zircaloy claddings is not clear. Temperatures were from 292 to 325°C and failure times observed were up to 300 hours. However, cladding stresses (induced by internal gas pressure) were very high, viz., 45,000 to 80,000 psi. What is not clear is whether similar failures would occur at stresses of 20,000 psi and below at much longer times, i.e., years, and whether similar failures would be observed at temperatures well below 300°C for the hundreds to thousands of years that are characteristic of our repository conditions. In particular, some threshold stress probably would be required to initiate the cracking mechanism, as is observed in other crack-propagating failure mechanisms.

In fact, Chung points out that strain aging, i.e., the interaction of oxygen and dislocations resulting in brittle-phase Zr_3O agglomerates, maximizes in the vicinity of 300°C. Below about 250 to 300°C, temperature recombination of radiation-induced vacancies and (oxygen) interstitials predominates. At temperatures above 300 to 350°C radiation-induced defects are highly mobile and anneal out at sinks. So it is primarily close to 300°C (275 to 325°C) where this embrittlement effect may be a problem. Further work on SCC may at the same time determine whether one can disregard this potential failure mechanism in the face of the (probably) overriding SCC mechanism.

Delayed Hydriding and Other Hydride Failure Modes

Delayed fracture due to hydriding in Zircaloy is another potential failure mechanism. The solubility of hydrogen in zirconium alloys is about 60 ppm at 300°C, but only 1 ppm at 20°C (Sawatzky and Wilkins, 1967; Simpson and Cann, 1979; Cann and Atrons, 1980). When the solubility is exceeded at any particular temperature, brittle hydrides precipitate. Hydrogen is present in the PWR cooling water. In addition, oxidation of Zircaloy in the water releases H_2 , part of which may diffuse into the Zircaloy and react to form dispersed particles of zirconium hydride. Normally the presence of hydride is not a problem. However, driven by the stress gradient at crack tips, hydrogen can migrate and form brittle zirconium hydride at these tips. At high enough stresses, the crack will propagate at some velocity, and given a sufficiently long time, may end in failure of the cladding.

Failure due to the presence of hydrides would especially tend to arise if a combination of hydrogen concentration, stress, and temperature occurs as follows. Normally hydrides precipitate as platelets in circumferential orientations, due probably to the texture arising from tube fabrication. At moderately low hydrogen concentrations (e.g., less than 300 or 400 ppm) these circumferentially oriented hydride precipitates are not a problem. However, if a large temperature gradient exists within a Zircaloy tube, hydride decomposes in the hot region and the hydrogen thus placed in solution migrates by diffusion to the cold region where hydride reprecipitates. If hoop stresses are sufficiently high (e.g., 90 to 95 MPa), hydride will precipitate with a radial orientation. These radially oriented brittle hydrides form an

easier pathway for cracks, given these same high hoop stresses. Thus, in addition to hydrogen availability, both high stress and a large temperature gradient are necessary. Such a failure is described below.

In practice, hydrides have been observed in PWR claddings, but failures in Zircaloy clearly attributed to delayed hydride cracking had not been observed in reactors until recently. Delayed failure due to hydriding has been recorded in Zr-2.5% Nb pressure tubes in Pickering-3 and -4 CANDU (heavy water) reactors, but no cracking had been reported in the literature for Zircaloy-2 pressure tubes in Pickering-1 and -2 reactors (Puls et al., 1982; Johnson, 1977). However, a Zircaloy-2 pressure tube did fail recently (August 1983) in Pickering Unit 2 reactor (L. A. Simpson, private communication, Feb. 2, 1984). Observation was that the failure was related to a cold spot due to bowing and subsequent contact of the hot Zircaloy tube with a colder surface. Hydrogen in the Zircaloy apparently migrated to the cold spot and a sufficiently high concentration of radially oriented zirconium hydride formed there. A long crack developed and sudden failure occurred. Hydride blisters were observed on the Zircaloy. Although reported in local newspapers in Canada, details have not yet been reported in the technical literature (L. A. Simpson, *ibid.*).

A series of papers deals with delayed hydride cracking (Puls et al., 1982; Hillner, 1982; Dutton, 1978; Dutton et al., 1977; Simpson and Puls, 1979; Simpson and Cann, 1979). Cracking failure requires movement of the cracks, which in turn requires high stress intensity factors. In particular, Puls et al. (1982) experimentally showed that for Zr-2.5% Nb the threshold stress intensity factor is $6.0 \text{ MPa}\cdot\text{m}^{1/2}$, and is independent of temperature up to about 300°C, the highest temperature under study in this paper. Above 250°C (approx.) crack propagation has not been observed in unirradiated Zircaloy-2, presumably because of appreciable plastic flow. (L.A. Simpson, personal communication, Jan. 6, 1984). Hydrogen contents ranged up to 200 ppm, with no observable differences between 100 and 200 ppm. Even at 400 ppm, no measurable difference in the threshold for crack propagation was observed (L. A. Simpson, *ibid.*). Although fewer data are available for Zircaloy-2, earlier tests reported showed that the threshold of stress intensity for crack propagation in the unirradiated material is 50 to 100% higher than that for

Zr-2.5% Nb. Coleman and Ambler (1977) determined that cracks initiated in smooth Zr-2.5% Nb at high stresses (725 MPa, 105,000 psi) and after two thermal cycles. Under the same conditions, Zircaloy-2 deformed plastically with no cracking. The work showed that the stress intensity threshold (K_{IC}) for Zircaloy-2 is higher than for Zr-2.5% Nb. Furthermore, K_{IC} increases as temperatures drop.

More recent tests on Zircaloy-2 underway at Chalk River had shown a threshold value of $10 \text{ MPa}\cdot\text{m}^{1/2}$ for compact tension tests, but $6.0 \pm 1.0 \text{ MPa}\cdot\text{m}^{1/2}$ for round notch tests (C. Ellis, personal communication, February 10, 1984). Further tests are continuing at Chalk River. Most recently, the belief was expressed that the threshold stress intensity for crack propagation is about the same for Zircaloy-2 as for Zr-2.5% Nb (L. A. Simpson, personal communication, June 5, 1984).

The following analysis was conducted to establish that the hydrogen content does not exceed 400 ppm (the value mentioned above) in the repository case. Johnson, Gilbert, and Guenther (1983) reported that the hydrogen content of spent fuel claddings ranges from 80 to 150 ppm. A comprehensive study by Garzarolli et al. (1982) showed hydrogen contents less than 50 ppm in spent PWR fuel pins, even at high burnups (50 GWD/tU). Consequently, we can establish that hydriding of Zircaloy-2 claddings in the repository is not likely to result in delayed failure if we can show that the additional hydrogen pickup does not exceed about 250 ppm.

When Zircaloy is oxidized by water, the stoichiometric release of hydrogen is 1/8 the weight gain due to oxygen. In practice the hydrogen actually absorbed by the Zircaloy is only a fraction of the hydrogen released. Typical absorption ratios for PWR reactors in practice are about 1/3 (Kass, 1970). However, this occurs in the absence of oxygen, since hydrogen is intentionally added to PWR water to suppress oxidation of the system components. In the presence of oxygen, the ratio of hydrogen absorption to hydrogen released is less than 0.1 (Hillner, 1964). A detailed study by Garzarolli et al. (1982) showed hydrogen pickup fractions of 3 to 9%, with a mean value of 6%. These observations are for corrosion by liquid water.

In oxygenated steam, Cox (1962) shows a reduction in hydrogen pickup when compared to that in pure steam. In particular, the quantity of H_2 absorbed is about 20% of the quantity theoretically released from the steam.

Oxidation of Zircaloy during 10,000 years in the repository was calculated in an earlier section of this report (film thickness gain of 17 μm). For the equivalent amount of oxygen, assuming oxidation was by H_2O alone, the hydrogen absorbed would be about 100 ppm. In practice, very likely a substantial part of the Zircaloy oxidation would be from air itself, in which case hydrogen would not be generated.

Thus, the anticipated maximum hydrogen content in spent fuel claddings during 10,000 years is 250 ppm. One caveat here is that if large temperature gradients are present, hydrogen concentrations could become high at colder regions. However, we anticipate that gradients in the Zircaloy claddings would be small in the repository canisters. Further experimental work is needed for longer times to establish the temperature and stress limits of delayed hydride failures.

Next, to determine whether delayed hydride cracking is expected in Zircaloy spent fuel claddings, the stress intensity factor K are compared with the threshold value cited above. Unfortunately, determining K is not straightforward. Instead, one must know or estimate the likely range of crack dimensions to determine K . In the absence of detailed data, Blackburn et al. (1978) used a broad range of crack lengths that seemed reasonable and conservative. However, they used a maximum crack depth equal to half the cladding thickness. This may be an excessively conservative assumption.

There is some controversy about the maximum crack depth to use in these calculations. Tasooji, Einziger, and Miller (1982), using the SCIGG model (see above), calculated that the maximum crack depth for unbreached claddings after reactor operation is 20% of the cladding wall thickness. Deeper cracks would cause breaching during reactor operation.

On the other hand, several spent fuel pins from Maine Yankee were found to have cracks as deep as 50 to 65% of the wall thickness. However, the fuel rods in Maine Yankee failed at relatively low burnups, and, as mentioned before, UO_2 fuel had densified, increasing the thermal resistance and fuel temperature. In general Maine Yankee fuel rods are not representative of other (even early) reactor fuel rods.

Table 7 lists several calculations for our case, following the procedure outlined by Blackburn et al. (1978). These are for crack lengths ten times the crack depth.

TABLE 7.

Crack depth % of wall thickness	Hoop stress, psi (MPa)	K (325°C)	K (280°C)
20	14,000 (95)	2.2	2.0
20	20,000 (137)	3.15	2.9
50	14,000 (95)	5.4	5.0
50	20,000 (137)	7.7	7.1

These values for K are to be compared with $6.0 \text{ MPa}\cdot\text{m}^{1/2}$ cited above. They appear to show that delayed hydride failure by crack propagation would not occur if initial crack depths are 0.2 of the wall thickness, even at a stress 40% higher than our conservative assumption of 14,000 psi. However, if crack depths reach 0.5 of a wall thickness, the results appear more marginal for some tubes. The equivalent K values are somewhat lower if one considers Simpson's observation that crack failures were not experimentally observed above 250°C for Zircaloy containing at least up to 400 ppm hydrogen (L. A. Simpson, personal communication January 6, 1984).

Because the threshold stress intensity for delayed hydride cracking is $6.0 \text{ MPa}\cdot\text{m}^{1/2}$ and because upper extreme gas pressures and hoop stresses were used, delayed hydride cracking would not be expected to occur in 10,000 years

if one accepts maximum crack depths 0.2 of the cladding thickness and a corresponding critical stress intensity factor of 3.3. If, however, the crack results mentioned above for Maine Yankee are not merely "rare" results (i.e., under 0.1% of all spent fuel), delayed hydride cracking could conceivably occur during the repository lifetime for 1% or more of spent fuel pins.

We are left with a dilemma that requires further investigation. The maximum crack depths in spent fuel claddings should be determined. The Maine Yankee results are not likely to be typical, but because some fuel rods have cracks that extend 50% of the cladding depth, it must be determined whether 1 or 0.1% or even fewer of the spent fuel rods are affected.

Failure because of reorientation of hydride precipitates (see above) does not seem credible because of the anticipated absence of large longitudinal temperature gradients in Zircaloy-clad tubes placed in the repository.

Another source of delayed hydride failure is hydrogen generated within the fuel pins, which Blackburn et al. (1978) refers to as "internal hydriding." In the past this was an important failure mechanism in operating LWR fuel rods. The source of the hydrogen was small quantities of water accompanying the UO_2 pellets. Since 1972, manufactured fuel pins have been evacuated before sealing to remove water vapor, so the problem no longer exists. Many claddings hydrided in this manner have failed in service. The survivors, when exposed to long burnups, have had ample opportunity for the hydrogen to diffuse outward at reactor operating temperatures. The few questionable fuel pins are those early pins that have seen relatively short burnups and have therefore experienced inadequate time for outward diffusion of hydrogen. These pins constitute a very small fraction of spent fuel, and at any rate few if any of these are expected to fail in the long term for reasons similar to those given for external hydriding. Blackburn et al. (1978) reaches the same conclusion.

Another caveat about hydriding must be made. In recent work, Einziger and Kohli (1984) found that hydrides had predominantly radial orientation after slow cooling under a hoop stress of 145 MPa at 323°C. A pin similarly tested but cooled with no hoop stress showed only circumferential orientation. At

intermediate stresses, viz., 13 to 26 MPa, no radial reorientation was observed, even for slow cooling. It is therefore uncertain as to whether stresses from 26 to 145 MPa would cause radial reorientation of hydrides. Also, since the cooling rate was 5°C/hour, one may ask whether the cooling rates anticipated in the repository (1°C/year and less) would give rise to radially oriented hydride at lower stresses. Note that more rapid cooldown rates (10°C/hour and above) do not result in radial orientation (Einziger et al., 1982). Further experiments are needed to determine whether there is a critical stress for re-orientation of hydrides and if so, how it is affected by the cooling rate.

Oxidation of UO_2

In connection with cladding ruptures, the oxidation of UO_2 fuel is often considered. This report deals only with the initial penetration of the cladding, since work is going on elsewhere on the effect of cladding penetration defects on containment of radionuclides. Therefore, oxidation of UO_2 to less dense U_3O_8 as a result of contact with external air implies that penetration has occurred. We need only to consider oxidation of UO_2 internal to the cladding and its possible effect on the cladding integrity. The void volume in a fuel rod is too small to permit significant oxidation of UO_2 , and at any rate the fill gas is helium. Complete oxidation of UO_2 to form U_3O_8 would require 103 g of O_2 (72 liters at 1 atm and 0°C), which is not credible for our conditions.

Miscellaneous

A multi-year test of a fuel assembly has been underway at the Nevada Test Site (called the Fuel Temperature Test). Several months after emplacement, Kr-85 was detected, indicating that one of the pins had breached (T. Hakl, personal communication, November 17, 1983). The pins in this fuel assembly had been handled and then re-assembled. The peak temperature was 275°C and the pins were stored in dry air. The question now is, did the pin have an incipient defect that subsequently corroded through in the air environment, or was the pin damaged during disassembly, handling, and re-assembly, which then caused subsequent breaching? The answer is not yet available. Note that

failure of fuel pins during storage in air had not been observed in any previous tests (Johnson, Gilbert, and Guenther, 1983).

CONCLUSIONS

There are a number of possible failure mechanisms for Zircaloy claddings on spent fuel during a 10,000-year lifetime in a tuff repository. These are discussed in sequence.

1. Calculations show that depth of oxidation would not penetrate cladding, even in the presence of the ions in the local water. Additional experimental work would be desirable on the effect of fluoride ions.
2. Mechanical overload should not be a problem.
3. Stress (creep) rupture appears unlikely based on Larson-Miller type calculations and comparisons of such calculations with some experimental observations on spent fuel claddings.
4. Most of the data appear to deny that delayed hydride cracking would be a problem. However, some limited data on crack depths raise questions about this conclusion. More data are needed on the statistics of large cracks ($\sim 50\%$ of wall thickness). Furthermore, the effect of slow cooling of Zircaloy in the repository on radial re-orienting of hydrides must be studied, in light of indications by Einziger and Kohli (1984) that slow cooling under stress favors this re-orientation.
5. Stress corrosion cracking is the least understood of the potential failure mechanisms. Although there is evidence that failure would not occur under repository conditions, other analyses raise the possibility that failure may occur in a minority of claddings. Temperatures would constantly decrease, significantly reducing the likelihood of failure if the pins survive for the first 50 or 100 years. Further experimental work is called for, with a special need for sufficient data to make probabilistic calculations.

It is also of note that Johnson and Gilbert (1983) conclude that there is sufficient evidence to support licensing of extended dry storage (up to 100 years) at temperatures up to 380°C. Tests and demonstrations are said to be underway to determine whether storage even above 400°C is viable. Because the highest temperature history (the most critical part) of the repository life falls within 100 years, and because the initial temperatures of claddings are well below 380°C, most of their arguments about Zircaloy also apply to Zircaloy claddings in the repository.

RECOMMENDATIONS

The following recommendations are offered:

1. To confirm that low concentrations of fluoride ions do not enhance Zircaloy corrosion, and to determine the threshold for attack, some additional tests are called for. These would determine the effect on Zircaloy of 2 to 1000 ppm fluoride in 100°C aqueous solution.
2. More experimental work should be done to define conditions under which SCC will occur, with sufficient data to allow reasonable probabilistic estimates of failure.
3. Data on the statistics of maximum crack depths should be taken for a range of spent fuel rods.
4. Further experimental work is needed for longer times than currently available data to establish temperature and stress limits of delayed hydride failure. Also the effect of slow cooling under stress on hydride re-orientation should be determined since radial hydrides can increase hydride cracking failures.
5. Close liaison should be established with ongoing work on dry interim storage at PNL, HEDL, and West Germany and Canada.
6. Liaison should also be maintained with EPRI, which has funded and continues to fund work on SCC, hydriding, oxidation, and other potential failure modes for Zircaloy cladding.
7. Work on delayed hydride cracking of Zircaloy is of considerable concern to Ontario Power in Canada, and the ongoing work at Chalk River and Whiteshell should be followed closely.

8. More data are needed to establish survival and failure of claddings on a probabilistic basis. Work funded by EPRI will be of value in this respect, but more is required to firmly establish spent fuel Zircaloy claddings as long-term barriers.
9. Breaching of the fuel pin in the EMAD test should be followed up to determine whether this was due to mechanical damage or failure of an incipient defect that had developed during reactor operation.

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