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Zircaloy Cladding Performance Under Spent Fuel Disposal Conditions

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EXECUTIVE SUMMARY

Spent fuel cladding integrity is an important component of the Department of Energy (DOE) licensing strategy for spent fuel waste packages at Yucca Mountain over the entire operational life of the repository.

The Brookhaven National Laboratory (BNL) Waste Materials and Environment Modeling (WMEM) Program has been assigned the task of helping the DOE formulate and certify analytical tools needed to support and/or strengthen the Waste Package Licensing Strategy. One objective of the WMEM program is to perform qualitative and quantitative analyses of irradiated Zircaloy cladding. This progress report presents the early findings of an on-going literature evaluation and the results of the numerical implementation of two models of Zircaloy creep. The report only addresses cladding degradation modes within intact, dry waste containers. Additional degradation modes will be considered when the study is expanded to include moist environments and partly failed containers. Further updates of the present analyses will also be provided.

During the early stages of spent fuel isolation, the temperature inside the fuel rods is predicted to reach a maximum value of roughly 320° C. This temperature level will be maintained for a few decades, after which it will *slowly* decrease. Cladding temperatures will still be as high as 200° C one hundred and fifty years after disposal of the waste. These relatively high temperatures will cause the internal pressure of PWR fuel rods to reach pressure levels in the range of 35 to 130 atm depending on burnup, on the degree of initial pressurization of the fuel rods, and on the fission gas fraction which is not retained in the UO₂ pellets. By comparison, the internal pressures of PWR fuel rods during reactor operation for a period varying from 3 to 5 years are in the range of 38 to 150 atm. Unlike reactor operating conditions, however, there will be no external pressure to reduce the ΔP across the cladding wall during isolation. These unbalanced internal pressurization conditions are rather unique in the LWR fuel cycle. Similar conditions are obtained only during the dry storage of spent fuel. The basic difference between a dry storage and a dry isolation situation is that, in the former case, the initial temperature can be as high as 370° C, but it will decrease to below 200° C within a few years.

The Nuclear Regulatory Commission (NRC) has identified three potential failure modes for irradiated Zircaloy cladding while in dry storage: (a) creep rupture, (b) delayed hydride cracking (DHC), and (c) fuel-side stress corrosion cracking (FSSCC). Of these, only creep rupture was deemed capable of producing "gross rupture" of the cladding which could hinder later fuel handling and transportation operations.

BNL's preliminary conclusions on DHC agree with those of the NRC and others, in that it is believed that, for the overwhelming majority of fuel rods, DHC is not likely to be an important mode of failure. The Zircaloy cladding material of the fuel rods will contain hydrogen in amounts which will vary with the extent of fuel burnup, but will always lead to the formation of hydrides in the cladding. The hydrides will initially form in a predominantly circumferential orientation. If these hydrides do not reorient themselves radially during dry storage and isolation, failure due to DHC is considered extremely unlikely, even under worst-case conditions. In general, the stresses likely in spent fuel pin cladding are less than those usually considered necessary to cause significant reorientation, although an observation on an actual pin has indicated that reorientation could occur at lower stresses than originally thought. In actuality, it is recognized that some reorientation into the radial direction could conceivably result, the degree of which would be dependent on, among other factors, stress and temperature. Even though this should prove to be the case, the stress levels in the cladding will still be insufficient to initiate DHC, even under worst-case conditions, based on currently proposed threshold stress values.

With respect to FSSCC, the preliminary conclusions are again essentially in accord with those of the NRC, in that this is not believed to be an important mode of failure during storage and isolation. In the current evaluation, the assumption has been made that FSSCC requires the presence of iodine, although it is recognized that the actual situation is very complex and other elements may well contribute to the phenomenon. Based on observations on unirradiated materials, it is conceivable that iodine may be present in sufficient concentration to facilitate stress corrosion cracking but the stress levels in the cladding will be substantially below the threshold stress for the process. Even under "worst-case" conditions, failure due to FSSCC of only a very small fraction of spent fuel pins is considered extremely unlikely. At the present time, the susceptibility

of *irradiated* Zircalloys to FSSCC has not been evaluated and it is conceivable that this preliminary conclusion may be modified at a later date.

Creep rupture is potentially the most relevant failure mode as measurable Zircaloy creep takes place at relatively low stresses. Experimental studies of pre-irradiated and internally pressurized cladding tube samples have clearly demonstrated the occurrence of positive cladding hoop strains at 350° C under a tensile hoop stress of 50 MPa. Furthermore, the hoop strains continued to increase throughout 8,000 h of testing.

In their safety evaluation of spent fuel dry storage, the NRC has indicated that, where possible, creep modeling should be mechanistic. To that end, both the NRC and a DOE-sponsored dry-storage study program have implemented a diffusion-controlled cavity growth (DCCG) model to estimate the amount of grain boundary decohesion that would occur in cladding due to creep with the passage of time. The reference DCCG model was originally proposed in 1975 by Raj and Ashby (R&A) for predicting the intergranular fracture of metals at elevated temperatures. The model assumes that a fixed number of cavities exist initially. These cavities grow and eventually coalesce as stress is applied.

At BNL, we have implemented the original R&A model for the conditions expected during spent fuel isolation. Using the peak fuel temperature profile presented in the Yucca Mountain Site Characterization Plan (SCP) and the parameter values utilized by the NRC in their dry storage analysis, we found that the predicted amount of decohesion of the Zircaloy will exceed 15%, the maximum allowed by the NRC during dry storage. However, decreasing the temperature profile by 20° C would cause the predicted amount of decohesion to be less than the NRC limit. Sensitivity analyses with the model indicate that the predicted amount of decohesion is quite sensitive to all parameters tested and, therefore, the model is not an effective method for screening important variables.

The DCCG model has never been validated against actual data. The existing data on cavity nucleation in Zircaloy suggest that stable cavities are only rarely formed in Zircaloy-2 and -4 during reactor irradiation and that stress-induced cavities in unirradiated Zircaloys only appear at relatively large strains. For these reasons, it is not clear that the DCCG model provides meaningful predictions.

An experimental correlation which relates hoop strain, stress, temperature, and time is presently used by German researchers in support of spent fuel dry storage studies. This empirical correlation is based on isothermal, isostress, unirradiated Zircaloy creep data. At BNL, we have generalized the correlation to account for variations in temperature and stress with time. This generalized correlation has been used to determine the sensitivity of predicted hoop strain to variations in temperature, stress, and the empirical coefficients. Using the peak fuel temperature profile presented in the SCP, the original recommended values for the correlation coefficients, and the expected maximum value for the hoop stress, the model predicts a maximum strain of 0.125%. The sensitivity analysis indicates that it is unlikely that the variation in any single parameter from the recommended values will cause the strain to exceed 1%.

The correlation developed by the German fits their data well but it cannot be extrapolated with confidence to very long times. Other models based on theoretical grounds and experimental data are available which exhibit different, but probably more reasonable long term trends. At this time, we have not examined these models nor the data which support them in detail. This will be a subject of future study. Indeed, the experimental data base on creep behavior of internally pressurized Zircaloy tubes, although not very large, is comprised of more than the data used by the German to develop their correlation. Data exist for irradiated and unirradiated samples under a range of temperatures and stress levels. All of the data need to be reviewed in a systematic, comprehensive manner and compared with the predictions of the available models.

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LIST OF ABBREVIATIONS

DCCG	-	Diffusion Controlled Cavity Growth
DHC	-	Delayed Hydride Cracking
DOE	-	Department of Energy
EFPD	-	Effective Full Power Days
FSSCC	-	Fuel Side SCC
IDS	-	Inerted Dry Storage
ISCC	-	Iodine-induced Stress Corrosion Cracking
ISFSI	-	Independent Spent Fuel Storage Installation
MRS	-	Monitored Retrievable Storage
NNWSI	-	Nevada Nuclear Waste Site Investigations
NRC	-	Nuclear Regulatory Commission
PCI	-	Particle Cladding Interactions
SCC	-	Stress Corrosion Cracking
SCP	-	Site Characterization Plan
SER	-	Safety Evaluation Report
TSAR	-	Topical Safety Analysis Report

1. INTRODUCTION

Spent fuel cladding integrity is an important component of the Department of Energy (DOE) licensing strategy for spent fuel waste packages at Yucca Mountain over the 10,000 years design life of the repository. Credit for cladding performance is sought for both the expected case and the bounding case of Issue 1.4 (Substantially Complete Containment by the Waste Package) (Table 1) and for the bounding case and alternative cases of Issue 1.5 (Controlled Release of Radionuclides from the Waste Package) (Tables 2a and 2b).

The Brookhaven National Laboratory (BNL) Waste Materials and Environment Modeling (WMEM) Program has been assigned the task of helping the DOE formulate and certify analytical tools needed to support and/or strengthen the Waste Package Licensing Strategy. One objective of the WMEM program is to perform qualitative and quantitative analyses of irradiated Zircaloy cladding. Scope of the activity is to examine the technical literature on Zircaloy degradation and corrosion modes, to investigate implications to spent fuel isolation of the NRC position on cladding performance in allied fields, to indicate which failure modes are important and why, to apply models developed by the NRC and others in order to obtain reliable estimates of irradiated cladding performance, and to identify further data and modeling needs.

This progress report presents the early findings of an on-going literature evaluation. The report only addresses cladding degradation modes within intact, dry waste containers. Additional degradation modes will be considered when the study will advance to include moist environments and partly failed containers. Further updates of the present analyses will also be provided.

2. REFERENCE CONDITIONS

As long as the waste containers remain intact, the irradiated cladding will be exposed to a dry, inert gas atmosphere, possibly argon [SCP, 1988]. The inert atmo-

Table 1 Reference approach for Issue 1.4 (containment by waste package) [SCP, 1988].

Table 2.a DOE's Reference approach to resolving Issue 1.5 [SCP, 1988].

Table 2.b Alternative approaches to resolving Issue 1.5, assuming case of maximum water flux per package (20 liters per year) [SCP, 1988].

sphere is necessary to prevent the oxidation to U_3O_8 of the UO_2 contained in rods with failed cladding [SCP, 1988]¹.

The temperature of the fuel cladding is predicted to reach an early, maximum value of roughly 320°C after which it will slowly decrease. Temperatures inside the waste containers will be as high as 200°C one hundred and fifty years after disposal of the waste (Fig. 1). These relatively high temperatures will cause the internal pressure of the hottest fuel rods to reach pressure levels comparable with those achieved during reactor operation. In particular, based on the in-reactor values reported in Table 3, the internal pressure of PWR fuel rods under disposal conditions may reach values in the range of 35 to 130 atm, depending on burnup and on the degree of fission gas release from the fuel pellets². Unlike reactor operating conditions, there will be no significant external pressure to reduce the ΔP across the cladding wall. The resulting hoop stress on PWR cladding will be about eight times the internal pressure.

The above conditions are rather unique in the LWR fuel cycle and resemble those realized during interim, dry inerted storage of spent fuel regarding which a relatively large body of recent literature is available [Chin, 1989; Gilbert, 1988; Gilbert, 1989a; Peehs, 1986a], including the NRC licensing position on two dry storage cask facilities [Roberts, 1987; Levy, 1987]. The dry storage option is being increasingly pursued in the United States as the utilities find it more difficult to store the spent fuel in the reactor pools [Roberts, 1988 and 1989; Kapitz, 1989; File, 1989]. Dry storage of spent fuel has also been licensed in Canada, the Federal Republic of Germany, and Switzerland. The availability of a NRC licensing position on dry, inert gas storage of spent fuel should provide useful indications on avenues that could be explored for resolving licensing issues relating to what extent irradiated cladding may still be considered to be intact by the time a container fails.

¹ Not all leaking rods are identified and separately stored when they are discharged from the reactor. In older fuel (through the 1970's) one rod in one hundred would develop a pinhole defect. Later, fuel rods failures have been limited to about two to five in ten thousands through tighter fuel fabrication controls.

² In this country, PWR fuel rods represent the great majority of spent fuel rods and operate with higher internal pressures and thinner walls than BWR fuel rods.

Figure 1 Example of temperature histories of waste package components and host rock for a vertically emplaced spent fuel container [SCP, 1988].
(Note: "peak fuel" indicates "peak cladding temperature")

Table 3

Irradiation and Pool Storage Conditions for Water Reactor Fuels^a [IAEA, 1982]

Item	In reactor			In pool
	PWR	BWR	HWR	
Fuel centre temperature (°C)	1200–1700	1400–1800	1300–1700	100
ID clad temperature (°C)	340–370	320–360	300–350	30–60 ^b
Water temperature (°C)	300–330	260–330	260–300	20–50
Pressure inside fuel rod (atm)	38–150	5–49	23–100	(c)
Pressure outside fuel rod (atm)	140–160	70	70–110	2
Fission gases released to rod filler gas (%)	1–13	1–11	2–18	(d)
Assembly burn-up (GW·d/t U)	35	27	7	same
OD heat fluxes (W/cm ²)	100	70	100	0.03 ^e
Neutron flux, > 1 MeV (max.) (n/cm ² ·s)	(5–6) × 10 ¹³	(4–6) × 10 ¹³	(4–6) × 10 ¹³	10 ⁵
Gamma field (max.) (R/h)	~ 10 ⁹	~ 10 ⁹	~ 10 ⁹	10 ^{5e}

^a Peak values during normal operation.

^b Depends on water temperature and decreases with age of spent fuel.

^c One-half of the in-reactor pressure.

^d Additional fission gas release during storage is negligible.

^e Decreases with age of spent fuel.

An early assessment [Blackburn, 1978] identified the following potential cladding degradation mechanisms and causes for failure during dry storage:

1. Creep (stress) rupture
2. Mechanical overload
3. Fuel side stress corrosion cracking (FSSCC)
4. Fracture of flawed cladding
5. Delayed hydrogen cracking (DHC) and fatigue
6. Internal hydriding
7. Oxidation (internal of the UO₂ and external of the cladding proper)

Following the analysis of Rothman [Rothman, 1984] one can add one more failure mode to the above list, namely:

8. Alternative Pellet-Cladding Interaction (PCI)

The NRC has identified only creep rupture, DHC, and FSSCC as important failure modes during the dry storage of spent fuel (Section 3 of this report). The licenses that the NRC have granted allow temperature limits of 400° C and 370° C for five-year-old BWR and PWR fuel, respectively, based on applicant's suggested maximum hoop stresses of 60.7 and 66 MPa, respectively [NRC, 1985; Levy, 1987].

This progress report addresses the NRC position on irradiated cladding degradation while in dry storage and presents preliminary reviews of the creep rupture, DHC, and FSCC degradation modes within intact, dry containers identifying available models and data. Implementation of these models along with an update of the present findings, will appear in future progress reports.

Additional degradation modes will be considered when the study will address moist environments and partly failed containers.

3. THE NRC POSITION

In 1985 the NRC issued a favorable safety evaluation report (SER) of the spent fuel dry storage cask Castor V/21 manufactured by General Nuclear Systems, Inc. [NRC, 1985]. Based on that report a license was granted later to Virginia Power to operate an Independent Spent Fuel Storage Installation (ISFSI) at its Surry Power Plant.

Pursuant 10 CFR Part 72 Section 72(h), which regulated that *"The fuel cladding shall be protected against degradation and gross ruptures³,"* the NRC indicated that:

"For protection to be adequate, the design of the cask should be such that degradation after at least a twenty-year storage life should not preclude the ability of the cladding to resist gross rupture during normal operations associated with cask unloading and subsequent fuel rod handling operations.

After reviewing the current research relating to spent fuel cladding damage mechanisms, the reviewers concluded that a diffusion controlled cavity growth (DCCG) mechanism was the only mechanism of damage for dry storage applicable to the storage conditions of the fuel rods that could cause degradation and gross rupture of the cladding. Under the influence of stress and temperature, this damage mechanism progresses by nucleation and growth of cavities along grain boundaries. This damage mechanism is serious since it can progress without external evidence of damage, may not cause pin holes or through cracks to relieve the internal pressure, and manifests itself by a sudden non-ductile type of fracture. The staff has therefore paid particular attention to evaluating the potential for cladding damage from this mechanism for the conditions of storage specified in this TSAR." [NRC, 1985, p. 12].

While it is interesting to see how manifest the NRC concern is regarding creep damage, the indication that *"avoidance of gross ruptures"* should be related to subsequent operations with the fuel is also interesting. The same indication certainly applies to the potential licensing of the MRS facility [Roberts, 1989] and might also be invoked for the mandated waste retrievability option for 50 years from the beginning of waste acceptance operations at the repository.

³ Text later amended to read: *"The spent fuel cladding must be protected during dry storage against degradation that leads to gross ruptures or the fuel must be otherwise confined such that degradation of the fuel during storage will not pose operational safety problems with respect to its removal from storage."* [FR, 1988]

In this document the NRC indicates further that the Larson-Miller approach for extrapolating short-term creep damage data to the long term is not acceptable. Namely:

"Creep rupture is a potential failure mode under dry storage conditions. Researchers have demonstrated that using a Larson-Miller approach, temperature limits from 380°C (716° F) to 400° C (752° F) could be tolerated for creep rupture lives well beyond that required for interim storage of spent fuel. The Larson-Miller approach, however, is somewhat empirical ... predictions based on a Larson-Miller approach are clouded with sufficient uncertainty to warrant a more fundamental approach to cladding degradation under creep conditions." [NRC, 1985, p. 33].

The Larson-Miller approach is at the heart of the analyses based on which the DOE's Site Characterization Plan (SCP) regards creep rupture to be unimportant (see Sections 3 and 5.1.1 in this document).

The NRC utilized a diffusion-controlled cavity growth model (DCCG) to analyze the accumulation of creep damage with stress and temperature. As a measure of damage, the NRC considered the fraction of grain boundary area undergoing decohesion according to a model developed by Raj and Ashby [Raj, 1974]. A fractional decohesion of less than 15% over twenty years was considered sufficient for granting a license. Namely:

"The progress of damage based upon the applied methods indicated the area of decohesion after 20 years of storage would be less than 15%. Based upon the degree of conservatism maintained throughout the analysis, it can be concluded that this level of damage is insignificant and would not be exceeded." [NRC, 1985, p. 33].

The NRC model has been reviewed recently [Levy, 1987] and shown to be in substantial agreement⁴ with a more complex model for Zircaloy degradation developed at PNL and based on deformation and fracture maps developed by Chin and co-workers (Section 5.1.2). A computer code, named DATING, implementing Chin's suggested equations is to be released [Gilbert, 1989b] through the National Energy Software Center at Argonne National Laboratory. A report illustrating the code is available [Simonen, 1988]. The NRC licensing model and licensing position has been recently re-presented, unchanged, in the open literature [Schwartz, 1989].

In other parts of the Castor V/21 SER the NRC clarifies its position on other failure modes. With regard to stress corrosion cracking of the cladding, the NRC notes that:

"Stress corrosion cracking (SCC) occurs as a result of a synergistic combination of a susceptible material, an aggressive environment and high stress. The corrosive environment associated with SCC of fuel rods has been attributed to fission products generated during reactor irradiation....SCC may also be related to pellet cladding interaction (PCI), this has only been observed during reactor operation due, in part, to the large external pressure on the fuel rods. The only known cause of cladding failure due to SCC occurred in a reactor during a ramp-up. No other failures from this cause are known to have occurred either during pool storage or under dry storage conditions. One explanation may be the pellet temperatures during dry storage are much lower than those in a reactor. Consequently, the accumulation of fresh fission products at the cladding is slowly reduced during dry storage. Furthermore, the activation of SCC requires stress levels substantially above those that can reasonably be expected to prevail under dry storage conditions. The possibility exists, however, that cracks may be present that were initiated during reactor operation. Under these conditions, the stresses generated at the crack tips may be large enough to cause crack extension. However, should such a crack penetrate the

⁴ Levy did not realize that he was actually utilizing a *modified* NRC model, therefore, his conclusions may not be valid.

cladding, it is likely that the internal pressure will be relieved and, as a consequence, effectively terminate the progress of the SCC damage mechanism. The staff concludes, therefore, the SCC is not a damage mechanism that can lead to gross rupture of the fuel and cladding." [NRC, 1985, pp. 31-32].

When the above criteria are applied to the Yucca Mountain Project, it appears that, if the DOE is to seek credit for cladding integrity, the question should be addressed of the number of failures that could take place due to crack propagation from cracks which were produced during reactor operation. Cracks could also be produced during rod consolidation and handling operations, as implied by a rod consolidation study [EPRI, 1989]. Unfortunately one should be made aware that *"little data is (sic) available on the flaw size distribution of irradiated Zircaloy cladding"* [Tarn, 1986]. The latter item will be addressed in future progress reports.

FSCC is addressed in Section 5.3 of this report.

Another failure mode, delayed hydride cracking, is addressed by the NRC as follows:

"...the hoop stresses in the cladding are not expected to be high enough to cause a radial orientation of the hydride and consequent crack initiation. It is remotely possible that pre-existing cracks under stress can induce the diffusion of oxygen to the crack tips where substantially higher concentrations could precipitate hydride in a manner that would encourage crack extension. However, as is the case of SCC, crack propagation would result in a loss of fuel rod internal pressure and termination of the damage mechanism. The staff concludes, therefore, the delayed hydriding is not a damage mechanism that can lead to gross rupture of the fuel rod cladding." [NRC, 1985, pp. 32-33]

DHC is reviewed in Section 5.2 of this report.

One last item to be considered is that the NRC relates "failure" to "gross rupture" of the cladding. Such failures, if they were to occur, would hinder spent fuel handling operations. The SCP licensing strategy for spent fuel waste packages (Tables 1, 2a and 2b) appears to be more stringent. Although no final position has been adopted, in this case pinholes or microscopic through-cracks might be construed as cladding failures. This needs to be taken into account when drawing conclusions as to the relative importance of different cladding degradation modes.

4. THE POSITION EXPRESSED IN THE SCP

According to Chapter 7 of the SCP, only DHC is of concern during the dry, inert-gas isolation period, while FSSCC and stress rupture are deemed not to be important. This contradicts a large body of literature [Blackburn, 1978; Peehs, 1980; 1982; NRC, 1985; Kaspar, 1985; Tarn, 1986; Chin, 1986; Cunningham, 1987; Chin, 1989; Schwartz, 1989] which identifies creep or stress rupture⁵ as the rate limiting failure mode during the dry, inert phase. To that effect, it must be noticed that the SCP analyses are based on experimental work utilizing the Larson-Miller parameter extrapolation approach. The latter has been found unacceptable by several reviewers (see Section 5.1.1 in this document) including the NRC.

In accordance with the indications of Chapter 7, Chapter 8 of the SCP indicates that the "planned test matrix" only contemplates checking the mechanical strength of the cladding under a wide range of hydride densities and orientations. When these tests are performed with overpressurized cladding, they may yield information on the role of stress (creep) rupture.

⁵ The SCP refers explicitly to *stress rupture* which occurs "when internal pressure from the gas inside the fuel rod exceeds the strength of the cladding material. Failure occurs after a period of time under stress and depends on the stress applied, which is a function of the temperature." Most of the available analyses concentrate, however, on creep rupture, i.e., they consider the contribution of creep to the failure process.

5. REVIEW OF FAILURE MODES AND THEIR MODELING APPROACHES

5.1 Creep Rupture

Failure by creep rupture is the end result of accumulation of damage during creep and is directly related to the presence of relatively high gas pressures within the fuel rods. The presence of stress in general, and high hoop stress in particular, may combine with the presence or growth of microscopic cavities/cracks within the material which produce an effective thinning of the cladding wall and therefore an acceleration of the creep phenomenon. Thus, a necessary condition for creep rupture is a rod which is still pressurized, while incipient defects represent a cause for creep rupture acceleration. There exist several approaches to modeling creep rupture. One approach, which has been already commented upon, utilizes a Larson-Miller parameter extrapolation of short term data to the long term; another approach is mechanistic in nature, e.g., the modeling approach taken by the NRC and briefly mentioned earlier; a third approach combines basic creep engineering equations with information from microstructural analyses; and a fourth approach, which has been implemented in Germany (and possibly other countries), utilizes empirical correlations derived from laboratory test data.

5.1.1 The Larson-Miller approach to data extrapolation

Both analyses referred to in the SCP [Rothman, 1984; Einziger, 1983], which consider stress-, and therefore, creep-rupture unimportant, utilize the Larson-Miller parameter to extrapolate short-term data to the long-term. Larson-Miller's is only one of many approaches used to correlate the combined effect of stress-and-temperature to time-to-rupture in engineering materials [Finnie, 1959]. This method of extrapolating data becomes questionable when extrapolation is required to time scales much larger than the test data. A large error may result even from a small degree of extrapolation, although this might be offset by taking conservative values for the reference data⁶. The

⁶ Einziger indeed utilized "...a conservatively modified Larson-Miller curve to provide a lower bound on permissible maximum dry-storage temperatures, assuming creep rupture as the life limiting mechanism." According to Einziger, "If hydride reorientation can be ruled out during dry storage, 305° C is a conservative lower bound, based on the creep rupture mechanism, for the maximum storage temperature of rods with irradiation hardened cladding to ensure a 100-yr cladding lifetime in an inert atmosphere."

assessment made by Finnie in 1959 is still valid nowadays, namely:

"There is, of course, a limitation by which the testing time can be decreased ... The loading conditions may strongly influence the rupture life in short-time tests, and even more important, the temperature required in short-time tests may be sufficient to cause grain growth, phase changes, or other effects in the material. Conversely, such effects as recrystallization, precipitation, and oxidation which may not be revealed by short-time tests can lead to faulty prediction. Extrapolation beyond the tested values of the parameters is also uncertain." [Finnie, 1959, p. 248].

The more recent assessment by Cunningham [Cunningham, 1987], which is inspired in turn by the work of Chin and co-workers [Chin, 1986] (see also [Chin, 1989]) states that:

"Empirical models such as the Larson-Miller parameter approach (Blackburn et al., 1978) overestimate the rupture times for dry storage temperatures and stress. The empirical models incorrectly assume that behavior evaluated at high temperature and stress levels, with high temperature and stress dependencies, may be adequately extrapolated to low temperature and stress levels. However, the temperature and stress dependencies found at high temperatures and stresses do not exist at low levels; therefore, empirical models underestimate the creep rate at dry storage conditions and overestimate failure times."

The NRC position on the utilization of the Larson-Miller approach is likewise negative and it has been reported earlier in Section 3 of the present document. It thus appears unlikely that a license application based only on Larson-Miller interpreted data would be acceptable, if credit were sought for the performance of the cladding.

5.1.2 Mechanistic modeling approaches

Recent mechanistic modeling approaches of creep rupture examine the detailed processes of creep degradation. Chin and co-workers appear to be the authors who have applied most consistently a mechanistic modeling approach to Zircaloy creep rupture. To that effect they have produced deformation and fracture maps of the material in the unirradiated state⁷ over a wide range of temperatures and stress levels [Chin, 1989].

In particular, with reference to Figures 2 and 3, respectively, nine creep deformation processes and four fracture mechanisms have been addressed. Among the fracture mechanisms, diffusion-controlled cavity growth dominates in the stress-temperature region expected for spent fuel isolation.

Associated with each fracture mechanism is an equation⁸ for estimating time-to-failure (Tables 4.a and 4.b) which may depend on the strain rate, $d\epsilon/dt$. When this is the case, the strain rate is obtained from the creep deformation map or its associated equations.

In Chin's approach, the time-to-failure expressions for each mechanism are to be combined with a life fraction rule to calculate the amount of useful life expended. The life fraction rule is expressed as follows:

$$\sum_{i=1}^N \frac{\Delta t_i}{\tau_i} = 1,$$

⁷ "Unfortunately, definitive postirradiation rupture data describing the low stress, low temperature, and long term failure behavior of irradiated Zircaloy cladding do not exist," [Chin, 1989]. This statement, however, should be reconsidered in the light of the data reported in Section 5.1.4 of this document and of the work of Griffiths [Griffiths 1988a; 1988b], Yang [Yang, 1988], [Einzinger, 1983] and others.

⁸ As Chin acknowledges "there is much debate over the equations describing different fracture mechanisms," [Chin, 1986].

Figure 2 Deformation map for Zircaloy with constant stress and strain rate contours (strain rate is in s^{-1}) adapted from [Chin, 1989].

Figure 3 Fracture map for Zircaloy showing dominant fracture mechanisms adapted from [Chin, 1989].

Table 4.a

Fracture Equations

Theoretical shear strength	$\sigma_{th} = \left(\frac{E\gamma_f}{a_0} \right)^{1/2} = \frac{E}{10}$
Transgranular fracture	$t_f^{TG} = \left[\epsilon_n + \left(\frac{1}{4.937} \right) \left(\frac{n}{n-1} \right) \ln \left(\frac{0.38}{f_v^{1/2}} - 1 \right) \right] \dot{\epsilon}^{-1}$
Triple-point cracking	$t_f^{TP} = \frac{\gamma_f}{Ed\xi} \left(\frac{\sigma}{E} \right)^{-1} \dot{\epsilon}^{-1}$
Cavitation-diffusional growth	$t_f^{CD} = \frac{2.525 \times 10^{-3} l^3}{\delta D_{ogb} b^2 \exp \left(\frac{-Q_{gb}}{RT} \right)} \left(\frac{kT}{Eb} \right) \left(\frac{\sigma}{E} \right)^{-1}$
Cavitation-power law growth	$t_f^{CP} = \left[\frac{(1 - 0.78 P_0 l_0)}{4.87} \right] \dot{\epsilon}^{-1}$

Table 4.b

Symbols and Coefficient Values for Fracture Equations

t_f	= time to fracture (s)
ϵ_n	= hole nucleation strain = 0.08
f_v	= volume fraction of intragranular inclusions = 0.025
P_0	= average particle diameter = 10 nm (100 Å)
l_0	= particle spacing along boundary = 2.0×10^{-6} m
ξ	= $\dot{\epsilon}_{GBS}/\dot{\epsilon}$ = contribution of grain boundary strain rate to total strain rate = 0.2
l	= average cavity spacing = 2.6×10^{-6} m (6/grain segment)
δ	= width of grain boundary = 1.6×10^{-8} m (50 Burger's vectors)
γ_f	= free surface energy created by fracture = 35 J/m ²
a_0	= lattice spacing (m)
σ_{th}	= maximum theoretical stress

D_{ogb} = Grain boundary self-diffusion coefficient = 3.89×10^{-6} m²/sec.

Q_{gb} = Activation energy for grain boundary diffusion = 175 kJ/mol

b = Burger's vector = 3.23×10^{-10} m

E = Young's modulus

where Δt_i is the time spent at the i -th temperature and τ_i is the time necessary to fracture a specimen under isothermal and isostress conditions due to each specific mechanism starting from zero damage. When the summation of the life fractions, $\Delta t_i/\tau_i$, reaches one, the material is assumed to have failed.

5.1.2.1 Diffusion-controlled cavity growth

Focusing our attention on the diffusion-controlled growth of voids, as it has been reported (also by the NRC) to dominate the predictions under inert storage conditions, one may observe that, in metals, cavitation failure is experimentally observed under conditions of relatively low stress and high temperatures. Most commonly, cavities appear on boundaries which lie roughly perpendicular to the maximum tensile stress direction. Their presence reduces the section and so accelerates the creep which, in turn, increases the rate at which the damage grows. At low stresses the damage is void-like; at high stresses, the voids may link to give grain boundary cracks. Many pure metals and industrial alloys can fracture by this mechanism alone, including the important nickel-base superalloys and the ferritic and austenitic steels, though it is more usual for other mechanisms to contribute also [Ashby, 1984]. The holes take on a variety of shapes depending on their spacing and on the temperature and strain rate.

Cavity nucleation under an applied stress occurs during grain boundary sliding at sites where the stress concentration is sufficiently high, such as at grain boundary corners, steps, and second phase particles along the boundaries (Fig. 4a). The experimental evidence quoted by the NRC and Chin of stress-induced cavities has been reported by Keusseyan [Keusseyan, 1985], who observed 0.1 μm or larger voids in creep-tested, unirradiated specimens of Zircaloy-2 and Zircaloy-4. The Zircaloy-2 data were obtained within a temperature range of 350 to 400°C with initial stresses between 72.4 and 132 MPa (Table 5 and Figures 4b and 4c). The grain boundary cavities in Zircaloy-4 were found after subjecting the specimens to creep for 10 days at 375°C with an initial stress of 132 MPa. The temperatures at which these tests were performed are not foreseen to be reached at Yucca Mountain. Also, the stress levels that were utilized in these tests represent the extreme upper range of stress values that can be achieved in spent fuel under disposal conditions. It must be further noticed that extrapolating Keusseyan's data

Figure 4a Schematic diagram of grain boundary cavity nucleation sites at grain boundary corners, steps and second phase particles.

Table 5

Summary of Experimental Results on Cavity Nucleation Rate in
Unirradiated Zircaloy-2

$T(^{\circ}\text{C})$	σ_0 (MPa)	$\dot{c}$ (1/sec)	$\dot{n}(10^{-10}\text{mm}^{-2}\cdot\text{sec}^{-1})$
350	118	1×10^{-7}	2.53
350	132	3.5×10^{-7}	2.395
375	118	3.26×10^{-7}	2.63
375	132	6.7×10^{-7}	2.208
400	72.4	1×10^{-8}	0.1
400	92.4	5×10^{-8}	0.8
400	116	8×10^{-7}	6.04
400	132	3×10^{-6}	0.2

Figure 4b Creep cavity nucleation data for Zircaloy-2 at 350°C and 375°C.

Figure 4c Creep cavity nucleation data for Zircaloy-2 at 400°C.

of Figures 4b and 4c towards lower temperatures and stress levels, one would expect cavities to be formed only with creep strains in excess of 1%. The latter value is probably not going to be exceeded under dry, spent-fuel isolation conditions as a 1% hoop strain has been proposed by German researchers (see Section 5.1.4) as the maximum allowable value for the hoop strain during dry storage of the fuel. Further data on stress-induced cavity nucleation appear to be lacking.

Neutron irradiation at temperatures above 400° C can also induce the nucleation of cavities in zirconium and Zircaloy-2 [Griffiths, 1988a and 1988b]. This phenomenon is much less pronounced in Zircaloy-2 which shows instead a high concentration of vacancy c-component loops which are thought to compete for vacancy point defects. A recent examination of irradiation-induced defects in neutron irradiated Zircaloy-4 [Yang, 1988] has also shown the development of c dislocations, but has failed to observe the presence of cavities. c-component loops formed during neutron irradiation are indeed more common than previously thought. They have been observed at temperatures between 285 and 500° C and range in size from about 0.1 to 1.0 μm in diameter depending on the temperature. According to Griffiths [Griffiths, 1988a], in many cases they are directly responsible for increased irradiation-induced growth and creep.

Models of creep due to cavity growth

The nucleation process of intergranular cavities is not well understood [Tarn, 1986], therefore cavitation models normally assume a fixed initial number of cavities with growth beginning upon the application of stress. This is the approach taken by the NRC and Chin and co-workers.

Both the NRC and Chin implement a diffusion-controlled cavitation model derived from one paper by Raj and Ashby [Raj, 1975] (referred to as R&A, hereafter). The model has been obtained from theoretical considerations on the intergranular fracture of metals at elevated temperature⁹ and has not been validated against Zircaloy creep data.

⁹ The experimental data utilized to illustrate the theory refer to copper polycrystals with a grain size of 10 micrometers.

The model by R&A rests on the following assumptions:

1. A fixed initial number of voids are present in a periodic array which can grow as soon as stress is applied to the specimen;
2. Inclusion-free boundaries;
3. Only two-grain boundary junctions are present;
4. The stress is applied normally to the grain boundary;
5. Growth of the void volume occurs by diffusion of matter away from the void surface along the two-grain boundary.

A geometrical representation of the model is reported in Figure 5. Volume diffusion appears in the figure but it is not taken into account by the NRC and Chin, although an addendum to the boundary diffusion model, also suggested by R&A, would make it possible.

Figure 5 A periodic array of voids in a grain boundary. A tensile stress of σ_{∞} is applied normal to the boundary [Raj, 1975].

In terms of $A(t)$, the fractional amount of grain boundary area which has undergone decohesion by time t , the R&A model predicts the rate of decohesion to proceed as follows:

$$\frac{dA}{dt} = \frac{32}{3\pi} \frac{[F_B(\alpha)]^{3/2}}{F_V(\alpha)} \frac{\Omega D_B \delta}{k T} \sigma \rho^{3/2} f(A) \quad (1.a)$$

where

$$f(A) = \frac{1 - A}{\sqrt{A}} \frac{[1 - (r_c/r) (1-A)]}{-0.5 \ln(A) - 3/4 + A(1 - A/4)} \quad (1.b)$$

Equation (1.a) is to be solved with the initial condition:

$$A(0) = A_{\min} = \frac{r_c^2 F_B(\alpha) \rho}{\pi} \quad (1.c)$$

In the equations above, the indicated parameters are interpreted as follows:

- α - contact angle to the grain boundary; $\alpha = \cos^{-1}(\gamma_B/2\gamma)$, where γ_B is the energy per unit area of the grain boundary surface and γ is the energy per unit area of the free surface of the void,
- Ω - atomic volume of metal,
- ρ - number of voids per unit area in the grain boundary;
 $\rho = 1/(2\ell)^2$, where 2ℓ is the average distance between cavities,
- δ - boundary thickness,
- σ - externally applied stress,
- D_B - grain boundary self-diffusion coefficient,
- k - Boltzmann constant,
- r - radius of curvature of the void surface,
- r_c - critical radius for void nucleation; $r_c = 2\gamma/\sigma$, where γ is the surface free energy per unit area of the matrix material,

and:

$$F_B(\alpha) = \pi \sin^2(\alpha),$$

$$F_V(\alpha) = \frac{2\pi}{3} [2 - 3 \cos(\alpha) + \cos^3(\alpha)]$$

The functions F_V and F_B are related to the void volume, V , and to the boundary area, B , it replaces through the following relations:

$$V = r^3 F_V(\alpha)$$

and

$$B = r^2 F_B(\alpha).$$

Chin's equation for time-to-failure, t_f^{CD} , under cavitation diffusion conditions (Tables 4.a and 4.b) appears to have been obtained from Equation (1.a) upon integrating it under *constant* temperature and stress conditions between $A_{min}=0$ and $A(t_f)=1$ after the introduction of suitable values for the dihedral angle, α , and for r_c . The latter values are not reported in the original papers. The important observation, however, is that Chin's expression for t_f^{CD} does not display a dependence on the area of decohesion.¹⁰

The NRC [NRC, 1985] re-expresses Equation (1.a) as follows¹¹:

$$\int_{A_i}^{A_f} \frac{dA}{f(A)} = \int_0^{t_f} G(t) dt, \quad (2.a)$$

¹⁰Note, that in Chin's expression for t_f^{CD} , decohesion is supposed to start from zero damage in each temperature and stress-level interval considered. Since the rate of damage accumulation in the R&A model depends on the degree of damage already accumulated at a given time, Chin's application of the life fraction rule may result in non-conservative, non-realistic predictions of damage (see also Section 5.1.5.1).

¹¹While Equation (2.a) is formally correct, the NRC report has obvious typos in the expression for $G(t)$, Equation (2.b), and in the expression for $f(A)$.

where

$$G(t) = \frac{32}{3\sqrt{\pi}} \frac{[F_B(\alpha)]^{3/2}}{F_v(\alpha)} \frac{\Omega D_B(t) \delta}{k T(t)} \sigma(t) \rho^{3/2} \quad (2.b)$$

The NRC reports that *"Much of the review effort focused on establishing the values of the parameters of the above expressions. Where there was wide divergence in reported values, the value that led to the most conservative result was selected."* The selected values and expressions were:

$$\begin{aligned} \alpha &= 50^\circ, \\ \Omega &= 3.37 \cdot 10^{-29} \text{ m}^3/\text{atom}, \\ \delta &= 9.69 \cdot 10^{-10} \text{ m}, \\ 2\ell &= 10^{-5} \text{ m}, \end{aligned}$$

and:

$$D_B = 5.9 \cdot 10^{-6} \exp(-131/RT) \text{ m}^2/\text{sec},$$

where R is the gas constant in units of $\text{kJ/mol}^\circ\text{K}$. The NRC calculational approach has been recently presented in the open literature [Schwartz, 1989]. A further observation is that the NRC only allows up to 15% decohesion, i.e., $A_t = 0.15$ in Equation (2.a).

Levy has compared the predictions of a *modified* NRC model, whereby $A_i=0$ and $f(A)=1$ in Equation (2.a), with the predictions from Chin's model. He concluded that the predictions of the NRC model and those of Chin's are compatible as long as the hoop stress is below 130 MPa [Levy, 1987]¹².

¹²Levy did not realize that he was actually utilizing a *modified* NRC model, therefore his conclusions are not valid.

5.1.3 A unified continuum and micromechanistic approach

Ashby and Dyson have recently proposed new sets of equations to describe creep damage accumulation in metals during tertiary creep [Ashby, 1984]. Their new approach combines ideas of continuum mechanics, typical of an engineering approach to creep design, with information based on microstructural observations or physical reasoning, typical of a materials science approach. The new approach represents further modeling development by one of the original authors (Ashby)¹³ of the model implemented by the NRC and Chin.

Ashby and Dyson (A&D, hereafter) distinguish four broad *categories* of creep-damage each one containing one or more than one *mechanism* of creep acceleration. These categories are:

1. **Damage through loss of external section:** This addresses deformation without volume change, e.g., during creep under a constant tensile load the section decreases, stress slowly increases, and the creep rate accelerates. In the absence of other damage mechanisms, failure occurs when the material necks to a point. Usually, other damage mechanisms intervene and failure occurs at a finite reduction in area.
2. **Damage through loss of internal section:** (a) formation of holes either within the grains or at grain boundaries (cavitation), and (b) growth of a single dominant crack.
3. **Damage by degradation of the microstructure:** (a) thermal-coarsening of particles which produces creep acceleration, and (b) substructure-induced acceleration of creep.

¹³Between 1975 and 1984 M. F. Ashby has produced other creep modeling papers one of which, with A. C. F. Cocks, is especially noted [Cocks, 1982] although it is not reviewed hereafter because it preceeds the 1984 report.

4. **Damage by gaseous-environmental attack:** (a) creep acceleration due to internal oxidation, (b) creep acceleration due to failure of external oxide.

A&D suggest that each of the above mechanisms can be described by a pair of coupled differential equations, one describing the rate of damage accumulation, the other describing the strain rate. Namely:

$$dA/dt = f(\sigma, T, A) \quad (3.a)$$

$$d\epsilon/dt = g(\sigma, T, A) \quad (3.b)$$

The time to failure, t_f , is obtained by integrating the first equation; the strain to failure, ϵ_f , and the creep damage tolerance, λ , by integrating the second.

The reference equation for hole growth by surface diffusion in the grain boundaries is:

$$f(\sigma, T, A) = \frac{16 \Omega D_B \delta \sigma^3}{k T (\sigma_0)^2} \rho^{3/2} A^{1/2} (1-A)^{-3} \quad (4)$$

where A is the fractional area of grain boundary decohesion, σ_0 is a temperature-dependent material property, and all other parameters are the same as for Equation (1.a) .

Besides its obvious relevance to creep modeling, the A&D report also indicates that important information about the dominant tertiary creep mechanisms of a material can be obtained simply from the shape and scale of the creep curve. With reference to Figure 6, this information is contained in the quantities C_m (the Monkman-Grant constant), ϵ_f , and λ , all of which can be read from a single creep curve. As an example, when creep occurs at constant stress, void growth mechanisms all lie within the areas delineated by $\lambda = 1$ and $\lambda = 2.5$. In this approach, careful microscopy would be utilized only for confirmation purposes.

Figure 6 Ashby and Dyson's diagnostic diagram for creep failure modes. [Ashby, 1984].

5.1.4 Experimentally-based creep correlation

Data on the creep behavior of pre-irradiated and internally pressurized Zircaloy have been generated in Germany¹⁴ in support of dry storage studies of spent fuel [Kaspar, 1985; Peehs, 1986a; Peehs, 1986b]. The post-pile creep program consisted of two sets of experiments.

In one set of experiments 14 PWR cladding samples were pre-irradiated in the research reactor Geestacht FRG-2 at a temperature of 400° C in the presence of a fast neutron flux of about $3 \cdot 10^{13}$ n/cm²sec with irradiation periods of 540 and 1170 h.

¹⁴Further creep data and models from other sources have been recently identified and will be analyzed in future progress reports.

During irradiation these samples were also kept under tensile and compressive hoop stresses varying between 70 and 120 MPa. After removal from the reactor the samples were creep-tested at 380° C for the first 1,000 h and at 395° C thereafter, up to 8,000 h, with a tensile hoop stress of 70 MPa. The resulting hoop strains as a function of time are reported in Figure 7a and are compared with the prediction of a strain-stress-temperature correlation obtained from internal-pressurization creep data of unirradiated Zircaloy at temperatures varying between 250 and 400° C with hoop stress levels of 150 MPa and 200 MPa [Peehs, 1986a]. The empirical correlation reads as follows:

$$\epsilon (\%) = 1.89 \cdot 10^{-3} \cdot \left[\frac{610}{T} - \frac{\ln(\sigma/450)}{\ln(t)} - 1 \right]^{-2.58} \quad (5)$$

where σ is the hoop stress in MPa, T is the reference temperature in degree Kelvin, and t is the time measured in hours.

The data of Figure 7a would show then that, up to a temperature of 400° C and for the relatively small neutron fluences ($\approx 10^{20}$ n/cm²) that were utilized, the irradiated material is more creep-resistant than the unirradiated material.

In the second set of experiments PWR cladding samples were pre-irradiated in the Obrigheim power plant. The irradiation lasted up to 5 reactor cycles corresponding to up to 1,500 days. The irradiation temperature was about 300° C. The samples had an initial internal overpressure, at room temperature, of 32 atm, which lead to an in-reactor compressive hoop stress of about 65 MPa. The total fast neutron fluence was in the range of 0.5 to $1 \cdot 10^{22}$ n/cm². These samples, except for two that lost the internal pressure, were later creep-tested at 350° C corresponding to an internal pressure of 69 atm and to a tensile hoop stress of 50 MPa. The resulting hoop strain data, along with the predictions of Equation (5), are reported in Figure 7b. As it can be seen, Equation (5), which is based on unirradiated Zircaloy data, predicts very closely the average of the data referring to the irradiated cladding. The slope of the curve, however, appears to decrease faster than that of the experimental data and it becomes questionable whether very long term predictions based on Equation (5) are realistic. Peehs and co-workers [Peehs, 1986a] are of the opinion that the latter is the case and have implemented

Figure 7a Hoop strain of pre-irradiated Zircaloy cladding creep-tested with a tensile hoop stress of 70 MPa. The absolute error of the strain data points is $\pm 0.05\%$.

Figure 7b Hoop strain of pre-irradiated Zircaloy cladding creep-tested with a tensile hoop stress of 50 MPa. The absolute error of the reported data points is $\pm 0.02\%$.

Equation (5) in a computer code, named TRAB, for predicting spent fuel dry storage behavior. These authors also assume a hoop strain safety value of 1% as a sufficient value to insure against any future creep rupture of the cladding.

Interestingly, when the two samples that lost pressurization while in-reactor were heated to 350° C, it was found that creep still occurred even though no stress was applied (Figure 8). This phenomenon has been explained with the accumulation of residual stresses during reactor operation which are able to manifest themselves once the reactor coolant overpressure is no longer present and the temperature has reached a high enough value. The existence of strain not related to a directly applied stress and having the same direction as the post-irradiation creep strain and still increasing after 8,000 hours at 350° C *"may consume some of the supposed conservatism"* [Kaspar, 1985] of Equation (5). It is not clear whether this effect would exist at 320° C, the present maximum envisioned temperature of the cladding under disposal conditions (Fig. 1).

Figure 8 Creep strain of 2 irradiated cladding samples without applied stress.

5.1.5 Sensitivity Analyses

Sensitivity analyses of Zircaloy performance were conducted using the R&A model discussed in Section 5.1.2.1 and Peehs' correlation, Section 5.1.4. These analyses were performed to determine predicted performance while using the temperature profile presented in the SCP, (Fig. 1), and to determine the key variables of each equation.

5.1.5.1 The R&A Model

The R&A model was developed in 1975 and was presented in Equations (1.a) - (1.c). This model attributes failure to the growth of pre-existing cavities along the grain boundaries. Variations of this model have been applied by the NRC [NRC, 1985; Schwartz, 1989] and Chin and co-workers [Chin, 1983; Chin, 1986; Chin, 1989; Santanam, 1989] and others [Levy, 1987; Simonen, 1988].

Although, the R&A model has gained wide acceptance, the model appears to lack an experimental basis with regard to Zircaloy performance. Serious shortcomings of the model include: 1) no experimental verification of the model has ever been attempted; 2) stable cavities are only rarely formed during reactor irradiation of Zircaloys; and 3) stress-induced cavity nucleation and growth has been observed in only one instance in unirradiated Zircaloys. In this case, the stress, temperature, and strains were atypical of spent fuel isolation conditions.

With these shortcomings in mind, we have implemented the R&A model as described in the original paper, that is, we have solved Equations (1.a) - (1.c) allowing for temporal changes in the temperature, the stress, and the diffusion coefficient.

The R&A model (Section 5.1.2.1) assumes a fixed initial number of cavities along the grain boundaries with growth beginning upon the application of stress. The growth rate is expressed as the fractional grain boundary area undergoing decohesion per unit time and depends on: 1) initial cavity spacing; 2) normal stress; 3) temperature; 4) grain boundary self-diffusion coefficient; 5) dihedral angle; 6) grain boundary thickness; and 7) the amount of decohesion already present. As more decohesion takes place, less

area is available to transmit the stress and higher stresses occur, which makes the differential equation non-linear. The NRC considers greater than 15% decohesion as a failure for dry storage systems.

We have conducted sensitivity studies on the effects of varying cavity spacing, temperature, initial pressure, and dihedral angle. In each of these studies, all parameters except one were held constant. The reference values for the relevant parameters were taken from the NRC analysis for inert dry storage with an exception for the dihedral angle. The latter was taken to be 75° and not 50°, for internal consistency with the original R&A model which assumes inclusion free boundaries.

For these calculations we assumed, as the reference, the peak fuel temperature profile of Figure 1, taken from the SCP. This profile peaks after four years at 322° C [O'Neal, 1984]. For conservatism it was assumed that the temperature is constant for the first four years. The internal pressure of the fuel rod was assumed to be related to the temperature through the ideal gas law. The hoop stress, σ , was calculated using the equation for an internally pressurized thick-walled vessel.

The base case parameters for the analysis are:

- $P = 8.25 \text{ MPa at } 370^\circ \text{ C, (NRC dry storage value)}$
- $\sigma = 65.4 \text{ MPa at } 322^\circ \text{ C,}$
- $\alpha = 75^\circ, \text{ dihedral angle,}$
- $\lambda = 10^{-5} \text{ m, cavity spacing (NRC dry storage value).}$

The diffusion coefficient, atomic volume, and the value of the Burger's vector are the NRC values presented in Section 5.1.2.1.

The results of the analyses suggest that the fractional decohesion area is sensitive to all the parameters tested. It is most sensitive to cavity spacing (Fig. 9). The results indicate that in the reference case, the NRC failure criterion would be violated after about 20 years. Figure 9 also shows that the rate of decohesion increases dramatically

Figure 9 Fractional Decohesion versus time for various values of cavity spacing, λ .

above approximately 40% decohesion. This increase is occurring during a period of decreasing temperature and stress and is caused by the increase of the area dependent term, $f(A)$, in Equation (1.a) [see Appendix A].

The prediction that the base case using the SCP temperature would fail the NRC dry storage failure criterion contradicts the statement by Chin and co-workers [Santanam, 1989] that *"For typically stressed rods (70 - 100 MPa) with low fission gas release, initial storage temperatures of 340° C would be acceptable."* Potential reasons for this difference include: a) Use of different parameter values including the temperature profile. Chin used a temperature profile supplied by Rothman [Rothman, 1984] which had a slightly different time dependence than the SCP profile; b) The failure criterion used by Chin is 100% decohesion; c) The model used by Chin to predict time to failure is independent of decohesion area; and d) The life fraction rule used by Chin to account for changes in temperature and stress also does not account for changes in the rate of decohesion as a function of decohesion area.

Table 6 summarizes the results of our sensitivity analyses. This table presents the time at which the NRC dry storage failure criterion of 15% decohesion is reached for various test cases. The details of the analyses are presented in Appendix A.

Conclusions

In the R&A model, the predicted amount of decohesion is very sensitive to all parameters tested. Due to this sensitivity, the R&A model is not an effective method for screening important variables. If this model were indeed applicable, parameter values would have to be determined with a high degree of accuracy to obtain a meaningful estimate of decohesion. This may be extremely difficult. In the literature, the values used for the grain boundary diffusion coefficient vary by four orders of magnitude [NRC, 1985; Chin, 1986]; cavity spacing varies by two orders of magnitude [NRC, 1985; Chin, 1986]; and grain boundary thickness varies by a factor of twenty [NRC, 1985; Chin, 1986].

Table 6

Summary of R&A Model Sensitivity Analyses. The table presents the time at which the fractional decohesion area, $A(t)$, reaches 0.15 for various test cases.

<u>Test Case</u>	<u>Year at which $A(t) = 0.15$</u>
------------------	---

Dihedral Angle

$\alpha = 75^\circ$ (Base Case)	22.1
$\alpha = 68^\circ$	16.0
$\alpha = 60^\circ$	12.0
$\alpha = 50^\circ$	8.9

Pressure at 322°C

$P = 4.0$ MPa	>1000
$P = 7.6$ MPa (Base Case)	22.1
$P = 8.0$ MPa	20.2
$P = 12.0$	10.5

Cavity Spacing

$\lambda = 2 \cdot 10^{-6}$ m	0.1
$\lambda = 5 \cdot 10^{-6}$ m	1.9
$\lambda = 7.5 \cdot 10^{-6}$ m	6.7
$\lambda = 9 \cdot 10^{-6}$ m	13.0
$\lambda = 1 \cdot 10^{-5}$ m (Base Case)	22.1
$\lambda = 1.25 \cdot 10^{-5}$ m	>1000

Temperature

$T(0) = 250^\circ\text{C}^1$	37.1
$T(0) = 300^\circ\text{C}^1$	28.0
$T(0) = 322^\circ\text{C}$ (Base Case)	22.1
$T = \text{SCP Profile} + 10^\circ\text{C}$	11.0
$T = \text{SCP Profile} - 10^\circ\text{C}$	>1000
$T = \text{Constant} = 322^\circ\text{C}$	14.8

¹ In the base case, the initial temperature is assumed to be 322°C and remains constant for the first four years. In these test cases, the temperature was calculated by linear interpolation between $T(0)$ and $T(4 \text{ yrs}) = 322^\circ\text{C}$.

Application of the R&A model with the SCP peak fuel temperature profile and the conservative values used by the NRC in their dry storage analysis indicates that the Zircaloy will undergo more than 15% decohesion, the maximum allowed by NRC. However, decreasing the temperature profile by 20° C would cause the predicted amount of decohesion to be less than NRC limit¹⁵.

5.1.5.2 Peehs' Model for Predicting Hoop Strain

Modeling of strain due to creep was performed using the empirical correlation developed by Peehs and co-workers. This correlation was developed using experimental data for internally pressurized unirradiated Zircaloy tube samples under inert dry storage conditions [See Section 5.1.4]. This equation considers time, temperature, and stress to be the important variables in determining strain and was presented previously in Equation (5).

For convenience, Equation (5) is repeated here in terms of the experimentally determined empirical correlation coefficients.

$$\epsilon(\%) = A[B/T - \ln(\sigma/C)/\ln(t) - 1]^m \quad (5.a)$$

where ϵ is the percent strain, σ is the hoop stress (MPa), T is the temperature in °K, t is the time in hours, and A , B , C , and m are experimentally determined constants.

The constants for Peehs' correlation were obtained from experiments at temperatures varying between 250 and 400° C with hoop stress levels of 150 and 200 MPa (typical peak hoop stresses expected in spent fuel disposal will range from 60 - 130 MPa and typical peak temperatures will be less than 330° C). Peehs' values for the constants are $A = 1.89 \cdot 10^{-3}$; $B = 610$; $C = 450$; and $m = 2.58$.

¹⁵The NRC assumes that the dihedral angle is 50° C, not 75° C as in the reference case for our studies. This is the reason for the difference between Table 6 where it is reported that a 10° C decrease in the temperature profile would insure that the NRC criterion is not exceeded.

As Peehs' correlation is based on data obtained from tests performed under isothermal and isostress conditions, the correlation was transformed to account for variations in temperature and pressure using a generalization technique developed by Pescatore [Pescatore, 1983]. In this approach, the rate of strain is re-expressed as a function of accumulated strain and of the environmental variables (temperature and stress) [See Appendix A].

A detailed sensitivity analysis was performed for the predicted strain as a function of changes in temperature, pressure, and of all the empirical constants of Equation (5.a). The results of this analysis are presented in Appendix A.

Peehs' correlation is fairly insensitive to changes in any of the parameters tested. For any reasonable change in the parameters, the predicted amount of strain would not exceed 1%. Using a constant temperature of 330° C (approximately the maximum **peak** temperature expected in the fuel rods) and an internal pressure of 130 MPa (the expected maximum **peak** pressure), the correlation predicts only 0.96% strain after 1000 years. For dry storage Peehs recommends that the strain be limited to 1%.

Discussion of Peehs' Correlation

To check for consistency with independent data, Peehs' correlation was applied to data from an irradiated, whole-rod test at 323° C with a hoop stress of 150 MPa [Einziger, 1983]. The value measured by Einziger was $0.16 \pm 0.06\%$. Using Peehs' correlation and the test duration time of 2101 hours gives an estimated strain of 0.18%, which is within the range of experimental error in the measured value.

Other correlations have been developed to predict the observed strain in internally pressurized Zircaloy rods [Matsuo, 1987; Murty, 1977]. They both used an approach based on a "*quasitheoretical*" model for predicting strain developed by Dorn. This model breaks the total creep strain into two components: a) a primary (transient) creep strain which accounts for the relatively fast initial strain rate and b) steady-state creep strain which accounts for long term creep. The steady state creep leads to a linearly increasing amount of strain with time.

Peehs' correlation is not based on mechanistic principles and has a number of issues that need to be resolved before it may be used to make long term predictions. These issues include:

- 1) For an isothermal system Peehs' correlation predicts that if the temperature is below 287° C the strain will **never** reach 1% at any stress level.
- 2) At large times, the correlation becomes independent of stress, which may not be physically correct.
- 3) As discussed in Section 5.1.4, Peehs' correlation fits the average irradiated Zircaloy data well, however, the slope of the correlation appears to decrease faster than that of the data. That is, the correlation is better at early times. This brings into question whether long term predictions based on Peehs' correlation are realistic.
- 4) Peehs' correlation has the predicted strain increase with the logarithm of time. This contrasts with the model employed by Matsuo which predicts a linear increase with strain in time. The difference will be significant for extrapolation of the model to hundreds of years based on data for at most a few thousand hours.
- 5) Kaspar [Kaspar, 1985] states that the Peehs' correlation is valid only over the range of time, temperatures, and stresses that the data were obtained. He does not offer an opinion on whether the correlation can be used for long term predictions, but notes that its supposed conservatism may be diminished when it is applied to predicting creep of irradiated cladding (see Section 5.1.4).

Conclusions

Peehs' model for predicting creep strain as a function of temperature and hoop stress has been modified to account for variations in these properties with time. Using the SCP temperature profile, the recommended values for the coefficients in Peehs' model, and expected values for the hoop stress, the model predicts a maximum strain of 0.125%. Based on sensitivity analyses with the model, it is unlikely that the variation in any single parameter from the reference value will cause the strain to exceed 1% (the maximum value recommended by Peehs for dry storage).

The creep strain data obtained by Peehs and co-workers are encouraging for demonstrating that creep rupture will not be a long term problem under repository conditions.

Peehs' correlation fits the German data well, however, it cannot be extrapolated with confidence to very long times. Other models based on theoretical grounds are available which exhibit different, but, probably more reasonable trends. At this time, we have not examined these models nor the data which support them in detail. This will be a subject of future study.

5.1.6 Conclusions

Experimental studies of pre-irradiated and internally pressurized cladding tube samples have clearly demonstrated the occurrence of positive cladding hoop strains at 350° C under a tensile hoop stress of 50 MPa. The hoop strain had not yet reached its final value after 8,000 hr of testing.

In the safety evaluation of a spent fuel dry storage, the Nuclear Regulatory Commission (NRC) has indicated that where possible, creep rupture modeling should be mechanistic. To that effect, both the NRC and a DOE-sponsored dry-storage study program have implemented a diffusion-controlled cavity growth (DCCG) model to estimate the amount of grain boundary decohesion that would occur in cladding due to

creep with the passage of time. The reference DCCG model was originally proposed in 1975 by Raj and Ashby (R&A) for predicting the intergranular fracture of metals at elevated temperatures. The model assumes that a fixed number of cavities exist initially. These cavities grow and eventually coalesce as stress is applied.

At BNL, we have implemented the original R&A model for the conditions expected during spent fuel isolation. Using the peak fuel temperature profile presented in the SCP (Fig. 1), and the conservative values utilized by the NRC in their dry storage analysis, we found that the predicted amount of decohesion of the Zircaloy will exceed 15%, the maximum allowed by the NRC. However, decreasing the temperature profile by 20° C would cause the predicted amount of decohesion to be less than the NRC limit. Sensitivity analyses with the model indicate that the predicted amount of decohesion is quite sensitive to all parameters tested and, therefore, the model is not an effective method for screening important variables.

The DCCG model has never been validated against actual data. The existing data on cavity nucleation in Zircaloy suggest that stable cavities are only rarely formed in Zircaloy-2 and -4 during reactor irradiation and that stress-induced cavities in unirradiated Zircaloys only appear at relatively large strains. For these reasons, it is not clear that the DCCG model provides meaningful predictions.

An experimental correlation which relates hoop strain, stress, temperature, and time is presently used by German researchers in support of spent fuel dry storage studies. This empirical correlation is based on isothermal, isostress, unirradiated Zircaloy creep data. At BNL, we have generalized the correlation to account for variations in temperature and stress with time. This generalized correlation has been used to determine the sensitivity of predicted hoop strain to variations in temperature, stress, and the empirical coefficients. Using the peak fuel temperature profile presented in the SCP (Fig. 1), the original recommended values for the correlation coefficients, and the expected maximum value for the hoop stress, the model predicts a maximum strain of 0.125%. The sensitivity analysis indicates that it is unlikely that the variation in any single parameter from the recommended values will cause the strain to exceed 1%.

The correlation developed by the Germans fits their data well, however, it cannot be extrapolated with confidence to very long times. Other models based on theoretical grounds and experimental data are available which exhibit different, but probably more reasonable long term trends. At this time, we have not examined these models nor the data which support them in detail. This will be a subject of future study.

The total data base on creep behavior of internally pressurized Zircaloy tubes, although not very large, is comprised of more than the data used by the German's to develop their correlation. Data exist for irradiated and unirradiated samples under a range of temperatures and stress levels. All of the data need to be reviewed in a systematic, comprehensive manner and compared with the predictions of the available models. Areas that require further work include analysis of significance of the data; determination of upper and lower bounding correlations; and determination of correlations based separately on the irradiated and on the unirradiated data.

5.2 Delayed Hydride Cracking

5.2.1 Hydrogen pickup in Zirconium and its alloys

The propensity of zirconium for absorbing hydrogen has been known for a hundred years, having first been reported by Winkler [Winkler, 1890]. Since that time numerous studies have been devoted to examining the reaction between the two elements and the phases thereby formed. Beck [Beck, 1962] reviewed previous data on the binary alloy system, refined them with his own observations and produced a Zr-H phase diagram which is basically the one still in use today. In its simplified form, this is shown in Figure 10 [Northwood, 1983].

Of particular interest in the present case is the solubility of hydrogen in α -Zr which has an hexagonal, close-packed structure. The data of Kearns [Kearns, 1967] provide such information on pure Zr, Zircaloy-2 and Zircaloy-4, indicating that the terminal solid solubility of hydrogen in alpha Zr varies from about 40 ppm at 260° C to about 650 ppm at 550° C. The presence of the small amounts of alloying elements in the Zircalloys has

Figure 10 Zr-H phase diagram [Northwood, 1983].

little effect on the solubility limit, which could be represented by an Arrhenius equation of the form:

$$\text{Solubility limit (ppm)} = 1.2 \times 10^5 \exp (-4303/T) \quad (6)$$

where T is the temperature in kelvin.

These observations were confirmed by Sawatzky and Wilkins [Sawatzky, 1967] who also extended them to include the hydrogen solubility in Zr-2.5 wt% Nb. More recent data, involving lower hydrogen contents, have been reviewed by Northwood and Kosasih [Northwood, 1983] who concluded that, although there were indications of deviations from the Kearns relationship at contents less than about 10 ppm, the evidence was not conclusive. In their opinion, there is only one solubility-temperature relationship for all hydrogen concentrations up to the eutectoid temperature of 550° C.

When the solubility limit is exceeded at temperatures below 550°C, the material becomes a two phase structure, consisting of hydrides in a matrix of α -Zr. In the past there has been some difference of opinion on whether the gamma hydride (with a body-centered tetragonal structure) or the delta hydride (face centered cubic structure) is the more stable form. However, the consensus nowadays is that the latter is the most stable hydride in the system (see, for example, [Ivey, 1985]). The composition of the gamma hydride is approximately ZrH [Mishra, 1972], that of delta approximately ZrH_{1.6} [Beck, 1962]. The latter phase is extremely brittle and its presence in alloys, even in small amounts, can have an embrittling effect [Northwood, 1983]. It is this aspect which is of particular concern to designers of fuel pins.

In recognition of this, ASTM B 353-83 ("Standard Specification for Wrought Zirconium and Zirconium Alloy Seamless and Welded Tubes for Nuclear Service") imposes a maximum limit of 25 ppm on hydrogen content. Typically, finished clad tubing might contain 10 ppm hydrogen [Pyecha, 1985; Cheadle, 1987]. Thus, although the material probably contains a small amount of hydride at room temperature, this will be dissolved when the clad temperature rises during reactor operation. If it is assumed that the coolant outlet temperature for a typical PWR is 330°C and that there is a temperature drop of 20°C between the clad and the coolant [Duderstadt, 1976], then the clad external temperature will be about 350°C (this is in line with the value quoted in [Stehle, 1975]). At this temperature, the terminal solid solubility of hydrogen is of the order of 125 ppm. If we assume that there is an average temperature gradient of about 20°C across the clad itself, this would mean the temperature at the inner surface would be about 370°C (see also Table 3). At this temperature the solubility limit is about 155 ppm¹⁶. Thus, if the hydrogen content of the clad exceeds 155 ppm, hydride formation will occur at normal reactor operating temperatures and the mechanical properties of the cladding will begin to be affected. However, even if the content remains substantially below this value, hydride formation may still occur when the reactor is in a shutdown mode for refueling or maintenance. As the coolant at such times will probably be around

¹⁶It should be noted that this value is lower than the 200 ppm quoted in [Pyecha, 1985] but no details are provided on how their higher figure was obtained.

60° C, with cladding temperatures somewhat higher (80° C plus), the hydrogen solubility limit will be much less than 10 ppm. However, as pointed out [Northwood, 1983], the alpha phase is capable of supersaturation with hydrogen and thus hydride may not precipitate at temperatures suggested by the phase diagram for the Zr-H system.

The actual extent of change in mechanical properties is dependent on several factors, including the orientation and distribution of hydride platelets and the operating temperature. Figure 11 [Lin, 1979] gives an overall picture of the effect of hydrogen content of Zircaloy-4 on the room temperature tensile properties. The continuing loss of ductility as the hydrogen concentration increases is readily apparent. For example, 600 ppm hydrogen produces perhaps a slight increase in tensile and yield strength but the elongation is decreased to about 3/4 of the initial value while the reduction of area is only half the value it is when the hydrogen content is less than 20 ppm. Corresponding data obtained at higher test temperatures have not been located but it has been shown that the hydride, which is brittle at room temperature, apparently becomes ductile at temperatures above about 150° C [Evans, 1966]. Thus, at these higher temperatures, the hydrogen content has less effect on the ductility and, during normal reactor operation at full power, factors other than temperature are more important in determining how much ductility is present. According to Pickman [Pickman, 1972], embrittlement due to hydrides at these temperatures *"depends in a complex manner on the texture of the tube, the stress system, the amount, distribution and orientation of the hydride, the temperature and the "relative size" effect."* The embrittlement experienced at the lower temperatures is nevertheless important in fuel pin design, which must take into account low power and refueling operations as well as full power operation. According to [Stehle, 1975], designers usually limit hydrogen pick-up to 500-600 ppm. In support of this, [Pyecha, 1985] cites results from ex-reactor tests which show that *"sufficient margins in cladding ductility are maintained in cladding having hydrogen concentrations of 500 ppm or less."*

Figure 11 Effect of hydrogen content on the tensile properties of Zircaloy-4 [Lin, 1975].

5.2.2 Mechanisms and conditions for DHC

The previous paragraphs indicate that the presence of hydrides in zirconium and zirconium alloys affects the ductility of the material, bringing about large decreases in the elongation and reduction of area values measured in tensile tests. The tensile strength of the material tends to be less affected; for example, [Lin, 1979] found that the room temperature yield strength gradually increased as the hydrogen content increased while the ultimate tensile strength increased up to about 400 ppm hydrogen then gradually decreased at higher levels. However, there is also a time-dependent process which can take place; this is delayed hydride cracking (DHC), sometimes called hydrogen-induced delayed cracking. The phenomenon was noted in the early 1960s [Weinstein, 1964] and has since been the subject of many investigations. Summary

reviews have been presented by Coleman and Ambler [Coleman, 1979] and Northwood and Kosasih [Northwood, 1983], among others.

Most of the recent research into DHC has been performed in Canada. Part of this intense interest derived from experiences with failures in pressure tubes (made of Zr-2.5 wt% Nb) in CANDU reactors [Perryman, 1978]. The processes that comprise DHC are now thought to be identified and efforts have concentrated on modelling the mechanisms. The model which has received the most attention is that first proposed by Dutton et al. [Dutton, 1977]. Since that time, it has undergone several developments and refinements, and a recent review of its status was published by Eadie and Smith [Eadie, 1988]. The Dutton-Puls model does not adequately explain some of the experimental observations, in particular the existence of a threshold stress or stress intensity factor below which no cracks will propagate, and a more qualitative treatment has been proposed by Sawatzky [Sawatzky, 1986], a description of which may be found in a report by Cunningham et al. [Cunningham, 1987].

The basic sequence of events which lead to DHC are:

- (a) diffusion of hydrogen to a notch or crack tip
- (b) formation of brittle hydride
- (c) application (or continued existence) of a tensile force
- (d) cracking of the hydride and extension of the crack
- (e) repeat of the process at the new crack tip.

That this mechanism of crack growth does occur has been confirmed in an electron optical study involving zirconium, Zr-2.5 wt% Nb and Zircaloy-2 [Cann, 1980]. However, the likelihood of it occurring in a particular instance is dependent on several parameters. Elimination or minimization of any one of the parameters can prevent the occurrence of DHC, as has been discussed by Cheadle et al. [Cheadle, 1987].

The presence of hydrogen is obviously the most important parameter. Although tight controls during fabrication can reduce the hydrogen content to less than 10 ppm, conditions will be such that, during reactor operation, it will soon increase and eventually exceed the terminal solid solubility, thus giving rise to hydride formation.

The rate at which hydrides form is dictated by, among other things, the rate at which hydrogen is picked up, the rate at which it can diffuse in the material and the availability of favorable sites for nucleation. The relative rates at which hydrogen can be picked up by the various zirconium alloys has been discussed in the previous paragraph. Once absorbed by the alloy, the diffusion of hydrogen is dependent on three parameters: the gradients of concentration, temperature, and stress [Northwood, 1983]. Hydrogen in zirconium alloys will diffuse down a concentration gradient or a thermal gradient but up a stress gradient. When the hydrogen concentration finally reaches the solubility limit, consideration must be given to the presence and concentration of flaws as these are the sites which will most likely favor nucleation of hydrides. According to [Cheadle, 1987], effective flaws can range in size from small surface perturbations to large weld or forming defects. Following from this, it is apparent that the microstructure of the material (crystallographic texture, phase distribution, etc.) also affects the characteristics of hydride formation. For example, in the absence of applied stress, the texture inherent in extruded tubing will dictate that hydrides form in the circumferential and axial direction, rather than in the radial direction.

The formation of hydrides does not, *per se*, indicate whether DHC will occur. Crack initiation is dependent on the size of the hydride platelet, the stress (or stress intensity factor) present, and the temperatures involved. A summary of the conditions required for initiating DHC in three zirconium alloys is given in Table 6 (from [Cheadle, 1987]). The critical (or threshold) stress intensity factors (K_{IH}) are slightly different from values quoted in other sources but not radically so. Simpson and Puls [Simpson, 1979] show values from 6 to 8 MPa.m^{0.5} for Zr-2.5 wt% Nb in the temperature range 108-300°C, while Puls et al. [Puls, 1982] indicate that K_{IH} for Zircaloy-2 is of the order of 10 MPa.m^{0.5}.

TABLE 6
Requirements for Initiating DHC in Zirconium Alloys
[Cheadle, 1987]

Material Condition	Temperature, K	Zircaloy-2,-4	Zr-2.5 wt% Nb
Smooth surfaces and notches ≤ 0.1 mm	290	no cracking	≥ 550 MPa
	525	no cracking	≥ 250 MPa
	cycling	300 MPa	≥ 250 MPa
	between 290 and 525		
Notches ≥ 0.2 mm	350	$14 \text{ MPa} \cdot \text{m}^{0.5}$	$\geq 4.5 \text{ MPa} \cdot \text{m}^{0.5}$
	525	$14 \text{ MPa} \cdot \text{m}^{0.5}$	$\geq 10.0 \text{ MPa} \cdot \text{m}^{0.5}$
	cycling	$5 \text{ MPa} \cdot \text{m}^{0.5}$	$\geq 4.5 \text{ MPa} \cdot \text{m}^{0.5}$
	between 290 and 525		

Having established that cracking can be initiated, it then must be established whether the cracks will propagate and how fast. Somewhat surprisingly, the rate of propagation is virtually independent of stress or the stress intensity factor once a crack has begun to propagate. This is illustrated by Figure 12 (taken from [Cheadle, 1987]), a schematic diagram of the dependence of crack velocity on the stress intensity factor. Essentially, no cracking or crack growth will occur for stress intensity factors below a certain value (the threshold stress intensity factor, K_{IH}). Once this value has been reached, crack propagation increases very rapidly as the stress intensity factor becomes larger, up to a crack velocity value of V_c . The velocity then remains stable at V_c despite further increases in the stress intensity until a critical value, K_{IC} , is reached, after which

Figure 12 Schematic diagram of the dependence of crack velocity on stress intensity factor [Cheadle, 1987].

rapid unstable crack growth occurs. Thus, it can be assumed that, for all intents, once a crack has formed, it will continue to propagate and at a constant velocity as long as the stress intensity factor remains at or slightly above K_{IH} .

The value of K_{IH} is generally independent of temperature over the approximate range 20-300° C though Coleman and Ambler [Coleman, 1979] indicate that values may be higher at temperatures around 250° C than at lower temperatures. In addition, as can be noted in Table 6, thermal cycling can apparently reduce it. On the other hand, Simpson [Simpson, 1979] shows that V_c , the crack velocity, is strongly dependent on temperature in the Arrhenius manner, increasing as the temperature is raised. The relationship between crack velocity and temperature is, however, not simple and the same authors noted that the direction of approach to the test temperature (i.e., via heating or cooling) considerably affected the reproducibility of the data. The most erratic results were obtained when the specimen was brought up to the test temperature. Ambler [Ambler, 1984] examined the phenomenon in Zr-2.5 wt% Nb in more detail,

concluding that it only occurs above a certain critical temperature and is related to loss of constraint by the hydrides during heating. When specimens were cooled to the test temperature, the crack growth rates in [Ambler, 1984] are in very good agreement with those in [Simpson, 1979] (see Fig. 13).

Stress and temperature also serve a role in determining hydride morphology and orientation. As mentioned earlier, in the absence of applied stress, the strong texture normally present in the clad tubing dictates that the hydride platelets form with their normals in the radial direction, the platelets themselves being aligned in the circumferential direction. However, by application of stress under certain conditions, it is possible to reorient the hydrides such that the platelets begin to align themselves radially. Louthan and Marshall [Louthan, 1963] demonstrated that, in Zircaloy-2 tubing fabricated by a particular technique, hydrides could begin to undergo reorientation at 400° C at stresses as low as 35 MPa. However, by changing the fabrication method, the level was raised to 150 MPa. Marshall, in two later papers ([Marshall, 1967a] and [Marshall, 1967b]), expanded this work. He found that the susceptibility to hydride reorientation was very high for tubing made by hot reduction, it being possible to obtain 70% reorientation in a specimen containing 50 ppm hydrogen after 1 hour at 350° C under a circumferential stress of 83 MPa. Increasing the stress to 124 MPa resulted in virtually 100% reorientation. In contrast, cold-formed tubing (which now constitutes the basis of most clad specifications) underwent much less reorientation under the same conditions, with, on average, about one third of the circumferentially-oriented plates becoming radially oriented with a stress of 124 MPa. This was only fractionally increased when the stress was raised to 165 MPa. Application of a stress of 220 MPa at 300° C to the same tubing produced less than 50% reorientation. Ells, in an early review of hydride precipitation in zirconium alloys [Ells, 1968], concluded that *"If it is desirable to fabricate zirconium alloy tubes to operate under internal pressurization and to avoid formation of radial hydrides, then in the later stages of production it is necessary to have a large amount of compressive strain in the radial direction. Cold drawing with small*

Figure 13 Steady-state crack growth rate-temperature relationship for specimens furnace-cooled from 623 K [Ambler, 1984].

reduction in diameter and shear forming are particularly suitable for favourable hydride orientation ..." Hardie and Shanahan [Hardie, 1975] conducted a comprehensive study of hydride reorientation in Zr-2.5 wt% Nb, varying such parameters as temperature, stress and hydrogen content. The last of these parameters is of particular interest in that [Hardie, 1975] demonstrated that reorientation only took place with the hydrides which went into solution. Thus, complete reorientation could be achieved with material containing 100 ppm hydrogen by holding at a stress of 200 MPa at 400°C. With 300 ppm hydrogen, the same conditions would only produce about 30% reorientation. Similarly, if the material containing 100 ppm hydrogen was held at a stress of 200 MPa at 300°C, less than 40% reorientation was observed. It was also noted that the minimum stress necessary to bring about some orientation, albeit of only a few percent, could be as low as 50 MPa, depending on the other parameters. Cheadle et al. [Cheadle, 1984] determined that, for thermal treatments at 300°C, a minimum applied stress of 175 MPa was required to reorient most of the hydrides in Zircaloy-2 containing

100 ppm hydrogen, while Zr-2.5 wt% Nb required a stress of 400 MPa. Northwood [Northwood, 1979] also performed hydride reorientation but the conditions are not specified in detail. However, he does state that some reorienting was achieved in Zr-2.5 wt% Nb through thermal cycling material containing 100 ppm hydrogen at a stress of 420 MPa. As he also describes the need for all the hydrogen to be in solution for this to occur, it can be inferred that the temperatures involved in this instance were 340-350° C, based of the solubility data of Kearns [Kearns, 1967]. Hydride reorientation was also performed on Zircaloy-2 containing 90 ppm hydrogen but the stress required is not mentioned. Complete solution of the 90 ppm hydrogen would require a temperature of about 330° C. Most recently, Puls [Puls, 1988] used the conditions summarized in Table 7 to reorient hydrides in both Zircaloy-2 and Zr-2.5 wt% Nb.

To our knowledge, hydride reorientation in actual spent fuel cladding has only been noted on one occasion [Einziger, 1983]. In this instance, a fuel pin, the cladding of which contained up to 90 ppm hydrogen, was internally pressurized to give a hoop stress of about 145 MPa at 323° C. This set of conditions was found to be sufficient to cause considerable hydride reorientation. Four similar fuel pins which were being tested at the same time, but which had lost their pressurization prior to the final cooldown, showed little or no reorientation of the hydrides. In an earlier set of whole rod tests involving low hoop stresses (estimated less than 30 MPa at 320° C), some agglomeration of hydrides was noted but there was no reorientation from the original alignment in the circumferential direction [Einziger, 1982]. The significance of the observed reorientation lies in the conditions surrounding its occurrence, which, at first glance, appear somewhat anomalous when compared with those predicted from the laboratory experiments described in the previous paragraph. [Cheadle, 1984] and [Puls, 1988] indicate that a stress in the range 175-200 MPa is required at this temperature, whereas the specimen in question had an estimated hoop stress of 145 MPa. In fact, the reorientation might have been achieved with an even lower stress. As this test involved a sealed, pressurized tube, the hoop stress will have decreased as the specimen cooled. Thus, if the precipitation of hydrides commenced at a lower temperature than 323° C, then the stress forcing the radial orientation would have been lower than 145 MPa. The reasons why

TABLE 7
Conditions Used to Reorient Hydrides
 (from [Puls, 1988])

Temperature	Stress	Cooling Rate
Sufficient to dissolve most hydrides:	1. Near yield at hydride precipitation temperature	1. Slow (furnace cool): "large" hydrides or
(1) 200-250°C at low [H] (20 ppm)	2. Sufficient to reorient most hydrides:	2. Fast (bench cool): "small" hydrides
(2) 300-350°C at high [H] (100 ppm)	a. Zircaloy-2: 200 MPa b. Zr-2.5 Nb: 250 MPa	

the orientation took place at lower-than-expected stress is not known but the observation casts some uncertainty on the application of data obtained on unirradiated material to cases involving spent fuel pins.

5.2.3 The DHC data base

A recent summary of in-service failures of reactor components due to DHC can be found [Cheadle, 1987], from which it appears that most (but not all) involved components made of Zr-2.5 wt% Nb. The paper also includes mention of two instances of cracking encountered in the chemical industry, again involving Zr-2.5 wt% Nb. In some of the cases, similar components made of Zircaloy-2 did not fail.

Details on the failure of some experimental fuel elements are given in [Simpson, 1974]. Cracking in this instance took place at the welds between the Zr-2.5 wt% Nb cladding and the similar end caps, during storage at room temperature. After evaluation of the cracks and the design, it was decided that DHC had resulted when the residual stresses from the welding process and those present in the sharp notch at the weld joint had combined to produce a stress gradient up which the hydrogen could diffuse.

The most numerous examples of DHC in the nuclear industry can be found in the pressure tubes in the CANDU reactors, principally involving units at the Pickering power stations. The first instances of cracking were detected in 1974 and the subsequent steps taken to determine the cause and rectify the problem have been described in [Perryman, 1978]. As with the fuel cladding failure described in the previous paragraph, the cracking was thought to have been caused by the existence of high residual stresses, on this occasion induced in the pressure tubes by improper joint rolling. Perryman noted at that time that pressure tubes of Zircaloy-2, fabricated by an identical procedure, had not failed and postulated that this was attributable to the lower yield strength of the Zircaloy, particularly at reactor coolant operating temperatures. This would lead to lower residual stresses in the tube, especially after a thermal cycle in the reactor.

Several years later (in 1983), one of the Zircaloy-2 pressure tubes did fail by DHC [Price, 1985]. However, the cause was not the presence of residual stresses following the fabrication process. According to Cheadle [Cheadle, 1987], *"the primary cause of failure was the incorrect position of one of the spacers which separate the calandria tube from the pressure tube. The hot pressure tube sagged by creep into contact with the cold calandria tube. The resultant severe thermal gradient through the wall of the pressure tube concentrated the hydrogen at the cool zones and hydride blisters were formed."* Cracking occurred in some of the blisters and subsequently these cracks grew by DHC, and resulted in an unstable fracture.

Cheadle [Cheadle, 1987] also describes failure by DHC of three Zr-2.5 wt% Nb pressure tubes at the Bruce power station, the initial cause of the trouble being traceable back to the improper fabrication procedure.

DHC was also the cause of failure of some seam-welded calandria tubes made of a high-strength zirconium alloy, Excel (Zr-2.5Sn-0.8Mo-0.8Nb). In this case, Cheadle [Cheadle, 1987] identifies the source of the problem as an incorrect heat treatment and the absence of stress relief after the final forming operation. The alloy Excel has a much higher yield strength (930 MPa) than either Zircaloy-2 (627 MPa) or Zr-2.5 wt% Nb (780 MPa) [Puls, 1988] and consequently can sustain higher residual stresses. Thus, if the probability of DHC increases as the residual stresses become larger, then Excel, if not stress-relieved, would be expected to be more susceptible to this mode of failure than the other zirconium-based alloys.

Few details are available on the DHC failures observed with Zr-2.5 wt% Nb components in the chemical industry. In both the cases mentioned by Cheadle [Cheadle, 1987], cracking was associated with high residual stresses from welding operations.

5.2.3.1 Observations of spent fuel elements

Garzarolli et al. [Garzarolli, 1979] include, as one of the main causes of fuel element failure, locally enhanced pickup of hydrogen which, in turn, gives rise to high concentrations of hydrides. Garzarolli et al. make the point that "*as long as the hydrogen pickup is uniform, no significant consequences arise.*" Thus, there is an important distinction between these failures, which derive from locally enhanced hydrogen pickup, and DHC, which usually involves concentration of the hydrogen after it has been absorbed. None of the failures described by Garzarolli et al. are thought of as due to DHC. In fact, with the exception of the incident with the experimental fuel rods mentioned in the previous section, no instances could be found in which fuel rod failures (either during reactor operation or during storage) were identified as being due to DHC. However, before an assessment can be made of the likelihood of spent fuel rods failing by DHC in the future, information must be available on the condition of the fuel cladding at end of life. The definition of "end of life" is in itself a variable and changes with reactor type. According to a report on storage of water reactor spent fuel in water pools [IAEA, 1982], the average fuel rod burnup in a PWR at discharge is in the range

26-33 GWd/t. However, efforts are continually being made to extend fuel burnup ranges in order to increase reactor efficiency and future designs may see rods being discharged with burnups to 50 GWd/t. This will have obvious implications concerning the condition of the cladding on the spent fuel.

Although it is not a common procedure, several spent fuel rods from commercial reactors have been subjected to destructive and non-destructive examinations and some of the required information has been obtained.

Pyecha et al. [Pyecha, 1985] were interested from the point of view of developing advanced PWR fuel rod designs with extended burnup capability. The actual pins examined had been through four and five cycles of irradiation in Oconee 1 and 2 reactors. Peak hydrogen content in the Zircaloy-4 cladding after four cycles was 182 ppm; that after five cycles, 326 ppm. Low values were about 60 ppm and 106 ppm, respectively. Photomicrographs of representative hydride morphology after five cycles show the hydrides to be universally in a circumferential orientation, with no significant radial component observable. However, there are variations in hydride distribution. The density is greater near the clad outer surface (as might be expected from the temperature gradient across the wall thickness) but it also varies with circumferential orientation. The latter is perhaps a reflection of variations in temperature due to coolant flow differences.

Davis and Pasupathi [Davis 1981] examined five fuel rods after two reactor operating cycles in Turkey Point Unit 3. Hydrogen contents in the samples of Zircaloy-4 cladding analysed are all less than 100 ppm, with the lowest average content (36 ppm) being found in the bottom half of the fuel rod. The highest average content (77 ppm) was associated with the top of the rod. Microstructural examination reveals mostly circumferential hydrides but with some radial hydrides, most of which appeared to connect with the circumferential ones. The density of hydrides varies with axial location, as would be expected from the variations in hydrogen content in the same direction. It also appears that the hydrides form nearer the inner surface of the cladding rather than the outer.

Atkin [Atkin, 1981] reports on the destructive examination of five fuel rods following four cycles of operation in Turkey Point Unit 3 (maximum clad surface temperatures estimated to be not greater than 340°C). Hydrogen concentrations in the Zircaloy-4 did not exceed 100 ppm, ranging from a low of around 30 ppm (near the bottom of one of the fuel rods) to a high of about 94 ppm (near the top of a rod). Transverse sections of the cladding show hydrides distributed fairly uniformly throughout the cross-section, although it is possible there is a slightly greater concentration near the outer surface. The orientation is predominantly circumferential, there being very few radially-oriented hydrides reported. The longitudinal variation in hydrogen concentration is also reflected in the size and distribution of hydrides along the length of the rod, with there being fewer and smaller ones in the bottom half.

The data on hydrogen pickup described above are summarized in Table 8 and in Figures 14 and 15. It is readily apparent, in Figure 14, that while fuel rods continue to be discharged from the reactor with burnups less than about 33 GWd/t, hydrogen concentrations will accumulate to no more than about 100 ppm. However, the current trend is towards higher burnups which, in turn, will result in ever increasing hydrogen contents.

It is of some interest to compare the data in Figure 15, obtained on Zircaloy-4, with similar data [Price, 1985] reported on Zircaloy-2 and Zr-2.5 wt% Nb pressure tube material, shown, respectively, in Figures 16 and 17. All three curves show an initial period of relatively low hydrogen pickup then a change to a more rapid rate. The length on the initial period is dictated by, among other factors, the temperatures to which the material is exposed. In the case of the pressure tubes, these will be in the range 250-310°C, according to [Price, 1985], and thus significantly lower than those experienced by the fuel cladding, the outer surface of which will be at about 340°C during full power operation. It is not surprising, therefore, that the initial period lasts for 1500-2000 effective full power days (EFPD) with the Zircaloy-2 pressure tubes but only around 500 EFPD in the case of the Zircaloy-4 cladding. At the same time, as far as it can be deduced, the change in rate occurs for both materials when the hydrogen concentration is in the range 20-40 ppm. The difference between the Zircaloy-2 initial

TABLE 8
Hydrogen Concentrations in Spent Fuel Cladding

Reference	Reactor	Burnup	Eff. Full	<u>Hydrogen Conc., ppm</u>	
	Cycles	MWd/MTU	Power Days	Minimum	Maximum
[Davis, 1981]	2	27	827	36	77
[Atkin, 1981]	3	31	851	31	94
[Pyecha, 1985]	4	43	1150	60	182
[Pyecha, 1985]	5	55	1554	106	326

period and that of the Zr-2.5 wt% Nb is probably a reflection of the reduced tendency of the latter material to absorb hydrogen produced by the corrosion reaction.

The other observation of note is that essentially all the hydrides seen in the cladding have been circumferentially oriented. Very few have been detected with a radial orientation.

5.2.4 Maximum achievable cladding hoop stress during spent fuel isolation

At the end of its useful life in a reactor, a fuel rod is removed and placed in either water storage or inerted dry storage (IDS). It will remain there for perhaps up to 50 years before finally being disposed of in a repository. During that time, the temperatures in the rod will remain elevated but decline with the passage of time. An example of this while the fuel is in IDS is shown in Figure 18, taken from [Levy, 1987], while the estimated temperature decay in the final repository is shown in Fig. 1. The rod will also be internally pressurized, thus maintaining the cladding in a state of stress. Because the pressure will change with temperature, the stress level in the cladding will drop as the fuel decays. However, as pointed out by Rothman [Rothman, 1984], the pressure will not decrease with temperature as fast as predicted by the ideal gas law due

Figure 14 Hydrogen content in Zircaloy-4 cladding as a function of Fuel Burn up.

to production of He generated by actinide decay. This becomes increasingly important from 1,000 years onwards. For conservatism Rothman suggests using the initial pressure and holding it constant for stress calculations oriented towards disposal conditions.

According to [Cunningham, 1987], the most common recommended maximum cladding temperature during IDS is 380° C but the report tends to favor variable limits based on several factors, including the time-temperature history during storage, internal gas pressure and modelling of potential failure mechanisms. The report also assumes that a *maximum* hoop stress for the cladding during IDS of 70 MPa at 400° C and a maximum stress intensity of 1.6 MPa.m^{0.5} for 5-year old PWR fuel.

Figure 15 Hydrogen content on Zircaloy-4 cladding as a function of Effective Full Power Days.

The value for maximum hoop stress given in [Cunningham, 1987] appears to have been derived from the average rod pressure of 6.5 MPa at 25° C, a cladding thickness of 0.1 cm (higher than typical PWR and BWR cladding) and the cladding inside diameter of 0.95 cm (more typical for PWR rods). Using values of 0.98 cm inside diameter and 0.06 cm thickness, typical for PWR fuel, and the equation for a uniformly pressurized thin shell gives a hoop stress of 120 MPa at 400° C. The use of an atypical cladding thickness by Cunningham leads to the large discrepancy in predicted hoop stress.

Figure 16 Corrosion and hydrogen pick-up of Zr-2.5 wt% Nb pressure tubes. [Price, 1985].

Figure 17 Corrosion and hydrogen pick-up in Zircaloy-2 pressure tubes [Price, 1985].

Figure 18 CASTOR V/21 cask temperature history [Levy, 1987]. Ambient air temperature represents the boundary condition to the thermal problem for the whole cask.

Levy [Levy, 1987] gives an upper bound value for the average rod pressure of 1707 psi (11.8 MPa) for a 15 x 15 PWR assembly with an average burnup of 33,000 MWd/MTHM at reactor operating temperatures. Assuming that the gas temperature inside the fuel rods is 370°C during reactor operations, the same value as the clad internal surface temperature as presented in Table 3, gives a maximum hoop stress of 96 MPa for PWR cladding with a diameter of 0.98 cm and a thickness of 0.06 cm. Levy [Levy, 1987] also estimated the peak pressure in the same rod with a burnup of 45,000 MWd/MTHM to be 2416 psi (16.7 MPa). The author points out that this pressure is higher than the typical PWR system pressure of 2250 psi. He emphasizes that this is only a hypothetical upper bound and does not imply operation at such a pressure. However, it is obvious that *"extended burnups will lead to higher than currently typical rod pressures in all fuel."*

The basic assumptions contained in [Rothman, 1984] include an initial cladding temperature of about 325°C, this being for 10 year old spent fuel, a cladding inside diameter of 0.98 cm, and a cladding thickness of 0.06 cm. The maximum internal pressure is assumed to be 1690 psi, from which he calculates the worst-case hoop stress of 95 MPa (14,000 psi)¹⁷.

The hoop stresses derived from [Rothman, 1984] may not actually be worst-case, if consideration is given to data contained in Table 3 indicating that the maximum pressure inside a PWR fuel rod during reactor operation is 150 atmospheres (15 MPa, 2180 psi). This is just below the typical PWR system pressure of 2250 psi and must be considered a worst-possible case. If it is assumed that this pressure exists at the maximum internal clad temperature of 370°C given in Table 3, then it can be calculated that at 330°C (the maximum clad temperature during the dry isolation phase) the pressure will be 14 MPa. This is equivalent to a hoop stress of 114 MPa, assuming a clad wall thickness of 0.06 mm and a fuel rod inner diameter of 0.98 cm.

¹⁷ 9.5 MPa is 13,800 psi not 14,000 psi as stated in Rothman.

Table 9 lists estimates of cladding hoop stress based on internal fuel rod gas pressures found in the literature. Hoop stresses are calculated using the thick wall formula. The ideal gas law was used to calculate pressure at 320° C. For PWR rods, the inner cladding diameter was assumed to be 0.98 cm and the thickness was 0.06 cm. For BWR rods, the inner cladding diameter was 1.24 cm and the thickness was 0.08 cm. For comparison purposes, these have been translated to the hoop stress that would occur at 320° C, which is approximately the expected peak temperature under disposal conditions. Most of the values for pressure in the table are based on theoretical calculations except a few for which measurements were taken.

The hoop stress calculations described above are based on using the formula for a uniformly pressurized thin shell. If the fuel pin is considered to be a thick-walled vessel (a not inappropriate assumption as the radius:thickness ratio is less than 10:1 - see [Roark, 1975]), then somewhat different values are obtained. For example, in the Rothman case, the maximum calculated hoop stress (at the inner surface of the clad) becomes 14,700 psi (101 MPa). The hoop stress will be lower throughout the rest of the clad wall, becoming lowest at the outer surface (13,000 psi, 89.6 MPa). The stresses in the other two principal directions (longitudinal and radial) will be much lower than the hoop stress. The longitudinal stress will be about half the value of the hoop stress, while the maximum radial stress will be approximately equal to the internal pressure but of opposite sign. In the worst-possible case derived from the Table 3 data, the maximum hoop stress calculated using the thick-walled vessel formula is 19,000 psi (131 MPa). The longitudinal stress at that point will be about 60 MPa and the radial stress 15 MPa.

Two points should be made about the maximum stresses discussed above. First, the number of pins which will actually be subjected to the worst-case conditions is expected to be very few. From Table 9, the hoop stresses in the average rods will be approximately 50% of that in the maximum rod. Because *"the peak rods represent less than the one percent of the rods in the core"* [Levy, 1987], any failures that might occur under the maximum conditions will be limited to relatively few pins. Second, as the radioactivity in the fuel continues to decay, the temperature will decline and the internal pressure will drop. This will occur most rapidly at early times when the temperature is

Table 9 Spent Fuel Cladding Hoop Stresses at 320°C

Press (MPa)	Temp (°C)	Hoop Stress (MPa) ¹ (at 320°C)	Comments	Reference
<u>PWR Fuel Rods</u>				
1.4-2.8	25	24.3-48.7	Average	[Locke, 1975] ⁴
1.7-3.8	25	29.6-62.6	Average	[Johnson, 1977] ⁴
8.25	370	66.1	Dry Storage	[GNSI, 1985]
8.9	370	71.3	Average ²	[Levy, 1987]
11.8	370	94.8	Max ² ; 33,000 MWd/MTHM	[Levy, 1987]
5.5	25	95.7	99% < 5.5	[Rothman, 1984]
5.8	25	100.1	Maximum	[RESAR3S, 1975] ⁴
11.7	322	101.8	Maximum	[Rothman, 1984]
6.5	25	112.2	Maximum	[Cunningham, 1987]
16.7	370	133.9	Max ² ; 45,000 MWd/MTHM	[Levy, 1987]
8.3	25	144.3	Atypical ³	[Johnson, 1977] ⁴
<u>BWR Fuel Rods</u>				
1.0	370	7.5	Average ² 8x8	[Levy, 1987]
1.4-2.0	25	20.7-29.6	Average	[Johnson, 1977] ⁴
1.83	25	30.3	Measured	[Blackburn, 1978]
7.5	370	58.0	Maximum ² 7x7	[Levy, 1987]

¹ Hoop stresses are calculated using the thick wall formula. The ideal gas law was used to calculate pressure at 320°C. For PWR rods, the inner cladding diameter was assumed to be 0.98 cm and the thickness was 0.06 cm. For BWR rods, the inner cladding diameter was 1.24 cm and the thickness was 0.08 cm.

² In the report by Levy the pressures are reported under average reactor operation conditions. The gas gap temperature is conservatively assumed to be 370°C for calculating pressures at lower temperatures in these cases.

³ This value was measured for Maine Yankee fuel which had been improperly fabricated leaving larger gaps between the fuel and clad. This lead to higher fuel temperatures and therefore higher fission gas release. *"The Yankee reactor fuel rods constitute well under 1% (likely much less than 0.1%) of all spent fuel anticipated at present"* [Rothman, 1984].

⁴ Referenced in [Rothman, 1984].

greatest. The pressure drop due to declining temperature will be offset somewhat by helium production within the rods. This may be significant after 1000 years [Rothman, 1984]. However, at that time temperatures will be much lower.

5.2.5 Conclusions

It is apparent from the observations described in the previous sections that, when fuel rods begin their life in storage, the cladding material will contain considerably more hydrogen than it had at the beginning of life. The actual amounts involved will vary with the time spent in the reactor; that is, the amount of fuel burnup and the number of EFPD experienced. These, in turn, will dictate whether or how long all the hydrogen will remain in solution during storage and when hydrides will form. Based on Figure 14, Zircaloy-4 cladding from a rod with a burnup of 33 GWd/t is likely to contain, on average, at least 100 ppm hydrogen. According to [Kearns, 1967], this would be equivalent to the terminal solid solubility of hydrogen at about 330°C (i.e., about the temperature assumed by Rothman at the beginning of repository storage). In practice, with efforts to extend the burnup of the fuel, hydrogen concentrations are likely to be much higher. A burnup of, say, 45 GWd/t could result in a hydrogen concentration of about 200 ppm, which is the solubility limit at 395°C. Thus, it is probable that cladding will already contain hydrides at the beginning of spent fuel isolation. As the cladding temperature declines, more hydrides will nucleate while those already in existence will grow.

From the aspect of overall ductility of the material, it has been demonstrated that a significant margin will exist even with hydrogen concentrations up to 500 ppm. This is applicable both at the higher temperatures of consideration, where the hydrides deform plastically, and at the lower temperatures, when the hydrides become brittle. However, of more relevance to considerations of DHC is the orientation of the hydride platelets.

In the fuel cladding, the strong texture in the material leads to a predominantly circumferential orientation of the platelets. This is fortuitous in that the stresses normal to this (the longitudinal and radial stresses) are not the highest in the cladding. The longitudinal component of the clad stress is estimated to be no greater than about 60 MPa while the radial stress is unlikely to exceed about 15 MPa (the latter will also be a compressive stress, not tensile). These values are much less than those normally considered necessary to cause DHC (see Table 6).

One other phenomenon must be taken into account - that of the possibility of the hydrides becoming reoriented such that the platelet normals lie in the circumferential direction. The conditions required for this to occur depend on several factors but typically, for Zircaloy-2 containing about 100 ppm hydrogen, these include a temperature of 300-350°C and a stress in the range 175-200 MPa. (Fuel pins with extended burn-up, and therefore more hydrogen, will probably require higher temperatures because one of the factors which determines the amount of reorientation which can take place is how much of the hydrogen will be in solution in the Zircaloy when the stress is applied.) While the necessary temperature conditions will exist, at least for a short time, during the dry isolation phase of the fuel pins, the stipulated stresses appear to be higher than the estimated maximum hoop stress in the cladding (and much higher than the average hoop stress). Thus, the possibility of significant hydride reorientation occurring appears unlikely. However, the only observation on reorientation in actual spent fuel pin cladding indicates that the phenomenon can occur at lower stresses than with unirradiated material. Whether this is an anomalous observation or whether the threshold stress for reorientation, particularly with irradiated material, is lower than originally thought can only be established by the acquisition of more information on spent fuel pin material.

In the event that reorientation should occur, the hydrides will then be subjected to tensile stresses possibly as high as 131 MPa along the platelet normals. Such stress levels will still be insufficient to initiate DHC, based on the guidelines contained in Table 6. If the assumption is made that K_{IH} for the Zircaloys is $5 \text{ MPa}\cdot\text{m}^{0.5}$, a stress of

131 MPa would require a crack of length about 1.2 mm for DHC to become active. As the wall thickness of PWR cladding is only of the order of 0.6-0.7 mm, the situation could never arise.

Conceivably, it might be postulated that the value currently being assumed for K_{IH} for the Zircalloys is not valid and that the real threshold stress intensity factor is much lower, so much so that a radially-oriented hydride could undergo DHC under the maximum stress conditions described above. However, it is by no means certain that this would lead to clad failure. For example, unless most of the hydrides are oriented in the radial direction, the crack would probably propagate only a short distance before encountering a circumferentially-oriented platelet. At this point, further progress would be directed in the tangential direction both because this is the direction of the highest stress (hydrogen diffuses up the stress gradient) and because the new hydride platelet is tangentially oriented. In addition, it should be remembered that the maximum stress will only be present for a relatively short period of time. As the initial radioactive inventory in the fuel decays, temperature will drop and will be accompanied, at least initially, by a proportional decrease in pressure/stress. Thus, although the initial stress in the cladding may equal the threshold stress, subsequent decay-induced changes would lower the stress below the critical value and crack propagation would cease. It might be argued that the crack propagation rate might exceed the rate of stress decrease and thus the stress intensity at the crack tip would always be in excess of the threshold value. This calculation has not been performed. However, this only becomes relevant if most of the hydrides are oriented radially and crack progress can continue unimpeded through the wall thickness.

Considering that peak condition fuel rods are only a very small percentage of the total number of fuel rods, it is concluded preliminarily that delayed hydrogen cracking is not likely to be an important mode of failure for the overwhelming majority of spent fuel pins during storage and final disposition. Perhaps the only uncertainty derives from lack of knowledge of the effect of radiation on the mechanisms of DHC and hydride reorientation. A scenario might be developed whereby radiation could bring about a decrease in the value of K_{IH} and so allow DHC to proceed. If this was accompanied by a major reorientation of hydrides to the radial direction, then conceivably gross

rupture would be the end result. However, as the conditions required for reorientation do not appear to exist, this is a somewhat moot point.

5.3 Fuel Side Stress Corrosion Cracking

5.3.1 Introduction

Degradation of Zircaloy cladding can occur in many different ways, one of which is known as "pellet-cladding interaction" (PCI). Interest in this particular mode of failure arose originally from concern about the performance of fuel pins during power ramp conditions, when the cladding can be subjected to relatively rapid increases in temperature and stress. Although PCI is often used to describe a single failure mode, it is in fact a generic term applied to the several processes originating in the internal environment of the fuel pins. These can be subdivided into those based on mechanical effects and those deriving from chemical phenomena. As an example of the former, the thermal expansion coefficient of the fuel is greater than that of the cladding. Consequently, as the reactor is brought up to full power, the pellets will expand to make intimate contact with the cladding and, as friction forces prevent them from moving freely axially, cause increases in the stresses in the latter. The chemical processes which are thought to contribute to pellet-cladding interaction often have their basis in radiolysis and in the release of fission products. The fission products are many, of course, but only a few have been seriously considered as potentially damaging, via stress corrosion cracking, to Zircaloy, including cesium, cadmium and iodine. Several investigations, including those of [Wachob, 1977], [Hofmann, 1981] and [Shann, 1983], have been carried out in order to identify the critical species. Almost invariably, the results have indicated that iodine is the most likely responsible agent. Thus the following review and discussion is based on the assumption that FSSCC of Zircaloy cladding occurs only because of the presence of iodine, although it is recognized that the actual situation is very complex and other agents may well contribute to the failures. In fact, even ten years ago, Garzarolli et al. [Garzarolli, 1979], referring to the characteristics of PCI failures, stated that *"a final review ... would be a book rather than a few pages."* Research since that time has only served to emphasize the complexity of the process. The 1979 statement, if applied to the status in 1989, would be considered an understatement.

Because our ultimate goal is an assessment of the likelihood of the occurrence of iodine stress corrosion cracking during spent fuel isolation, the present review concentrates mainly on data obtained from tests other than those aimed at measuring conventional short-term tensile and burst properties. Results from this latter type of testing are discussed only inasmuch as they provide information which might be of relevance in evaluating the phenomenon as a whole (for example, the critical iodine concentration).

The various aspects of the phenomenon can be grouped in three broad categories: quantifiable data on failure conditions (stress, temperature, iodine concentration); effects of other factors (for example, irradiation, hydriding, material texture and chemical inhomogeneities); and modeling. In this progress report, the emphasis is on the data obtained on typical unirradiated material. The effects of other factors, although alluded to at times in the present report, will be discussed in a later report.

5.3.2 Failure Conditions in Unirradiated Materials

The first report of the susceptibility of Zircalloys (specifically, Zircaloy-2) to ISCC was by Rosenbaum [Rosenbaum, 1966]. The phenomenon was observed to occur at 300-400°C in a vacuum chamber filled with iodine at a pressure of about 53.2 kPa¹⁸. Stress (or, more accurately, strain) was imparted to tubular specimens by the insertion of a stainless steel mandrel which had negative clearance at room temperature. Cracking was observed to occur after times as short as 0.5 hours. Interestingly, tests carried out on wire in uniaxial tension failed to produce any cracking. The reasons for this negative observation were not immediately apparent but it was postulated that it might be associated with the metallurgical microstructure differences between the tubing and the wire.

¹⁸For consistency, the present report gives all the iodine partial pressures in Pa, irrespective of the units used in the original reference. 1 Pa (a N/m²) is approximately equal to 10⁻⁵ atm., or 0.0075 torr, or 1.45 x 10⁻⁴ psi.

Garlick and Wolfenden [Garlick, 1971], using the same type of test as [Rosenbaum, 1966] (mandrel in tube), found both Zircaloy-2 and Zircaloy-4 to be susceptible to ISCC over the temperature range 250-510° C and with a variety of iodine concentrations (up to 26.6 kPa or 10^{-3} g/cm³). Test times were relatively short (the maximum failure time observed was 60 hours) and it was estimated that the stress imposed of the tubing was near the yield strength. Not all of the many combinations of materials and test conditions resulted in cracking. Specimens subjected to some pre-test heat treatments (e.g., 1 hour at 650° C) were less prone to cracking than specimens in other material conditions. No cracking was observed in the few tests run at temperatures above 510° C or when the iodine concentration was less than 2×10^{-4} g/cm³ (initial pressure less than 4.4 kPa). In addition, supporting the observations of [Rosenbaum, 1966], no stress corrosion cracking occurred when the loading was uniaxial. However, the iodine vapor pressure was less than 26.6 kPa and there is no information on the magnitude of the loads involved. The authors emphasize that the test methods were not suitable for long-term testing and therefore did not allow determination of the ultimate threshold conditions for cracking.

The first reported attempt to define some of the threshold parameters for ISCC of Zircaloys is that of [Wood, 1972]. This report also initiated the method of expressing iodine concentrations in the SCC testing in terms of the surface area of the Zircaloy specimens (i.e., mass of iodine per unit surface area of specimen). This method is more commonly encountered than others but proponents exist who contend that other units of measurement, such as partial pressure of iodine and mass of iodine per unit system volume, are more appropriate. The merits of the various systems are discussed in another section in the present report. Most of the testing in [Wood, 1972] was carried out at 300° C and the majority of the tests involved a particular batch of Zircaloy-2 tubing which had been shown in preliminary testing to be most susceptible to ISCC. With one exception, all the tests were done with stressed slotted rings cut from the tubing. An initial series of tests indicated that the critical stress for crack nucleation and propagation was approximately 217 MPa when the iodine concentration was 20 mg/cm², this being based on tests of relatively short duration. Subsequent testing, using precracked specimens exposed to iodine at a vapor pressure of one atmosphere, pointed to the existence of a critical stress intensity (K_{ISCC}) of about 32 MPa.m^{1/2}, below which

a crack would not propagate. ISCC was also found to be sensitive to both temperature and iodine concentration. With a stress of 310 MPa and an iodine concentration of 3 mg/cm², the failure time increased as the temperature decreased from 300° C to about 230° C. At the same stress and with a temperature of 300° C, no failures occurred within 1000 hours when the iodine concentration was less than about 0.02 mg/cm². [Wood, 1972] also discusses other aspects of ISCC of Zircalloys, including the effects of irradiation and metallurgical condition but these will be considered at a later point in time.

[Garlick, 1973] investigated the ISCC of Zircaloy-2 tubing using both expanding mandrels and inert gas pressurization. The mandrel tests, at 340° C, were designed primarily to determine the effect of residual cold work (and hence the strength of the tubing) on the susceptibility to ISCC. The most susceptible materials were those with the highest strength levels while tubing in the fully annealed condition did not crack even under the most severe test conditions. The internal pressurization tests were conducted at 330° C and various pressures, and involved material with three different strength levels. Iodine was contained inside the tubes but the actual concentration is not given. Each test had a nominal constant internal pressure but, because bulging and wall-thinning occurred as the test progressed, the true applied stress near the end of a test was probably greater than the initial stress. However, with one exception, no information is provided on what these corrected stresses might be. For each material, failure times increased as the internal pressure decreased, until reaching a critical stress level below which no failure would occur, at least in the laboratory time frame. These critical levels were usually just above the yield strength of the material in question; for example, the critical stress for tubing with a yield strength of about 305 MPa appeared to be about 320 MPa.

Testing of Zircaloy-4 tubing in several conditions of fabrication and heat treatment are described in [Weinberg, 1974]. Of particular interest is a series of internal pressurization tests at 360° C and 427° C, using iodine concentrations of 0.08 and 0.25 mg/cm² and various stress levels. Failure times extended out to 1,600 hours but some tests were allowed to run for up to 2,400 hours then discontinued without failure occurring. In all instances, rupture strengths at 360° C at the longer times were reduced

by as much as 50% when iodine was present, ranging from about 100 MPa for material cold-worked 78% and stress-relieved to about 130 MPa for recrystallized material. The reduction was much more at 427° C, the long-term rupture strength of 15-20% cold-worked material dropping from about 150 MPa without iodine to about 50 MPa in the presence of 0.08 mg/cm² iodine.

[Wood, 1974] addressed several aspects of ISCC of zirconium-based alloys (including Zircalloys 2 and 4). All the tests were performed at 300° C using stressed slotted rings and with iodine concentrations up to 20 mg/cm². Results on unirradiated Zircalloys stressed to the yield point showed one particular batch of tubing to be susceptible to ISCC but with much variability in failure times (from 3 to 310 hours). None of the other five batches failed in tests out to 290 hours, although two became embrittled. Other results in [Wood 1974] (such as the effects of irradiation) will be discussed in a future report.

[van der Schaaf, 1974] described a variety of tests on Zircaloy-2 in the recrystallized condition and after 50% cold-working. One of the tests involved biaxial bending, in which a disc was deformed by a conical indenter with a spherical tip. Although this type of test is not suitable for determining the threshold stress for ISCC, the results can show the qualitative dependence of the stress on the amount of iodine available. Thus van der Schaaf was able to demonstrate that, at 300° C, the minimum stress for ISCC decreased as the amount of iodine available increased. From the data presented, it can be inferred that, at the highest stresses, the minimum iodine concentration necessary to produce SCC at this temperature was about 2 mg/cm², irrespective of material condition. For stresses about one half those required to cause fracture without the presence of iodine, the minimum iodine concentration would be about 25 mg/cm². Similarly, by holding the iodine concentration constant (at 25 mg/cm²), it was shown that this stress reduction factor of about one half remained constant over the temperature range 200-500° C. None of the biaxial bending tests exceeded 5 hours in length. In addition to these tests, some uniaxial creep tests were run for times out to 22 hours at, presumably, 300° C (the actual temperature is not given in the paper) and with stress levels of 330, 350 and 370 MPa. The results from these tests indicated that there was no influence of the amount of iodine on the time to rupture, in line with the

observations of [Rosenbaum, 1966]. A third type of test, involving stressed slotted rings, also failed to reveal evidence of ISCC at 300°C, even though stresses near the yield strength were imposed while iodine concentrations ranged up to 20 mg/cm² and test times extended to 100 hours.

Wood et al. [Wood, 1975] performed a series of ISCC tests on Zircaloy-2 using both tube and plate specimens. Cracking was observed with the tubular specimens when stressed to near the yield strength at temperatures in the range 225-300°C. However, similar tests at lower temperatures (22-200°C) produced no cracks. The plate specimens were subjected to fracture toughness testing but little information is provided on the quantitative aspects of the test results. ISCC was observed to proceed at the three temperatures examined (22, 100 and 300°C), but only at 300°C are the actual stress intensities mentioned. Even here, the information is limited to "*stress intensity varied from 29-9 MN.m^{-3/2} as the cracks grew at 300°C.*" No quantitative estimates are provided of the iodine concentrations in any of the tests.

Busby et al., at the Bettis Atomic Power Laboratory, investigated the ISCC behavior of Zircaloy-4 tubing using pressurized tube specimens [Busby, 1975]. The results showed that an iodine concentration of 0.04 mg/cm² was sufficient to cause cracking at 360 and 400°C, but SCC appeared to be essentially independent of iodine concentration over the range 0.01-0.08 mg/cm². Threshold stress levels, below which SCC was not observed for test times up to 6000 hours, were in the range 130-165 MPa. The susceptibility to SCC, when it occurred, increased as the temperature increased from 360 to 400°C.

Kreyns, Spahr and McCauley [Kreyns, 1976] adopted a fracture mechanics approach to analyse the ISCC data reported in [Busby, 1975]. They calculated that K_{ISCC} was in the range 0.39-0.81 MPa.m^{0.5} between 360 and 400°C, values which are about an order of magnitude lower than those measured for delayed hydride cracking of Zircaloys.

Additional data from the Bettis program were reported by Tucker et al. [Tucker, 1976]. The studies in this case were focused on the effects of surface flaws and iodine concentration on the ISCC of stress-relieved Zircaloy-4 tubing at 360 and 400° C, using the method of internal pressurization. Failure times ranged from as low as 8.5 hours (at 360° C, 294 MPa, 0.04 mg iodine/cm² Zircaloy surface) to 5007 hours (at 360° C, 241 MPa, 0.005 mg/cm²). Some tests at lower stress levels exceeded 5500 hours and were terminated before failure occurred. Tucker et al. attempted a quantitative evaluation of their data and produced two relationships which facilitated calculation of the threshold stress and the critical stress intensity, K_{ISCC} . They were then able to calculate threshold stresses for three types of surface inhomogeneities at 360, 382 and 400° C.

The Bettis program also produced similar (but more extensive) data on recrystallized Zircaloy-4 tubing [Polan, 1977]. Failure times ranged from as low as 8.5 hours (at 400° C, 276 MPa, 0.04 mg iodine/cm² Zircaloy surface) to 3180 hours (at 360° C, 207 MPa, 0.001 mg/cm²). Some tests at stress levels of 207 MPa and lower at 360 and 382° C exceeded 4500 hours and were terminated before failure occurred. As in [Tucker, 1976], expressions were developed which related the threshold stress for ISCC to the temperature, iodine concentration and flaw geometry.

Mandrel insertion followed by differential expansion was the favored mode of testing cold-worked Zircaloy-2 tubing in [Une, 1977]. The objectives included determination of the critical iodine concentration required for ISCC and its temperature dependence, and the minimum plastic strain to failure at temperatures from 250 to 450° C. The iodine concentration effects were measured at 300 and 350° C using short-time tests (maximum 8 hours), with concentrations expressed in terms of mass per unit specimen area and mass per unit gas volume. By comparing the data from two series of tests at 350° C in which the gas volumes and specimen size were varied, Une was able to infer that expressing the iodine in terms of free volume was the more appropriate method for describing its concentration. Thus the critical concentration at 350° C was determined to be 1.14 mg/cm³ (when expressed as a function of area, he obtained two values: 2.58 mg/cm² and 0.40 mg/cm²). At 300° C the critical value was 0.15 mg/cm³ (or 0.34 mg/cm²). Une also selected the circumferential plastic strain as another key parameter in ISCC (as opposed to stress or stress intensity, favored by others). From

these tests he deduced that ISCC occurred at plastic strains above 0.37% at 300° C and above 0.42% at 350° C, values which he found to be comparable with those obtained by other researchers. Other facets of ISCC reported in [Une, 1977] included the effect of heat treatment and the presence of an oxygen partial pressure in the iodine atmosphere.

[Wachob, 1977] described a series of stress corrosion cracking experiments performed using compact tension fracture mechanics specimens of stress-relieved Zircaloy-4 exposed to various halogen-containing environments at 360° C. Iodine and bromine were similarly aggressive and each appeared to have a threshold stress intensity of just under 9 MPa.m^{0.5}. However, it should be noted that the bromine concentration in the tests was much higher than that of the iodine (30 mg/cm² compared with 4.4 mg/cm²). Tests using mixed environments (iodine-plus-iron, iodine-plus-oxygen and iodine-plus-cadmium) showed no evidence of synergistic effects and crack growth rates were similar to those obtained in free halogen environments.

A comprehensive EPRI-NASA program on the SCC of Zircaloys was conducted simultaneously at several different laboratories and the results are described in [Cubiciotti, 1978]. The inside surfaces of irradiated fuel cladding were examined and it was found that several potentially aggressive substances were present in the fuel pin internal environment. Screening tests identified iodine as one of the most aggressive species and attempts were made to determine threshold conditions (stress, iodine concentration) for Zircaloy-4 (tubing and plate forms) and Zircaloy-2 (tubing only). Some of the data (on the plate material) have already been described ([Wachob, 1977]). Other data, on the tubing material (unflawed and preflawed, unirradiated and irradiated), are described in later paragraphs ([Jones, 1979] and [Jones, 1980]).

Some data on ISCC failure of Zircaloy were provided in [Garzarolli, 1978] (these data also appear in [Garzarolli, 1979], an extensive paper on the main causes of fuel element failure in general). Garzarolli et al. first described the results of constant uniaxial load tests, at 350° C and under constant iodine partial pressure, on straightened samples taken from the tangential direction of cladding tubes. The loads were 300 and 330 MPa and failure times ranged from less than one hour to in excess of 100 hours. The critical iodine concentration necessary to induce SCC (expressed as the iodine

partial pressure in three different atmospheres) was found to be somewhere in the range 4-40 Pa. The actual value appeared to be dependent on the presence or absence of passivating species (such as moisture) in the environment. The limited data shown did not conclusively prove this but the theory could explain the differences between the results obtained by the various researchers. The authors also reported that similar observations were made when tests were conducted with internally pressurized tubes. Other test data reported show a time-stress relation for the occurrence of ISCC in stress-relieved Zircaloy. The data in question were obtained from internally pressurized tubes at 350°C and exposed to rather high iodine concentrations. Failure times varied between 30 minutes and 500 hours. These stress-rupture tests indicated that the threshold stress for ISCC at 350°C was about 250 MPa.

Videm et al. ([Videm, 1979a] and [Videm, 1979b]) focused their studies on stress corrosion crack initiation and growth in Zircaloy-2 tubes which either had smooth surfaces or had been precracked. Again, because the program was designed to study effects during power ramping, the tests were of relatively short duration and none of the failure times in the tests on smooth specimens exceeded about 24 hours. All the tests involved internal pressurization with argon containing 0.06 mg/cm² iodine and were carried out at either 80°C or 340°C. During the tests, the gas pressure was kept constant which meant that the stress in the tubing continually changed as the strain incurred altered the tubing dimensions. Videm et al. recognized this and estimated both the initial and the final stresses for the smooth specimen tests. The data obtained on these specimens indicated that a threshold stress existed below which SCC would not occur and that this stress level was dependent on the material condition. Based on the average stress values (i.e., between the initial and the final stress in each test), the threshold stress at 340°C was about 320 MPa for recrystallized material. This increased as the amount of cold work in the material increased, reaching 360 MPa for stress-relieved material and 410 MPa for 60% cold worked material. Tests on precracked specimens showed that crack growth rates increased very rapidly as the stress intensity increased at both 80 and 340°C. The authors did not attempt to define a threshold stress intensity at either temperature, but extrapolation of the data indicates that the crack growth rate will become insignificant below certain stress intensities. If we define the level of "insignificance" to be 10⁻⁹ mm/s (equivalent about 3 mm/100 years),

this growth rate would require a stress intensity of about $3 \text{ MPa}\cdot\text{m}^{0.5}$ at 340°C and $8\text{-}9 \text{ MPa}\cdot\text{m}^{0.5}$ at 80°C . In addition, [Videm, 1979a] provided a series of stress-versus-time to failure curves for starting defects of different sizes. From these, it was concluded that stress-intensity-controlled crack growth takes over when the initial defect size is about 0.07 mm . [Videm, 1979a&b] also briefly examined the effect of irradiation on ISCC.

Tests to determine the stress threshold for ISCC of unirradiated Zircaloy-4 tubing were described in [Jones, 1979]. The conditions included internal pressurization at 360°C and an iodine concentration of $6 \text{ mg}/\text{cm}^2$. The pressurization tests were divided into three different types: simple pressure ramp (to determine burst strength); incremental pressurization (to approximately define the pressure/failure time relationship); and rapid pressure ramp followed by isopressure hold (to more accurately define that relationship). When consideration was taken of the uncertainty in the data, it became apparent that the data from the as-received (unflawed) material and those from the preflawed material could be fitted to a common curve to describe the hoop stress/failure time relationship at 360°C . This curve, in turn, indicated a threshold stress of about 295 MPa , below which ISCC would not occur. However, this was again based on data from relatively short tests, the longest failure time (for an unflawed specimen at a nominal stress of 310 MPa) being about 34 hours. Some longer time tests exist but in these no failures occurred. These included one test (on a preflawed specimen) of 168 hours at a nominal stress of 225 MPa followed by another 168 hours at 250 MPa . The longest time without failure on an unflawed specimen was 100 days (at 290 MPa). The preflawed specimens were also used to give some measure of the critical stress intensity but again failure times were much too short (generally, less than 20 hours) to allow meaningful long-term values to be obtained. The lowest stress intensity to cause failure (after 19.2 hours) in the presence of iodine was $4.6 \text{ MPa}\cdot\text{m}^{0.5}$. The authors expressed strong reservations about the use of stress intensity as a threshold criterion for ISCC failure of tubing under internal pressurization.

The prime objective of the work reported in [Peehs, 1979] was to define the iodine threshold concentration for ISCC in Zircaloy cladding. The tests, carried out mostly at 400°C , involved internal pressurization of the specimens with helium containing various quantities of iodine. Different stress levels were investigated but the criterion of whether

failure was due to ISCC was based on the relative uniform elongation compared to that of a specimen not exposed to iodine. Using this method, it was determined that ISCC began to occur at 400° C when the iodine concentration exceeded about 0.001 mg/cm². Furthermore, this threshold value was essentially independent of stress over the range 150-250 MPa. However, it appeared to be higher (about 0.005 mg/cm²) at 350° C. Rupture times in these tests varied from less than half an hour to about 1,200 hours.

The deformation and fracture behavior of Zircaloy-2 in an iodine environment were discussed in two papers by Une [Une, 1979a&b]. The first of these [Une, 1979a] was concerned with the uniaxial tensile properties under constant extension rate and thus the experiments will not be further described here. Tension tests were also the main mode of testing in [Une, 1979b] but under plane strain conditions, thus allowing an assessment of stress ratio effects. Data from these tests indicated that Zircaloy-2, whether in the stress-relieved condition or recrystallized, was most susceptible to ISCC at 350° C when the stress ratio (axial to tangential) was about 0.5 (this is the ratio present in closed-end tube burst tests). The program also included a series of tests with different iodine contents (partial pressures). The results from these tests indicated that severe ISCC occurs when the iodine partial pressure is equal to or greater than 532 Pa. Viewing the plot provided in [Une, 1979b], it can also be inferred that the critical partial pressure below which ISCC would not occur is about 133 Pa.

Sejnoha and Wood [Sejnoha, 1979], using stressed slotted rings of Zircaloy-4, were unable to induce cracking after 300 hours at 300° C in iodine vapor (concentration 10 mg/cm²) when the material was in either the annealed or the as-received condition. This included specimens with additional axial scribe marks on the inside surface and for stresses (at the start of testing) ranging approximately from 275 to 400 MPa. However, the introduction of sharp precracks (depths from 1 mm to 7.5 mm) caused crack propagation and failures in the annealed material when the combination of depth and applied stress was high enough. In addition, stress-relieving of the as-received material rendered it susceptible to cracking at applied initial stress levels equal to or above the yield strength at 300° C (about 300 MPa). Failure times when the initial stress was close to that of the yield strength were of the order of 200 hours.

[Cox, 1979] was devoted mainly to the effect of hydrides on ISCC of Zircalloys but included, in the introductory section, a plot of crack velocity versus stress intensity for Zircaloy-2 at 27° C. No details are provided and the data are probably taken from an earlier (unreferenced) paper or report. The graph indicates that the critical stress intensity for ISCC is about 11-13 MPa.m^{0.5} at this temperature.

[Jones, 1980] described more of the testing performed under the EPRI-NASA program [Cubicciotti, 1978], using the pressurization methods of [Jones 1979] and mostly with an iodine concentration of 6 mg/cm². Some of the data provided, on Zircaloy-4, were previously presented in [Jones, 1979] and will not be further discussed here. Most of the data, however, are on unirradiated Zircaloy-2 tubing, either stress-relieved or annealed, and at 320° C. A few tests were performed on the stress-relieved material at 360° C and these were used to establish that there was no significant difference between Zircaloy-2 and Zircaloy-4 in ISCC behavior. That is, at 360° C, the threshold stress for stress-relieved Zircaloy-2 is about 295 MPa. At 320° C, this threshold seems to be higher, perhaps 320 MPa. On the other hand, the annealed material appears to have a lower threshold (about 280 MPa) at this temperature. Again, it should be noted that the failure times involved were generally no greater than 100 hours, while the longest times at one stress without failure were 190 days at 275 MPa for the annealed material and 218 days at 320 MPa for the stress-relieved material. An attempt was also made to assess the effect of iodine concentration on the pressurized specimens. However, the sparsity of data (only two tests involved iodine concentrations other than 6 mg/cm²) prevent the formation of any meaningful conclusions.

The EPRI-funded program also produced the data on the ISCC susceptibility of two lots of commercial Zircaloy-2 tubing, reported in [Syrett, 1980]. The two lots, produced by different manufacturers but to exactly the same specification, proved to have very different responses to ISCC testing via internal pressurization. The tests, conducted at 320° C and with an iodine concentration of 60 mg/cm², varied in length from less than an hour to about 170 hours. Both lots were tested in the as-received (stress-relieved) condition but one appeared to have a threshold stress, under the test conditions, of

about 340 MPa while that of the second lot was near 240 MPa. Although the origin of the variability was not clear, Syrett et al. considered that the important factors were residual stress, surface condition and texture.

Data from a follow-up program designed to clarify the observations of [Syrett, 1980] were presented in [Syrett, 1981]. These data also came from internal pressurization tests at 320° C but the iodine concentration was lower (0.6 mg/cm²) than in the earlier tests. The test material was from a single heat of Zircaloy-2 which was formed into four lots of tubing with different basal textures. These textures proved to be very relevant to the ISCC susceptibility of the tubing and it was determined that the more radial the basal pole distribution was, the greater was the resistance to cracking. For example, the tubing with the most radial texture required a estimated hoop stress of about 360 MPa for failure in 100 hours, whereas that with the most tangential texture required an estimated stress of only about 240 MPa to cause failure in the same time. The SCC susceptibility was also affected to some extent by the surface condition and the presence of a lightly-etched-and-shot-peened surface on the tubing with the most tangential texture was to lower the estimated 100 hour failure stress to about 200 MPa. Actual failure times recorded in these series of tests were generally short, the longest being 105 hours and most of them less than 50 hours. There were also some tests which were discontinued before failure occurred. The longest of these ran for 214 hours.

Onchi and Tanaka [Onchi, 1981] investigated ISCC of both cold-worked and recrystallized Zircaloy-2 tubing at 300° C by means of the ring tension method. The tests included constant extension rate and constant loading modes in argon gas containing 2 mg/cm³ iodine, and used simple ring and groove ring specimens. Failure time in the constant load tests extended only as far as about 40 hours. The presence of iodine in the test environment was sufficient to lower the stress required to produce failure in a specific time by 30-40 MPa over the range examined. This was true for both the cold-worked and the recrystallized material, but it was noted that the time to failure for simple ring specimens of the former material was much more sensitive to the applied stress than that for the equivalent recrystallized material specimens. When groove ring specimens were tested, neither material condition showed much stress sensitivity of the failure time. However, these specimens appeared to have higher strength than the

simple specimens. For example, the authors estimated the threshold stress for simple specimens of the recrystallized material to be about 240 MPa and that for grooved ring specimens about 300 MPa. The equivalent values for the cold-worked material were estimated at 314 and 450 MPa.

[Hunt, 1981] described the results of tests on precracked split ring specimens of Zircaloy-4 exposed to iodine at 36 Pa partial pressure. The tests were conducted at temperatures in the range 20-200° C and the results reported in terms of whether or not failure occurred in 2000 hours. From the data available, Hunt et al. were able to construct a plot showing the variation of critical stress intensity for failure/non-failure with temperature. This indicated that, from 20 to 100° C, K_{ISCC} remained constant at just over 9 MPa.m^{0.5}. Above 100° C, K_{ISCC} decreased until, at 200° C, it has reached a value of about 3 MPa.m^{0.5}. Hunt et al. also report that greatly increasing the iodine concentration (to 4650 Pa) at 100° C caused the value of K_{ISCC} to drop from 9 MPa.m^{0.5} to 5 MPa.m^{0.5}.

Cox et al., in [Cox, 1981], discussed PCI failures with particular reference to the possibility that they may be caused by metal vapor embrittlement due to the presence of cesium and/or cadmium vapors. In the process, a graph was shown of the variation of critical stress intensity for crack propagation in iodine. No reference was cited for the source of the information but the data appear to be the same as those contained in [Hunt, 1981].

Knorr and co-workers have reported on the ISCC of Zircaloys in plate and tubing form. [Knorr, 1982a] described a series of crack propagation tests using conventional fracture mechanics specimens cut from plates of Zircaloy-2 and Zircaloy-4, both materials being available in two conditions (stress-relieved and recrystallized). All tests except one were carried out at 300° C under an iodine pressure (in an atmosphere of flowing argon) of 4 Pa, and times ranged from 113 to 284 hours. The lowest values measured for K_{ISCC} of the stress-relieved material were 5.5 MPa.m^{0.5} (Zircaloy-2) and 4.0 MPa.m^{0.5} (Zircaloy-4). The equivalent values for the recrystallized material were 4.7 MPa.m^{0.5} (Zircaloy-2) and 7.0 MPa.m^{0.5} (Zircaloy-4). However, the value of K_{ISCC} for both material conditions was heavily dependent on the crystallographic texture. As the

resolved fraction of basal poles parallel to the direction of crack opening decreased ("f" values dropped from near unity to near zero), the value of K_{ISCC} increased significantly.

[Knorr, 1982b] reported on the results of tube pressurization tests on Zircaloy-2 at 320° C and an iodine concentration of 0.1 mg/cm². One of the objectives of the program was to study the effects of texture on ISCC susceptibility and to this end two lots of tubing were tested. The lot with the lower "f" value (that is, its basal poles were aligned more perpendicular to the radial direction of the tube than were those of the other lot) proved to be the more susceptible to ISCC, both when in the as-received condition and after stress relief. It is difficult to determine the values for the threshold stress but conceivably they could be about 290-300 MPa for the stronger lot and around 200 MPa for the weaker lot. However, none of the failure times exceeded 90 hours and most were less than 40 hours. One test ran to 143 hours without the specimen failing.

Norrington, Haag and Wikstrom [Norrington, 1982] investigated the propagation of stress-corrosion cracks in internally pressurized cold-worked Zircaloy-2. The test conditions included a temperature of 300° C and an iodine concentration of 0.6 mg/cm³, with the material being available in three different grain sizes. The last item did not appear to significantly influence the relationship between crack propagation rate and stress intensity factor. This relationship, in fact, could be interpreted either as following a simple one which extended over the complete data range or as a more complex one involving a transition between two different mechanisms. The actual stress intensity factors calculated varied from a low of 4.1 MPa.m^{0.5} (crack propagation rate 5 x 10⁻⁸ mm/s) to a high of 10.9 MPa.m^{0.5} (5.3 x 10⁻⁵ mm/s). Test times varied from less than one hour to 168 hours.

[Pettersson, 1982] essentially dealt with stress corrosion crack growth in irradiated, fully recrystallized Zircaloy-2 tubing but did provide a couple of data points for unirradiated material. These were obtained at 300° C and with an iodine concentration of 0.6 mg/cm³, and with the same test method as [Norrington, 1982]. The short-time tests (the longest was 20 minutes) used stress intensity factors of 7.9 and 7.7 MPa.m^{0.5} to produce crack growth rates of 1.17 x 10⁻⁴ and 1.25 x 10⁻⁴ mm/s, respectively.

[Shann, 1983] reported on the stress corrosion cracking of stress-relieved Zircaloy-2 tubing when internally pressurized with argon containing iodine or metal iodides. In this instance, the experimenters decided to report iodine concentrations as partial pressures, rather than the amount of iodine per unit surface area of Zircaloy. Stress dependence tests at 300° C with an iodine pressure of 1.86 Pa indicated a threshold stress of about 300 MPa, based on relatively short failure times (less than 100 hours). These failure times were also dependent on the temperature: at a fixed nominal stress of 314 MPa, the failure time at 270° C was approximately twice that at 320° C. With both temperature and stress were held constant, it was possible to measure the dependence of the rupture time on the iodine concentration. The data from this series of tests indicated a threshold iodine pressure of just over 0.001 torr, below which ISCC would not occur.

[Crescimanno, 1984] described a fracture mechanics model for application to iodine-induced stress corrosion cracking of Zircaloy tubing. The authors did not themselves perform any testing but provided a comprehensive tabulation of relevant data obtained mostly at the Bettis Atomic Power Laboratory but with some data points from the Argonne National Laboratory. Most of the observations have been described earlier, in [Busby, 1975], [Tucker, 1976] and [Polan, 1977]. However, the paper did include some previously unreported data on recrystallized material tested at 316° C and an iodine concentration of 0.04 mg/cm². Of these tests, the longest failure time was 520 hours following a nominal stress of 207 MPa.

A program to obtain ISCC information of particular relevance to spent fuel storage situations was described by Peehs et al. ([Peehs, 1986a] and [Peehs, 1986b]). The program involved two series of tests on internally pressurized stress-relieved Zircaloy tubing. One of these, at 400° C, with three different stress levels and an iodine concentration of 0.01 mg/cm² has been completed and no failures were observed over a period of 360 days. The highest hoop stress in these tests was 150 MPa. The conditions in the other series of tests included two temperatures (100 and 300° C), two stress levels (62 and 95 MPa) and four iodine concentrations (0, 0.001, 0.003 and 0.01 mg/cm²). At the time the later of the two papers, [Peehs, 1986b], was written, no failures had been recorded and the test time had accumulated to 2,300 days.

A series of crack initiation and growth tests on five lots of fuel cladding (Zircaloy-4) have been reported in [Brunisholz, 1987]. The tests were carried out on pressurized tubes exposed to iodine vapor (at a concentration of 1.5 mg/cm^2) at 350°C and the time to failure measured as a function of applied hoop stress (both for unflawed and for precracked specimens). The presence of iodine generally increased the susceptibility of both types of specimen to cracking but the effect was much more noticeable with the precracked specimens. Test times did not exceed about 200 hours. It is difficult to determine if a threshold stress existed for the unflawed specimens but the lowest hoop stress at which an iodine-exposed specimen failed was about 260 MPa (recrystallized material). The equivalent value for the precracked specimens (crack size approximately 0.2 mm) was about 170 MPa. However, the latter set of data were most useful in providing estimates of the critical stress intensity, K_{ISCC} . This varied from 3.5 to $5.0 \text{ MPa}\cdot\text{m}^{0.5}$ for stress-relieved material, and was measured at 5.0 and $5.7 \text{ MPa}\cdot\text{m}^{0.5}$ for recrystallized material.

The effects of iodine concentration on the ISCC of stress-relieved Zircaloy-4 tube over the temperature range $330\text{-}400^\circ \text{C}$ have been reported by Ryu, Kang and Lee [Ryu, 1988]. All the tests were performed at one stress level, 475 MPa, obtained by internal pressurization. The failure time at 330°C and 475 MPa, without any iodine present, was 110 hours. This was progressively shortened as the iodine level was increased from 0.2 to 4.0 mg/cm^2 , being just over 9 hours at the highest iodine concentration. Failure times were also dependent on temperature. An iodine concentration of 0.2 mg/cm^2 caused failure in just over 60 hours at 330°C , in about 5 hours at 360°C and in just over an hour at 400°C . The authors calculated activation energies for the various facets of the deformation process (time to failure, strain at failure and average crack propagation rate) and concluded that the adsorption of iodine or iodides on the metal surface at the crack tip was the rate-controlling factor.

5.3.3 Discussion

The observations described in Section 5.3.2 are briefly summarized in Tables 10, 11 and 12. The following paragraphs discuss the importance of some individual parameters and, where possible, indicate critical values below which it appears that ISCC will not occur. These are then compared with the conditions extant during spent fuel isolation, and thus the likelihood of failure assessed. Of necessity, these evaluations are very preliminary in nature. In-depth discussions of the many different facets of the phenomenon have not been attempted at this time, nor has a thorough assessment of the models proposed to quantify ISCC.

5.3.3.1 Iodine Concentration

Although it is implicit that, for ISCC to occur, iodine must be present, it is not obvious from the data available what constitutes a critical concentration. Table 10 summarizes these data and makes it very apparent that defining the critical concentration is not simple. One reason for this is the lack of agreement on the most appropriate method of expressing the iodine concentration.

The method most often encountered is that in which the concentration is expressed in terms of mass of iodine per unit area of Zircaloy. Originally, this method was adopted as a matter of convenience because the testing was taking place in a closed system [Wood, 1972]. One obvious limitation of this occurs when the closed system contains other materials in addition to Zircaloy; in such instances, the other material may also absorb iodine and thus affect the total amount of iodine available to react with the Zircaloy. However, in an all-Zircaloy system, the method of expression has some merit. Cubiciotti et al. pointed out, in [Cubiciotti, 1982], that consideration should be given to whether iodine is active in a gaseous form or as a solid on the Zircaloy surface. If gaseous species are involved, then the concentration should be expressed with reference to the volume of gas. If the ISCC mechanism is dependent on the presence of a solid iodide, it would be appropriate to express the concentration as a function of the Zircaloy surface. After reviewing the data presented in [Peehs, 1979], Cubiciotti et al. concluded that the mechanism involved the formation of solid iodides on the Zircaloy surface and

TABLE 10

Minimum Iodine Concentrations for Cracking of Zircalloys

Reference	Method of Stress Application	Temp. (°C)	Time (h)	Iodine Conc. Parameter	Iodine mg/cm ²	Concentration mg/cm ³	Pa
[Wood, 1972]	Wedge	300	300	Area	0.02	0.2	--
[Une, 1977]	Mandrel	300	7	Volume	0.34	0.15	--
[van der Schaaf, 1974]	Indentor	300	5	Area	2	0.4	--
[Shann, 1983]	Pressure	320	40	Pressure	--	--	0.2
[Ryu, 1988]	Pressure	330	50	Area	0.6	--	--
[Garlick, 1971]	Mandrel	340	24	Pressure	--	0.22	4400
[Une, 1977]	Mandrel	350	2	Volume	2.58	1.14	22000
[Une, 1977]	Mandrel	350	2	Volume	0.40	1.15	22000
[Peehs, 1979]	Pressure	350	1160	Area	0.005	0.02	--
[Garzarolli, 1978]	Pressure	350	6	Pressure	--	--	5
[Garzarolli, 1978]	Pressure	350	100	Pressure	--	--	25
[Une, 1979b]	Tension	350	<1	Pressure	--	--	133
[Ryu, 1988]	Pressure	360	4	Area	1.0	--	--
[Peehs, 1979]	Pressure	400	50	Area	0.001	0.004	--
[Ryu, 1988]	Pressure	400	10	Area	2.0	--	--

Notes

- "Iodine Conc. Parameter" - the prime method of expressing the iodine concentration
- "Area": concentration referenced to the Zircaloy surface (mass per unit area)
 - "Volume": concentration referenced to the volume of the test system (mass per unit volume)
 - pressures in parentheses estimated, not measured

TABLE 11

Summary of Selected Observations of Cracking in "Constant" Stress Tests

Reference	Material; Condition	Temp. (°C)	Iodine Conc. (mg/cm ²)	Stress (MPa)	Failure Time (h)
[Wood, 1975]	Zr2; SR	225-300	not given	near YS	--
[Garlick, 1971]	Zr2; SR	250	(<26.6 Pa)	near YS	17
[Rosenbaum, 1966]	Zr2; ?	300-430	(≈53.2 Pa)	above YS	0.5
[Garlick, 1971]	Zr4; SR	300	(<26.6 Pa)	near YS	23
[Wood, 1972]	Zr2; CD	300	20	217	<3
[Wood, 1972]	Zr2; CD	300	20	232-290	0.1-0.5
[Wood, 1972]	Zr2; CD	300	(threshold 0.1-0.3)	310	3-300
[Wood, 1974]	Zr2; SR	300	20	near YS	3-310
[Une, 1977]	Zr2; CW	300	0.34	(0.37%)*	7
[Sejnoha, 1979]	Zr4; AN	300	10	260?	400
[Sejnoha, 1979]	Zr4; SR	300	10	295	220
[Onchi, 1981]	Zr2; CW	300	(2 mg/cm ³)	380	30
[Onchi, 1981]	Zr2; RX	300	(2 mg/cm ³)	230	40
[Shann, 1983]	Zr2; SR	300	(1.86 Pa)	300	≈50
[Crescimanno, 1984]	Zr4; RX	316	0.04	207	520
[Crescimanno, 1984]	Zr4; SR	316	0.04	276	61
[Garlick, 1971]	Zr2; SR	320	(1.3-26 kPa)	near YS	17
[Jones, 1980]	Zr2; SR	320	6	329	90
[Jones, 1980]	Zr2; AN	320	6	282	100
[Syrett, 1980]	Zr2; SR	320	60	348	96.5
[Syrett, 1980]	Zr2; SR	320	60	241	46.6
[Syrett, 1981]	Zr2; SR	320	6	283	34
[Syrett, 1981]	Zr2; SR	320	6	207	4.3
[Knorr, 1982b]	Zr2; AR	320	0.1	314	1790
[Knorr, 1982b]	Zr2; SR	320	0.1	345	1390
[Knorr, 1982b]	Zr2; AR	320	0.1	208	2710
[Knorr, 1982b]	Zr2; SR	320	0.1	221	5335
[Garlick, 1971]	Zr2; SR	325	(1.3-26 kPa)	near YS	16
[Garlick, 1971]	Zr2; SR	330	(1.3-26 kPa)	near YS	6
[Garlick, 1973]	Zr2; AN	330	---	320	7.4
[Garlick, 1973]	Zr2; SR	330	---	410	5.5
[Garlick, 1973]	Zr2; SR	330	---	510	7
[Ryu, 1988]	Zr4; SR	330	0.2	475	≈66
[Garlick, 1971]	Zr2; SR	340	(1.3-26 kPa)	near YS	5
[Garlick, 1971]	Zr4; SR	340	(1.3-26 kPa)	near YS	5
[Garlick, 1973]	Zr2; SR	340	---	near YS	--
[Videm, 1979a&b]	Zr2; RX	340	0.06	315	20
[Videm, 1979a&b]	Zr2; SR	340	0.06	370	14
[Videm, 1979a&b]	Zr2; CW	340	0.06	440	25

TABLE 11 (cont.)

Summary of Selected Observations of Cracking in "Constant" Stress Tests

Reference	Material; Condition	Temp. (°C)	Iodine Conc. (mg/cm ²)	Stress (MPa)	Failure Time (h)
[Garlick, 1971]	Zr2; SR	350	(1.3-26 kPa)	near YS	6
[Une, 1977]	Zr2; CW	350	2.58	(0.49%)*	2
[Peehs, 1979]	Zr?; SR	350	0.005	250	1160
[Garzarolli, 1978]	Zr?; SR	350	3 x 10 ⁶	250	170
[Une, 1979b]	Zr2; SR	350	(0.5-6.6 kPa)	355	<1
[Une, 1979b]	Zr2; RX	350	(0.5-6.6 kPa)	330	<1
[Garlick, 1971]	Zr2; SR	360	(<26.6 Pa)	near YS	17
[Garlick, 1971]	Zr4; SR	360	(<26.6 Pa)	near YS	18
[Weinberg, 1974]	Zr4; SR	360	0.25	100	1200
[Weinberg, 1974]	Zr4; RX	360	0.08-0.25	130	1600
[Weinberg, 1974]	Zr4; CW	360	0.08-0.25	115	1200
[Busby, 1975]	Zr4; SR	360	0.01-0.08	165	3500
[Busby, 1975]	Zr4; RX	360	0.005-0.08	165	66-280
[Tucker, 1976]	Zr4; SR	360	0.005-0.04	241	5007
[Polan, 1977]	Zr4; RX	360	0.001-0.04	172	122
[Jones, 1979]	Zr4; SR	360	6	310	34
[Ryu, 1988]	Zr4; SR	360	0.2	475	≈5.2
[Busby, 1975]	Zr4; SR	382	0.04	155	1050
[Polan, 1977]	Zr4; RX	382	0.001-0.04	172	49
[Garlick, 1971]	Zr2; SR	400	(<26.6 Pa)	near YS	2
[Busby, 1975]	Zr4; SR	400	0.01-0.04	130	4900
[Busby, 1975]	Zr4; RX	400	0.04	145	77-117
[Tucker, 1976]	Zr4; SR	360	0.005-0.04	172	5004
[Polan, 1977]	Zr4; RX	400	0.001-0.04	207	7.5
[Peehs, 1979]	Zr?; SR	400	0.001	150-250	50
[Ryu, 1988]	Zr4; SR	400	0.2	475	≈1.2
[Weinberg, 1974]	Zr4; CW	427	0.08	52	1100
[Garlick, 1971]	Zr2; SR	450	(1.3-26 kPa)	near YS	60
[Garlick, 1971]	Zr2; SR	510	(1.3-26 kPa)	near YS	16

Notes: Material: Zr2 - Zircaloy-2; Zr4 - Zircaloy-4;
 Zr? - Zircaloy (type not specified)
 Condition: SR - stress-relieved; CD - cold-drawn;
 CW - cold-worked; AN - annealed;
 RX - recrystallized; AR - as received
 Stress: YS - Yield stress

* Rupture strain; no stress given.

TABLE 12

Summary of Selected Observations on Stress Intensity Measurements

Reference	Material; Condition	Temp. (°C)	Iodine Conc. (mg/cm ²)	K _{ISCC} (MPa.m ^{0.5})	da/dt (mm/s)
[Wood, 1975]	Zr2; CW	22, 100	- ISCC but conditions not stated		
[Cox, 1979]	Zr2;	27	not given	11-13	10 ⁻⁹
[Videm, 1979a&b]	Zr2; RX	80	0.06	11	4x10 ⁻⁷
[Hunt, 1981]	Zr4;	25-100	(36 Pa)	9.3	---
[Hunt, 1981]	Zr4;	100	(1460 Pa)	5	---
[Hunt, 1981]	Zr4;	200	(36 Pa)	3	---
[Wood, 1972]	Zr2; CW	300	(100 kPa)	32	10 ⁻⁴
[Wood, 1975]	Zr2; CW	300	not given	9-29	10 ^{-5?}
[Knorr, 1982a]	Zr4; SR	300	(4 Pa)	4.0-15.7	2x10 ⁻⁵
[Knorr, 1982a]	Zr4; RX	300	(4 Pa)	7.0-12.3	5x10 ⁻⁶
[Knorr, 1982a]	Zr2; SR	300	(4 Pa)	3.5-17.3	10 ⁻⁵
[Knorr, 1982a]	Zr2; RX	300	(4 Pa)	4.7-11.6	10 ⁻⁵
[Norrington, 1982]	Zr2; CW	300	(0.6 mg/cm ³)	4.1	5x10 ⁻⁸
[Pettersson, 1982]	Zr2; RX	300	(0.6 mg/cm ³)	7.7	10 ⁻⁴
[Videm, 1979a&b]	Zr2; RX	340	0.06	4	2x10 ⁻⁷
[Videm, 1979a&b]	Zr2; SR	340	0.06	6	6x10 ⁻⁷
[Brunisholz, 1987]	Zr4; SR	350	1.5	3.4-5.0	10 ⁻⁶
[Brunisholz, 1987]	Zr4; RX	350	1.5	5.0-5.7	10 ⁻⁶
[Kreyns, 1976]	Zr4; SR	360	0.08	0.50	---
[Kreyns, 1976]	Zr4; RX	360	0.04	0.81	---
[Wachob, 1977]	Zr4; SR	360	4.4	9	4x10 ⁻⁷
[Jones, 1979]	Zr4; SR	360	0.6	4.6	6x10 ⁻⁸
[Kreyns, 1976]	Zr4; SR	382	0.04	0.46	---
[Kreyns, 1976]	Zr4; SR	400	0.04	0.39	---
[Kreyns, 1976]	Zr4; RX	400	0.04	0.70	---

Notes: Material: Zr2 - Zircaloy-2; Zr4 - Zircaloy-4;
Condition: SR - stress-relieved; CW - cold-worked;
RX - recrystallized.

thus it was appropriate to express the concentration on an areal basis. On the other hand, Une, in [Une, 1977], compared the data from two sets of tests under identical conditions of temperature and stress, but with different system volumes and specimen surface areas, and concluded that expressing the concentration on a volumetric basis produced a better correlation with the failure observations.

Yet another school of thought supports the use of partial pressure to define the iodine concentration. This was the method used in the very earliest tests reported, [Rosenbaum, 1966] and [Garlick, 1971]. It lost favor for a few years then reappeared, first in [Une, 1979a&b]. Unlike his earlier tests, reported in [Une, 1977], which involved placing a known amount of iodine in a closed system, the specimens in [Une, 1979a&b] were exposed to a flowing argon atmosphere containing iodine at a small partial pressure. Une gives no reason for this change of procedure but it can be inferred that he was concerned about the decrease in concentration over time in a closed system as the iodine is gradually absorbed and reacted. By using a flowing gas system he was able to maintain a constant partial pressure (and thus concentration) of iodine. Knorr et al., in [Knorr, 1982a], also used a flowing gas system to deliver iodine at a constant partial pressure, presumably for the same reason. Shann and Olander provide a very explicit justification for their use of partial pressure as a measure of iodine concentration in the tests described in [Shann, 1983]: *"In all previous experimental studies of iodine SCC of Zircaloy a known quantity of iodine was added to the inside of the sealed tube. The procedure precluded control and even knowledge of the iodine pressure contacting the metal and led to the practice of describing iodine availability in the thermodynamically meaningless units of mg/cm². In the present experiment, iodine and other SCC agents were delivered to the outside surface of the tube specimen in the form of a molecular beam with a well-defined equivalent pressure. The molecular beam impinged on a spot ≈ 5 mm in diameter on the tube and failure always occurred inside this spot."*

In weighing the merits of the various ways of expressing the iodine concentration, consideration must be given to the application in mind. While there is no doubt that there is more precise control and knowledge of the iodine concentration in the tests described in [Shann, 1983], the information acquired is, strictly speaking, primarily of academic interest in elucidating the mechanism of ISCC. The usefulness of the data in

helping to assess the likelihood of ISCC failure of a spent fuel pin is more questionable, ironically for some of the same reasons Shann and Olander used to justify their testing technique. The fuel pin is a closed system and the environment within is in a constant state of change. Fission product releases will tend to increase the iodine concentration at the same time as the species is being absorbed and reacted with the Zircaloy. Continual temperature change will bring concomitant changes in the partial pressure, while axial temperature variations may lead to increased condensation and absorption in the cooler regions of the pin. In effect, the uncertainties associated with the definition of the internal environment of a fuel pin at any one point in time far outweigh the precision provided by the testing technique. Thus, it would appear to be more appropriate to base assessments of ISCC in spent fuel pins on information acquired under more nearly prototypic conditions. With this premise in mind, attention has been directed toward the data obtained from closed system tests and where the iodine concentration has been expressed on an areal basis.

The data in Table 10 show the time to cracking varies with the iodine concentration and temperature (it is also dependent on stress but this is not evident in the Table 10 data). If we assume that the iodine concentrations listed in Table 10 are minimum values, below which ISCC does not occur irrespective of the values of other parameters, then we can write:

$$t_f = f(I, T, S) \quad (7)$$

where t_f is the failure time,
I is the iodine concentration,
T is the temperature, and
S is the stress.

Relationships involving failure time, iodine concentration, temperature and stress have been proposed by, among others, Tucker et al. [Tucker, 1976], Polan and Tucker [Polan, 1977] and Shann and Olander [Shann, 1983].

The maximum clad temperature during isolation is unlikely to reach 400° C, so, for the purposes of the present analysis, only the data obtained in the range 300-360° C will be used. In addition, if we make the temporary assumption that the temperature-stress component of equation 1 remains constant over this range, then a rough estimate can be obtained of the time-iodine concentration relationship by plotting t_f as a function of I . The result is shown in Figure 19 and it was found that the data fit best the equation:

$$t_f = 5.15 I^{-0.98} \quad (8)$$

where t_f is in hours and I is in mg/cm^2 . It is of interest to note that this inverse proportionality is very similar to that proposed in [Shann, 1983], but slightly different from that proposed in [Tucker, 1976] (where the exponent of "I" is -0.75) and that in [Polan, 1977] ("I" exponent -0.781). The data reported in [Peehs, 1979] also indicate that the time to failure is inversely proportional to the iodine concentration. Such differences may not be significant and probably could result from differences in test methods employed. [Cox, 1974] has already made the point that *"the lowest concentrations of iodine required to cause stress corrosion cracking differ with the various testing methods and the time-scales of the tests."*

Obviously, the paucity of data points does not allow much confidence in predictions of failure times in excess of the limits of the data base. However, such extrapolations can provide a very approximate indication of the amount of iodine needed for ISCC over relatively long periods. For example, the relationship of equation 8 predicts that an iodine concentration of $5 \times 10^{-5} \text{ mg}/\text{cm}^2$ would be needed for failure to occur in 10 years or $5 \times 10^{-6} \text{ mg}/\text{cm}^2$ for failure in 100 years. Both values are lower than any critical concentration identified in the literature.

Of obvious relevance at this point is the amount of iodine likely to become available in a spent fuel pin. Very rough estimates of this have been made in the past ([Cubiciotti, 1978], [Roberts, 1979] and [Miller, 1984]) using the equation:

$$I_2 \text{ (in mg/cm}^2\text{)} = 0.02 \cdot f_{bu} \cdot f_{igr} \quad (9)$$

Figure 19 Time to failure by ISCC for Zircaloy as a function of iodine concentration.

where f_{bu} is the fractional burnup of fissionable uranium atoms and f_{gr} is the fractional fission gas release.

The iodine concentration in this equation is the axially averaged total iodine concentration, not the amount which might be concentrated in small zones at each pellet-pellet interface. The latter value will be higher, depending on the widths assumed for these zones.

Using the above equation, [Miller, 1984] calculates that for a "worst case" condition -- a fuel rod with an end-of-life burnup of 30 GWD/MTU (i.e., a burnup fraction of about 0.03) and 50% fission gas release -- the iodine concentration will be 0.0003 mg/cm². This value is below any of the values observed experimentally but it should be recalled that the experimental data were obtained from tests over times relatively short compared with those expected during spent fuel isolation. However, it is about an order of magnitude higher than that predicted by equation (8) for storage for 10 years (and much higher than values calculated for longer times). Thus it would appear that, over the long term, enough iodine will be available in a very few pins to facilitate ISCC. Whether it will actually occur is dependent on the ISCC stress threshold which is discussed in a later section. For the "typical" case, [Miller, 1984] invokes a fuel rod with the same burnup (30 GWD/MTU) but only a 1% fission gas release. In this instance, the iodine concentration is calculated to be 6×10^{-6} mg/cm². This is less than the critical value predicted at 10 years but about the same magnitude as that calculated for 100 years. Again, even at this stage, there must be sufficient stress present for the cracking to occur. For fuel pins with extended burnup, the critical iodine concentrations will be reached earlier during isolation.

5.3.3.2 Potential threshold stress

It is apparent, from Section 5.3.3.1, that there will probably be enough iodine present in at least some spent fuel pins to facilitate SCC. Whether failure will occur will probably depend on, among other factors, if the stress present exceeds a critical value. It is recognized that the existence of a stress threshold is not universally accepted, it being indicated by several researchers that strain might be a better criterion, or perhaps

even strain rate (see [Jones, 1980]). However, for the sake of simplicity, the present report assumes that stress is the determining factor (the following section extends this to consideration of a critical stress intensity).

Table 11 summarizes the observations of ISCC under constant (more usually, initial) stress conditions. It should be noted that this table is not intended to be comprehensive to the extent of recording every combination of material and test conditions which resulted in cracking or failure. Rather, the emphasis, during the compilation, was toward recording only the lowest stresses and the longest failure times involved. For example, [Knorr, 1982b] provided data on two lots of Zircaloy-2 tubing, each lot being tested in three conditions and over a range of stresses at each condition. The four observations recorded in Table 11 represent the longest failure times for each lot of material in both the as-received and the stress-relieved condition, irrespective of internal surface condition.

Preliminary quantitative evaluation of the data in Table 11 has been done on a strictly empirical basis, in an attempt to identify, if possible, the minimum stress level (or levels) below which ISCC is unlikely to occur. Initially, ignoring all the variables involved (temperature, iodine concentration, material condition, etc.), the data were plotted as stress versus failure time. The resultant graph, covering the temperature range 300-400° C, is shown in Figure 20. At first glance, it appears that there is a gradual trend of increasing failure time as the stress decreases. That is, over the test conditions examined, the minimum stress for ISCC is a function of the exposure time. However, when consideration is given to the existence of a temperature dependence factor, as proposed, for example, in [Tucker, 1976], [Polan, 1977] and [Shann, 1983], a somewhat different picture emerges. Figure 21 plots only the data obtained in the temperature range 300-350° C, while Figure 22 covers the range 360-400° C. It would appear from these two figures that the time-dependency factor of the minimum stress for ISCC observed in Figure 20 derives essentially from the presence of the data from the higher temperature tests. It is noted, in passing, that a best-fit of the data in Figure 22 indicates that the failure time varies inversely with the stress to the power 3.96, a relationship virtually identical with that assumed in [Tucker, 1976] and [Polan, 1977]. In the lower temperature range (that is, the one with most relevance to spent fuel isolation conditions), there appears to be a much reduced variation with time of the "threshold"

Figure 20 Time to failure by ISCC for Zircaloy as a function of stress in the temperature range 300 - 400° C.

Figure 21 Time to failure by ISCC for Zircaloy as a function of stress in the temperature range 300 - 350°C.

Figure 22 Time to failure by ISCC for Zircaloy as a function of stress in the temperature range 360 - 400° C.

stress for ISCC. If this holds true for longer times, it infers that there is a minimum stress below which ISCC will not occur at these temperatures, even when consideration is given to the long times involved in isolation. This level is of the order of 200 MPa.

A threshold of 200 MPa for ISCC at the temperatures of consideration is much lower than values generally quoted in the literature. The results of internal pressurization tests in [Garlick, 1973] indicated that the threshold stress for recrystallized Zircaloy-2 was about 320 MPa, a value later repeated in the tests reported in [Videm, 1979a]. [Roberts, 1979] estimated a stress of about 280 MPa (for annealed material), while [Jones, 1980] surmised that the threshold for stress-relieved material was about 300 MPa. Shann and Olander [Shann, 1983] agreed with [Jones, 1980] on a value of 300 MPa for the threshold stress and stated that ISCC does not occur below this stress or above 380 MPa. [Onchi, 1981] estimated that the SCC threshold stress for cold-worked material was 314 MPa but found a lower value (240 MPa) for recrystallized material. [Garzarolli, 1978], noting the dependence of threshold stress on temperature and material condition, provided data indicating a value of about 250 MPa for stress-relieved material. Only in one of the early papers by Wood [Wood, 1972] is there mention of a critical stress, 217 MPa, comparable to that suggested by Figure 21.

In deciding whether or not a value of 200 MPa for the threshold stress is valid, consideration must be given to the data which lead to this possibility. There are eight data points which lie below 250 MPa and they derive from six sources: [Wood, 1972], [Syrett, 1980], [Syrett, 1981], [Onchi, 1981], [Knorr, 1982b] and [Crescimanno, 1984].

The [Wood, 1972] data were obtained from tests of stressed slotted rings exposed to a relatively large iodine concentration (20 mg/cm²). Wood pointed out that the material used was selected from eight batches with different material conditions and that the particular batch tested had been shown to be that most susceptible to ISCC in preliminary tests. No reasons were advanced to explain the increased susceptibility and no indications were given of the relative magnitude of this difference from the other batches. The condition of the material was described as "cold drawn, 16 passes plus interim anneals" in [Wood, 1972] and, assuming it is the same material, as "cold drawn and stress relieved" in [Wood, 1975]. Its yield strength at room temperature was 522

MPa [Wood, 1972] and that at 300° C 310 MPa [Wood, 1975]. A review of the literature indicates that ISCC threshold stresses are dependent on several parameters. One of these is the yield-strength of the material, a property which reflects the processing history, and, generally, it has been observed that the threshold stress is not too dissimilar to the yield strength at the test temperature. The [Wood, 1972] observations do not conform to this general pattern, the apparent threshold stress being only two thirds of the yield strength at 300° C. Thus it appears reasonable to question whether this represents a true threshold stress. In particular, it should be pointed out that the tests, involving stressed slotted rings, would not be considered as prototypic of fuel elements as those which used internally pressurized tubes.

The two low data points produced by Syrett and co-workers ([Syrett, 1980] and [Syrett, 1981]) resulted from a series of tests to determine the effect of various material conditions on the ISCC susceptibility of Zircalloys. The low data point in each case was obtained from material with the most tangential texture, a condition now recognized as increasing the susceptibility to ISCC. In addition, the tubing which produced the low data point in [Syrett, 1981] had been subjected to a surface treatment which further enhanced the susceptibility to ISCC. The data points thus indicate material conditions which can be avoided in the manufacturing process and which will probably not be typical of most fuel claddings.

The [Onchi, 1981] data point, indicating a threshold stress of 230 MPa, was obtained from recrystallized material with a yield strength of 216 MPa and would appear to be in conformity with the general opinion that the threshold stress should be near to the yield strength. However, there are several problems associated with direct application of the observations from these tests to a typical fuel element situation. The tests were not of the internal pressurization type but, instead, uniaxial tension tests on ring specimens. The low data point was obtained from a simple ring specimen but an equivalent test on a grooved ring specimen of the same material produced a much higher threshold stress, 300 MPa. The yield strength, when measured with a grooved specimen, was similarly higher (270 MPa) than that obtained with a simple (ungrooved) specimen. No explanation is offered for these differences and the authors themselves use the value of 300 MPa for the threshold stress of the recrystallized material when comparing their data to those of

other researchers. Thus the meaning of the low data point is not clear at the present time and the point itself should probably be disregarded until the situation is clarified.

The two low data points, from [Knorr, 1982b] can probably be ignored for the present evaluation for reasons similar to those applied to the two data points obtained by Syrett and co-workers. Again, the object of the test program was to assess the effects of different textures and surface treatments on ISCC susceptibility. As with the [Syrett, 1980] and [Syrett, 1981] results, the tubing with the more tangential basal pole texture proved to be substantially more susceptible than the other, whose texture was much closer to that found in typical fuel element cladding. It was material from this "weaker" lot that produced the low data points. However, unlike [Syrett, 1981], no significant effect could be traced to any of the surface treatments investigated.

The remaining low data point below comes from the compilation in [Crescimanno, 1984] and no other information is available in that source on the general characteristics of the material. Evaluation of this data point is being withheld until the original data source has been reviewed.

Summarizing the above observations, it is possible that the threshold stress, if it exists, for ISCC of Zircalloys in the temperature range 300-350° C could be as low as 200 MPa but the probability is that it is significantly higher. Although a generally acceptable typical value might be about 280-300 MPa, the adoption of the more conservative value of 250 MPa would seem preferable for analytical purposes. However, it should be emphasized that this is only a preliminary finding and applicable only to unirradiated material. A more in-depth evaluation, particularly one which considered ISCC of irradiated material, is required to confirm that this is a valid finding and that it is universally applicable.

In assessing the probability of failure of spent fuel elements during isolation, the actual value selected for the threshold stress may not be very relevant. In Section 5.2.4, it was estimated that the worst-case maximum hoop stress in a spent fuel element during isolation will be about 131 MPa. Slightly higher values might possibly occur in atypical cases but in no instance is any value greater than 150 MPa visualized. Such stress levels

(which will possibly be present in only a very small fraction of the total number of elements) are considerably below any of the ISCC threshold stresses discussed above. Thus it is reasonable to assume that, though there may be sufficient iodine available in the fuel elements to allow SCC to take place, the stresses present will be below the threshold level and ISCC will not occur.

5.3.3.3 Potential critical stress intensity

The previous section considered the existence of a threshold stress below which ISCC will not occur. Such a stress is of general application and does not reflect the sensitivity of the material to stress concentration at cracks, notches and other surface blemishes. These surface discontinuities may be present in the original material or the cracks might have been initiated during reactor operation, as noted in [NRC,1985]. To evaluate the stress concentration effect, it must be established if there is a critical stress intensity factor for the ISCC process and, if so, what its value is.

Table 12 summarizes the measurements of the stress intensity factor under conditions of ISCC at various temperatures up to 400°C. As with the constant stress data in Table 11, it should be noted that this table is not intended to be comprehensive to the extent of recording all data points available. For example, [Knorr, 1982a] provided data on two lots of Zircaloy-2, each lot being tested in both the stress-relieved and the recrystallized condition and with several combinations of orientation and specimen design. Table 12 shows only the range of ISCC critical stress intensity (K_{ISCC}) values recorded for each lot in each of the two material conditions.

Again, as with the constant stress data of Table 11, quantitative evaluation of the data in Table 12 has been done on a strictly empirical basis, in an attempt to identify, if possible, the minimum critical stress intensity factor(s). Recognizing the probable temperature dependence of K_{ISCC} , the data have been plotted as a function of temperature in Figure 23. The initial impression is that the critical stress intensity decreases relatively slowly, from about 10 MPa.m^{0.5} to a low of about 3.0 MPa.m^{0.5}, between room temperature and 350°C, but then falls to less than 1 MPa.m^{0.5} at the higher temperatures. Although these higher temperatures are beyond the range expected

Figure 23 Critical stress intensity for ISCC of Zircaloy as a function of temperature.

during isolation, it should be noted that all the K_{ISCC} values below 1 MPa.m^{0.5} are *calculated* values and derive from the same source, [Kreyns, 1976]. The authors in question did not perform a planned series of tests to measure K_{ISCC} values but, rather, took the data reported by [Busby, 1975] and interpreted them using a law which relates the crack growth rate to the fourth power of the stress intensity factor. Thus there must be some question regarding the validity of the high temperature data points, if only based on the indirect method of estimating them. It might also be noted that both [Tucker, 1976] and [Polan, 1977] include expressions which allow the calculation of K_{ISCC} values. Those authors did not tabulate the results of any such calculations but the K_{ISCC} values estimated using their equations are higher than those reported in [Kreyns, 1976].

Based on the experimental data available in the temperature range 300-350° C, it appears that the critical stress intensity for ISCC is probably in the range 3-4 MPa.m^{0.5}. This is in line with the value proposed in [Cunningham, 1987] and is slightly lower than that required for delayed hydride cracking (Section 5.2 of this report). If the worst-case maximum hoop stress in a spent fuel element in isolation is 131 MPa (Section 5.2.4), then it is possible to estimate the size of the crack or defect necessary to produce a stress intensity factor in excess of the critical value. This can be done by applying the equation [Rolfe, 1977]:

$$K_i = 1.12 \cdot (\text{stress}) \cdot (\pi a)^{0.5} \quad (10)$$

where K_i is the stress intensity factor and $2a$ is equal to the crack length. Assigning K_i a value of 3 MPa.m^{0.5} and with the stress at 131 MPa, the critical crack length is calculated to be 0.27 mm. A crack of this length would extend approximately 40% through the cladding wall and is unlikely to be found in all but a fraction of a percent of spent fuel rods. [Tasooji, 1984] estimated that 1% of spent fuel rods would have a defect greater than 0.13 mm deep (20% of wall thickness), but there is some question of the validity of the statistical analysis and the estimates are thought to be too high. Thus, although the possibility exists that the critical stress intensity will be exceeded in some fuel rods, the actual number affected will probably be very small when account is taken of the very low probability of finding a rod with both a crack of the requisite size and a hoop stress of sufficient magnitude.

5.3.4 Conclusions

From the observations on unirradiated Zircaloy and the very preliminary analysis described in the previous sections, it is apparent that iodine may be present in sufficient concentration to facilitate ISCC of spent fuel pins during the isolation period. This is based on the assumption that there exist critical iodine concentrations below which cracking will not occur and it is concluded that there is an inverse proportionality between the time to failure and the concentration, at least over the temperature range 300-360° C.

The time to failure is also determined by, among other factors, the stress present in the cladding (or, perhaps more pertinently, the strain) and the cladding temperature. A very rough empirical analysis indicates that a critical stress exists below which ISCC does not occur and that the value of this stress is not less than 200 MPa in the temperature range 300-350° C. Over this range, the value does not appear to change much with temperature but in the range 360-400° C it decreases as the temperature increases. The critical value, or threshold stress, of 200 MPa is considerably in excess of the estimated maximum hoop stress in spent fuel cladding (burnup $\approx$ 30 GWD/MTU) under "worst case" conditions. Thus it is concluded that, if stress is the appropriate parameter to consider, failure during the isolation period of even a very small fraction of spent fuel pins due to ISCC is extremely unlikely. This conclusion is consistent with that developed by the NRC [NRC, 1985] which states that *"the activation of SCC requires stress levels substantially above those that can reasonably be expected to prevail under dry storage conditions."*

A similar very approximate analysis of stress intensity factor measurements indicates that the critical stress intensity for ISCC is in the range 3-4 MPa.m^{0.5} between 300 and 350° C. Assuming "worst case" conditions in a spent fuel pin, it was estimated that the equivalent critical crack length would be about 0.27 mm, or about 40% of the clad wall thickness. Such a condition is considered most unlikely except, possibly, in a very small fraction of spent fuel pins.

The overall preliminary conclusion is that, although conditions might conceivably exist in some spent fuel pins which could lead to ISCC at some time during the dry isolation period, this would affect, at the most, only a very small fraction of the total number of pins being held. However, it should be restated that this conclusion is based on observations on unirradiated material and that the effect of radiation on ISCC susceptibility has not been examined. Furthermore, it cannot be overemphasized that the data base which leads to this conclusion has other limitations, principally in terms of the test times involved. These are considerably shorter than the proposed times for storage and isolation, and there is a need for more long term data before full confidence can be placed in the analyses. To our knowledge, the only ongoing program in this area is that being conducted at Kraftwerk Union [Peehs, 1986a&b].

6. CONCLUSIONS

During the early stages of spent fuel isolation at Yucca Mountain, the temperature inside the fuel rods is predicted to reach a maximum value of roughly 320° C. This temperature level will be maintained for a few decades, after which it will *slowly* decrease. Cladding temperatures will still be as high as 200° C one hundred and fifty years after disposal of the waste. These relatively high temperatures will cause the internal pressure of PWR fuel rods to reach pressure levels in the range of 35 to 130 atm depending on burnup, on the degree of initial pressurization of the fuel rods, and on the fission gas fraction which is not retained in the UO₂ pellets. These levels are very slightly lower than the pressures inside the rods during reactor operation but, unlike reactor operating conditions, there will be no external pressure to reduce the ΔP across the cladding wall. These unbalanced internal pressurization conditions are rather unique in the LWR fuel cycle. Similar conditions are obtained only during the dry storage of spent fuel.

The NRC has identified three potential failure modes for irradiated Zircaloy cladding while in dry storage: (a) creep rupture, (b) delayed hydride cracking (DHC), and (c) fuel-side stress corrosion cracking (FSSSC). Of these, only creep rupture was deemed capable of producing "gross rupture" of the cladding which could hinder later fuel handling and transportation operations.

BNL's preliminary conclusions on DHC agree with those of the NRC and others, in that it is believed that, for the overwhelming majority of fuel rods, delayed hydride cracking is not likely to be an important mode of failure. The Zircaloy cladding material of the fuel rods will contain hydrogen in amounts which will vary with the extent of fuel burnup, but will always lead to the formation of hydrides in the cladding. These hydrides will initially form in a predominantly circumferential orientation. If the hydrides do not reorient themselves in the radial direction during dry storage and isolation, failure due to DHC is considered extremely unlikely, even under worst-case conditions. The stresses likely to exist in spent fuel pin cladding are less than those usually considered necessary to cause significant reorientation, although an observation on an actual pin has indicated that reorientation could occur at lower stresses than originally thought. However, even

though this should prove to be the case, the stress levels in the cladding will still be insufficient to initiate DHC, even under worst-case conditions, based on currently proposed threshold stress values.

With respect to FSSCC, the preliminary conclusions are again essentially in accord with those of the NRC, in that this is not believed to be an important mode of failure during storage and isolation. In the current evaluation, the assumption has been made that FSSCC requires the presence of iodine, although it is recognized that the actual situation is very complex and other elements may well contribute to the phenomenon. Based on observations on unirradiated materials, it is conceivable that iodine may be present in sufficient concentration to facilitate stress corrosion cracking but the stress levels in the cladding will be substantially below the threshold stress for the process. Even under "worst-case" conditions, failure due to FSSCC of only a very small fraction of spent fuel pins is considered extremely unlikely. At the present time, the susceptibility of *irradiated* Zircalloys to FSSCC has not been evaluated and it is conceivable that this preliminary conclusion may be modified at a later date.

Creep rupture is, potentially, the most relevant failure mode as measurable Zircaloy creep takes place at relatively low stresses. Experimental studies of pre-irradiated and internally pressurized cladding tube samples have clearly demonstrated the occurrence of positive cladding hoop strains at 350°C under a tensile hoop stress of 50 MPa. The hoop strain had apparently not yet reached its final value after 8,000 h of testing.

In the safety evaluation of a spent fuel dry storage, the NRC has indicated that, where possible, creep modeling should be mechanistic. To that effect, both the NRC and a DOE-sponsored dry-storage study program have implemented a diffusion-controlled cavity growth (DCCG) model to estimate the amount of grain boundary decohesion that would occur in cladding due to creep with the passage of time. The reference DCCG model was originally proposed in 1975 by Raj and Ashby (R&A) for predicting the intergranular fracture of metals at elevated temperatures. The model assumes that a fixed number of cavities exist initially. These cavities grow and eventually coalesce as stress is applied.

At BNL, we have implemented the original R&A model for the conditions expected during spent fuel isolation. Using the peak fuel temperature profile presented in the Yucca Mountain Site Characterization Plan (SCP) and the parameter values utilized by the NRC in their dry storage analysis, we found that the predicted amount of decohesion of the Zircaloy will exceed 15%, the maximum allowed by the NRC during dry storage. However, decreasing the temperature profile by 20° C would cause the predicted amount of decohesion to be less than the NRC limit. Sensitivity analyses with the model indicate that the predicted amount of decohesion is quite sensitive to all parameters tested and, therefore, the model is not an effective method for screening important variables.

The DCCG model has never been validated against actual data. The existing data on cavity nucleation in Zircaloy suggest that stable cavities are only rarely formed in Zircaloy-2 and -4 during reactor irradiation and that stress-induced cavities in unirradiated Zircaloys only appear at relatively large strains. For these reasons, it is not clear that the DCCG model provides meaningful predictions.

An experimental correlation which relates hoop strain, stress, temperature, and time is presently used by German researchers in support of spent fuel dry storage studies. This empirical correlation is based on isothermal, isostress, unirradiated Zircaloy creep data. At BNL, we have generalized the correlation to account for variations in temperature and stress with time. This generalized correlation has been used to determine the sensitivity of predicted hoop strain to variations in temperature, stress, and the empirical coefficients. Using the peak fuel temperature profile presented in the SCP, the original recommended values for the correlation coefficients, and the expected maximum value for the hoop stress, the model predicts a maximum strain of 0.125%. The sensitivity analysis indicates that it is unlikely that the variation in any single parameter from the recommended values will cause the strain to exceed 1%.

The correlation developed by the German fits their data well, however, it cannot be extrapolated with confidence to very long times. Other models based on theoretical grounds and experimental data are available which exhibit different, but probably more reasonable long term trends. At this time, we have not examined these models nor the data which support them in detail. This will be a subject of future study. Indeed, the

experimental data base on creep behavior of internally pressurized Zircaloy tubes, although not very large, is comprised of more than the data used by the German to develop their correlation. Data exist for irradiated and unirradiated samples under a range of temperatures and stress levels. All of the data need to be reviewed in a systematic, comprehensive manner and compared with the predictions of the available models.

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Appendix A

Sensitivity Analyses Results for the R&A Model and Peehs' Correlation

A.1 The R&A Model for Diffusion Controlled Cavity Growth

Diffusion-controlled growth of voids has been reported (by the NRC among others) to be the dominant mechanism for creep under inert dry storage conditions. A model for this process has been developed by Raj and Ashby in 1975. Variations of this model have been applied by the NRC and others in assessing Zircaloy degradation in dry storage.

We have implemented the Raj and Ashby model as described in their original paper. This model assumes a fixed initial number of cavities along the grain boundaries with growth beginning upon the application of stress. The growth rate can be expressed as a fractional area of decohesion along the grain boundary and depends on initial cavity spacing, normal stress, temperature, grain boundary self-diffusion coefficient, dihedral angle (the angle between the void and the grain boundary), the boundary thickness, and the amount of decohesion already present (as more decohesion occurs, less area is available to withstand pressure, therefore, higher stresses occur, this makes the differential equation non-linear). In the dry storage area, a fractional decohesion of greater than 0.15 is considered a failure by the NRC.

In terms of $A(t)$, the fractional amount of grain boundary area which has undergone decohesion by time t , the R&A model predicts the rate of decohesion to proceed as follows:

$$\frac{dA}{dt} = \frac{32}{3\pi} \frac{[\bar{F}_B(\alpha)]^{3/2}}{F_V(\alpha)} \frac{n D_B \delta}{k T} \sigma \rho^{3/2} f(A) \quad (A.1)$$

where

$$f(A) = \frac{1 - A}{\sqrt{A}} \frac{[1 - (r_c/r) (1-A)]}{-0.5 \ln(A) - 3/4 + A(1 - A/4)} \quad (A.2)$$

Equation (1.a) is to be solved with the initial condition:

$$A(0) = A_{\min} = \frac{r_c^2 F_B(\alpha) \rho}{\pi} \quad (A.3)$$

In the equations above, the indicated parameters are interpreted as follows:

- α - contact angle to the grain boundary; $\alpha = \cos^{-1}(\gamma_B/2\gamma)$, where γ_B is the energy per unit area of the grain boundary surface and γ is the energy per unit area of the free surface of the void,
- Ω - atomic volume of metal,
- ρ - number of voids per unit area in the grain boundary;
 $\rho = 1/(2\ell)^2$, where 2ℓ is the average distance between cavities,
- δ - boundary thickness,
- σ - externally applied stress,
- D_B - grain boundary self-diffusion coefficient,
- k - Boltzmann constant,
- r - radius of curvature of the void surface,
- r_c - critical radius for void nucleation; $r_c = 2\gamma/\sigma$, where γ is the surface free energy per unit area of the matrix material,

and:

$$F_B(\alpha) = \pi \sin^2(\alpha),$$

$$F_V(\alpha) = \frac{2\pi}{3} [2 - 3 \cos(\alpha) + \cos^3(\alpha)]$$

The functions F_V and F_B are related to the void volume, V , and to the boundary area, B , it replaces through the following relations:

$$V = r^3 F_V(\alpha)$$

and

$$B = r^2 F_B(\alpha).$$

We have conducted sensitivity studies on the effects of varying cavity spacing, temperature, initial pressure, and dihedral angle. In each of these studies, all parameters except one were held constant. The reference values for the equation were taken from the NRC analysis for inert dry storage with an exception for the dihedral angle. In these studies, the value was taken as 75° , not 50° , for internal consistency with the Raj and Ashby model which assumes inclusion free boundaries.

The effects of varying temperature are accounted for using the temperature profile presented in the SCP. This profile peaks at 4 years with a temperature of 322°C . For conservatism, the temperature is assumed to be 322°C for the first four years. The stress is assumed to be related to the temperature through the ideal gas law. The hoop stress, σ , was calculated using the equation for an internally pressurized thick-walled vessel with an inside diameter of 0.98 cm and a thickness of 0.06 cm. These values are within the expected range for PWR fuel rods.

The sensitivity analysis shows that the fractional decohesion area is sensitive to all of the parameters tested. It is most sensitive to cavity spacing. Changing the cavity spacing from $1.25 \cdot 10^{-5}$ to $7.5 \cdot 10^{-6}$ m resulted in a change in fractional decohesion from 0.1 in 100 years to 1.0 in 20 years, Figure A.1. A value of $1 \cdot 10^{-5}$ was used by the NRC in their dry storage analysis. In Figure A.1 it can be seen that the rate of decohesion begins to increase dramatically above 40% decohesion. This occurs even though the temperature and stress levels are decreasing. The increase in decohesion rate is caused by the sharp rate of increase in the $f(A)$ term, Equation (A.2), past the value of $A = 40\%$. This increase is shown in Figure A.2 which is a graph of $f(A)$ versus A . Since the rate of decohesion, Equation (A.1), is proportional to $f(A)$, it is clear that the

Figure A.1 The sensitivity of predicted fractional decohesion area to cavity spacing using the R&A model.

Figure A.2 The variation of the R&A model area dependent term, $f(A)$, with area.

area dependence in this model cannot be neglected. That is, the rate of decohesion depends strongly on the amount of decohesion present for a fixed temperature and stress level.

The influence of temperature is shown in Figures A.3 and A.4. Shifting the SCP temperature curve up by 10° C caused a doubling in the percent decohesion from 20 to 40% over 100 years. Although not shown, shifting the temperature profile down by 20° C while using the NRC values for the parameters (including a dihedral angle of 50°) leads to the decohesion being below 15%, the maximum value allowed by NRC for dry storage. Reducing the initial temperature to account for the time lag before the peak is reached had little influence on the predicted decohesion as evidenced in Figure (A.4)

Figure (A.5) displays the effect of the dihedral angle on predicted decohesion. Changing the dihedral angle from 75° to 50°, the value recommended by the NRC, caused the fractional decohesion to increase from 0.2 to 0.6 over 100 years.

Figure (A.6) demonstrates the effect of the initial pressure on decohesion. Four different pressures were used: a) 4 MPa at 322° C, a maximum value expected for typical BWR rods, b) 7.6 MPa at 322° C, the NRC dry storage recommended value, c) 8.0 MPa at 322° C, a typical peak value for PWR rods, and d) 12.0 MPa at 322° C, a maximum value for PWR rods. Only the lowest pressure rods have the predicted decohesion less than the NRC limit of 15%.

A.2 Peehs' Correlation for Predicting Hoop Strain

Modeling of strain due to creep was performed using the empirical correlation developed by Peehs and co-workers. This correlation was developed using experimental data for internally pressurized Zircaloy tube samples under inert dry storage conditions. This equation considers time, temperature, and stress to be the important variables in determining strain and takes the form:

Figure A.3 The sensitivity of predicted fractional decohesion area to temperature in the R&A model.

Figure A.4 The sensitivity of predicted fractional decohesion area to initial temperature in the R&A model.

Figure A.5 The sensitivity of predicted fractional decohesion area to the dihedral angle in the R&A model.

Figure A.6 The sensitivity of predicted fractional decohesion area to the initial pressure in the R&A model.

$$\epsilon (\%) = A[B/T - \ln(\sigma/C)/\ln(t) - 1]^{-m} \quad (\text{A.4})$$

where ϵ is the percent strain,

σ is the hoop stress (MPa)

T is the temperature in degrees Kelvin

t is the time (hours)

and A , B , C , and m are experimentally determined constants.

Peehs determined the constants from experiments on unirradiated Zircaloy at temperatures between 250 and 400°C with hoop stress levels of 150 and 200 MPa (typical peak hoop stresses expected in spent fuel disposal will range from 60 - 130 MPa and typical temperatures will be less than 330°C). Peehs' values for the constants are $A = 1.89 \cdot 10^{-3}$; $B = 610$; $C = 450$; and $m = 2.58$.

Peehs' correlation is based on data obtained from tests performed under isothermal and isostress conditions. The correlation was generalized to account for variations in temperature and pressure using a generalization technique developed by Pescatore [Pescatore, 1983]. In this approach, the rate of strain is re-expressed as a function of accumulated strain and of the environmental variables (temperature and stress). Namely:

$$\frac{d\epsilon}{dt} = F(\epsilon, \sigma, T) \quad (\text{A.5})$$

For Peehs' correlation Equation (A.3) takes the form:

$$\frac{d\epsilon}{dt} = \frac{-mA \{[(A/\epsilon)^{1/m}]^{-(m+1)} [\Phi]^2 (\sigma/C)^{1/\Phi}\}}{\ln(\sigma/C)} \quad (\text{A.6})$$

where $\Phi = [(A/\epsilon)^{1/m} - B/T + 1]$; and all other variables have been previously defined. Equation (A.6) is a non-linear first order differential equation.

In the sensitivity analysis the reference values for the empirical parameters were those mentioned earlier. The reference time-dependent temperature was determined from the profile provided in the Site Characterization Plan, Figure 19 in the body of this report. The peak temperature in this Figure is 322° C and occurs about 4 years after emplacement. For conservatism, it is assumed that the temperature is constant for the first 4 years. The reference hoop stress was determined from the equation for internal pressurization of a thick walled pressure vessel assuming a gas gap pressure of 8.25 MPa at 370° C. The value for gas pressure was chosen to be identical to the value used in the Topical Safety Analysis Report for dry storage in a CASTOR-V/21 dry storage cask. The value chosen for the cladding inside diameter was 0.98 cm, and the cladding thickness was 0.06 cm. These values are within the expected range for PWR fuel and give the highest hoop stress of all dimensions within the expected range. The gas pressure was adjusted for changes in temperature using the ideal gas law.

For the reference parameters, the strain reached a value of 0.125% after 20 years. After this time, the strain rate was so small that the total strain increased by less than $10^{-3}\%$ in the period of 20 - 1000 years. The cause for the decrease in strain rate is partially due to the decrease in temperature and stress and partially due to the increase in strain. (From equation (A.6) it can be seen that the strain rate decreases as the strain increases).

The effect of temperature on strain is presented in Figure A.7. Using the SCP profile with the exception that the temperature increased linearly from 300 to 322° C over the first four years had a minor impact on strain at 20 years as compared to the reference case. Although the strain was much lower in the initial years when the temperature was lower. Shifting the SCP temperature profile up by 10° C increased the predicted strain after 20 years from 0.125% to 0.16%. Although not shown on the graph, increasing the temperature profile 60° C, i.e., an initial temperature of 382° C, leads to 0.85% strain at 20 years. In all of these curves, the increase in strain is minimal after the first 10 years, therefore, the predicted strain at 20 years is essentially the maximum strain.

Figure A.7 The sensitivity in predicted percent strain to temperature in Peehs' correlation.

Figure A.8 displays the effect of changing the pressure on predicted strain. Gas pressures are expected to range from 2 MPa (typical average BWR rod pressure) to 11 MPa (typical peak PWR rod pressure according to Rothman, 1984). Increasing the initial pressure from the reference value of 7.63 MPa to 12 MPa increased the strain from 0.125 to 0.22% at 20 years. Decreasing the initial pressure to 4 MPa decreased the strain to 0.066%.

Figure A.9 displays the effect of changing the exponent m on predicted strain. Increasing the exponent from the reference value of 2.58 to 3.0 doubles the predicted strain to 0.25%. For the strain to reach 1% would require the exponent to have a value of 4.0. This value would greatly overpredict the strains at early times of the experimental data. Therefore, it is unlikely that the value could be that large.

Figure A.10 displays the effect of changing the temperature coefficient, B , in the correlation. Reducing the value from the reference value of 610 to 570 causes the predicted strain to increase from 0.125% to 0.37%. Decreasing the value further to 540 causes the strain to reach a value of 1% in 5 years. Reducing the temperature coefficient to 540 makes the temperature term, (B/T) , equivalent to a temperature of 673° K (400° C) with the recommended temperature coefficient.

Figure A.11 displays the effect of changing the stress coefficient, C , on predicted strain. Decreasing the value from the reference value of 450 to 350 increased the strain from 0.125% to 0.17%.

The expression for stress under varying temperatures and pressures is linear with respect to changes in the coefficient A . Doubling the value from 1.89×10^{-3} to 3.78×10^{-3} doubles the predicted stress from 0.125 to 0.25%.

Figure A.8 The sensitivity in predicted percent strain to initial pressure in Peehs' correlation.

Figure A.9 The sensitivity in predicted percent strain to changes in the exponent m in Peehs' correlation.

Figure A.10 The sensitivity in predicted percent strain to changes in the temperature coefficient, B, in Peehs' correlation.

Figure A.11 The sensitivity in predicted percent strain to changes in the stress coefficient, C , in Peehs' correlation.