

Attachment 2
Acceptance Criteria and Metal-Water Reaction Correlations

Acceptance Criteria (§50.46) and Metal-Water Reaction Correlations (Appendix K)

Background

The Commission is considering amending its regulations on the acceptance criteria for emergency core cooling systems (ECCS) to make the criteria applicable to all zirconium alloys used for fuel rod cladding rather than limiting the application to Zircaloy and ZIRLO as is currently the case. Of the five original acceptance criteria in §50.46, the two on coolable geometry and long-term cooling are performance-based and therefore need no change. The criterion on maximum hydrogen generation is prescriptive, but the combustible gas requirements are now considered in §50.44 so this requirement may be deleted from §50.46. The two remaining criteria are peak cladding temperature and maximum cladding oxidation, and these are both prescriptive and related to specific cladding alloys.

Peak Cladding Temperature

Peak cladding temperature was discussed extensively in the 1973 ECCS hearing, and the 2200°F value arose in connection with the 17% maximum cladding oxidation value. These numbers were a pair, related to ductility measurements that had been made at Oak Ridge National Laboratory. The 2200°F value was chosen because the relation between maximum cladding oxidation and ductility broke down for temperatures somewhere between 2200 and 2400°F (no data in between). It would, of course, have been possible to choose a higher peak cladding temperature and a correspondingly lower maximum cladding oxidation value. However, the Commission appeared to have another reason for not adopting a higher temperature based on statements that were included in the opinion that they issued.

Westinghouse proposed a maximum calculated temperature limit of at least 2700°F; Combustion Engineering and the Utility Group agreed on 2500°F as the peak allowable calculated temperature on the basis that much of the data on oxidation and its effects stops at 2500°F. Babcock and Wilcox suggested a more conservative 2400°F as the peak calculated temperature to be allowed, presumably because "significant eutectic reaction and an excessive metal-to-water reaction rate would be precluded below 2400°F." General Electric argued strongly that the limit should not be reduced to 2200°F; that 2700°F is really all right as far as embrittlement is concerned, but that the Interim Acceptance Criterion value of 2300°F should be retained. In addition to being consistent with their expressed desire not to change any of the criteria, the GE recommendation of retaining the 2300°F limit is intended to ensure that the core never "gets into regions where the metal-water reaction becomes a serious concern." (Ref. 1, p. 1097)

Thus, high oxidation rates, in addition to embrittlement, should be considered in making the desired rule change. There are two aspects of oxidation that need to be examined in doing this: one is the effect of temperature on oxidation, and the other is the effect of cladding alloy on oxidation.

(a) Temperature Effect

In 1973, the Baker-Just correlation was selected as the best correlation available and was included as a requirement in Appendix K. The Baker-Just equation was not without criticism, however, and one criticism in 1973 was that more recent data at that time yielded lower oxidation rates. The Commission had the following to say about that criticism.

Until new data are obtained and present doubts are resolved we believe it best to continue the use of the Baker-Just equation. It apparently gives about the correct results at 2000°F, and although it probably over-predicts the oxidation at 2200°F, this over-prediction does not exceed the range of the data available. (Ref. 1, p. 1103)

In other words, the Commission believed that the Baker-Just equation was reasonable up to 2200°F because of scatter in the data available at that time. The Baker-Just equation, as well as more recent correlations, can be represented as an Arrhenius relation ($e^{-Q/RT}$) with an activation energy Q and an exponential dependence on temperature T (R is the universal gas constant). Thus, the oxidation rate and, hence, the heat generation rate increase rapidly as temperature increases.

During the time period when high cladding temperatures occur, the heat sources are decay heat and the oxidation heat. As temperature increases, the oxidation heat becomes dominant such that the entire heat source increases rapidly with temperature. Experience has shown that cladding temperature calculations can be sensitive to this strong temperature dependence and that runaway temperature escalation can be predicted if the values of heat transfer from the fuel rods are too low. Therefore, in considering changes to the peak cladding temperature limit, it is desirable not to make this sensitivity worse.

We now know with a high degree of confidence that the Baker-Just equation is substantially conservative at 2200°F, and recent data exhibit very little scatter. A good representation of Zircaloy oxidation at this temperature is given by the Cathcart-Pawel correlation. If one examines the heat generation rate predicted with these two correlations, it is found that one needs a significantly higher temperature to get a given heat generation rate with the Cathcart-Pawel correlation than with the Baker-Just correlation. In particular, Cathcart-Pawel would give the same metal-water heat generation rate at 2307°F as Baker-Just would give at 2200°F (Ref. 2, Table 1). Thus, with regard to runaway temperature escalation, the peak cladding temperature could be raised to 2300°F without affecting this sensitivity and without reducing the margin that the Commission would have perceived in 1973.

To explore this sensitivity further, we performed more than 50 LOCA calculations with RELAP5/Mod3. In about half of the cases, the Baker-Just equation was used for the metal-water heat generation rate, and in the other half, the Cathcart-Pawel equation was used. Reactor power just prior to the LOCA was varied parametrically to simulate incremental variations in decay heat. The highest peak cladding temperature observed with the Baker-Just equation was about 2600°F; when the temperature went above this value, it continued to the melting point without turning around at some peak value. This indicated that runaway temperatures could not be prevented above about 2600°F for the parameters used in these calculations. The highest peak cladding temperature without runaway observed in

corresponding calculations with the Cathcart-Pawel equation was about 2700°F. Each series of calculations done with the two metal-water models always showed peak cladding temperatures without runaway to be at least 100°F higher with Cathcart-Pawel, which is consistent with the temperature difference in the rate equations. Thus in these calculations, the margin between 2300°F and the calculational instability using Cathcart-Pawel was always equal to or greater than the margin between 2200°F and the calculational instability using Baker-Just.

It is worth noting that there is no fundamental property of zirconium or zirconium-based alloys that makes them autocatalytic when they are oxidized in steam or in water. The reaction is always exothermic, and the heat of reaction is similar for all types of zirconium-based alloys. The rate of reaction increases smoothly, although strongly, with temperature. One discontinuous increase in rate does occur when ZrO_2 transforms from a tetragonal crystal structure to a cubic crystal structure at around 1577°C (2871°F), but this is well above the range of interest for a limit. Thus cladding temperature is a matter of heat balance, where heat transfer is the other half of the equation.

(b) Cladding Alloys

First, it should be noted that the Baker-Just equation was based on data from pure zirconium rather than an alloy, so a presumption was made in the beginning that the equation was also applicable to alloys. A review was recently done of relevant oxidation studies (Ref. 2), and the various investigators (and the metals they studied) are identified in Table 1.

Table 1. High-temperature oxidation measurements that were recently reviewed

Investigators	Metal
Baker and Just	Zr
Lemmon	Zr
White	Valoy (Zr-1.3Cr-0.1Fe)
Urbanic	Zircaloy-2, Zircaloy-4, Zr-2.5Nb
Cathcart et al.	Zircaloy-4
Chung and Kassner	Zircaloy-4
Grandjean et al.	Zircaloy-4
Yan et al.	Zircaloy-2
Waeckel and Jacques	Zircaloy-2
Le Bourhis	M5
Leech	ZIRLO
Yegorova et al.	E110 (Zr-1Nb)

It was found that all of these zirconium-based alloys exhibit about the same oxidation kinetics in the temperature range 1100-1500°C, particularly at 1204°C (2200°F). The explanation for this observation is that the dominant rate-controlling step in high-temperature oxidation is the diffusion of oxygen through the accumulating ZrO₂ oxide layer, and this may be about the same for all of the zirconium-based alloys.

Summarizing (a) and (b) above, it appears that the peak cladding temperature limit could be raised to 2300°F for all zirconium-based cladding alloys without increasing the sensitivity to runaway temperature escalations or reducing the margin that the Commission would have perceived in 1973. Of course, suitable embrittlement criteria, consisting of limits on peak cladding temperature and maximum cladding oxidation, need to be determined from mechanical tests, such as described below, and those tests could result in a limit below 2300°F just as the Oak Ridge ductility tests resulted in the 2200°F limit adopted by the Commission in 1973.

(It should be noted that embrittlement is a mechanical property, which is affected by diffusion of oxygen and hydrogen deep into the metal -- not just in the surface ZrO₂ layer -- and therefore may be dependent on the particular alloy in contrast to the alloy independence seen in the oxidation kinetics.)

Maximum Cladding Oxidation

At the conclusion of the 1973 ECCS hearing, the Commission's opinion was that retention of ductility in the Zircaloy cladding was the best guarantee of its remaining intact during a loss-of-coolant accident (LOCA). They further stated that the stress calculations, the measurements of strength and flexibility of oxidized rods, and the thermal shock tests all were reassuring, but their use for licensing purposes would involve an assumption of knowledge of the detailed process taking place in the core during a LOCA that they did not believe was justified (Ref. 1, p. 1098). Hence, the original 17% maximum cladding oxidation limit was derived from ring-compression tests performed on oxidized rings of Zircaloy cladding that were intended to show under what temperature and oxidation conditions residual ductility would be present after a LOCA. Figure 1 illustrates the ring-compression tests and the results that were obtained.

Unfortunately in 1980, ring-compression tests were shown to have a problem, although the 2200°F and 17% embrittlement criteria were shown to be conservative in that same study (Ref. 3). During a loss-of-coolant accident (LOCA), fuel rods are expected to balloon, rupture, and then oxidize as the temperature continues to rise up toward the peak cladding temperature. Oxidation on the inside of the cladding is also expected in the ruptured region, and maximum cladding oxidation is always found in that location. The regulation §50.46 requires calculation of double-sided oxidation in the ruptured region, and it is this amount of oxidation that is compared with the 17% limit to demonstrate ductility.

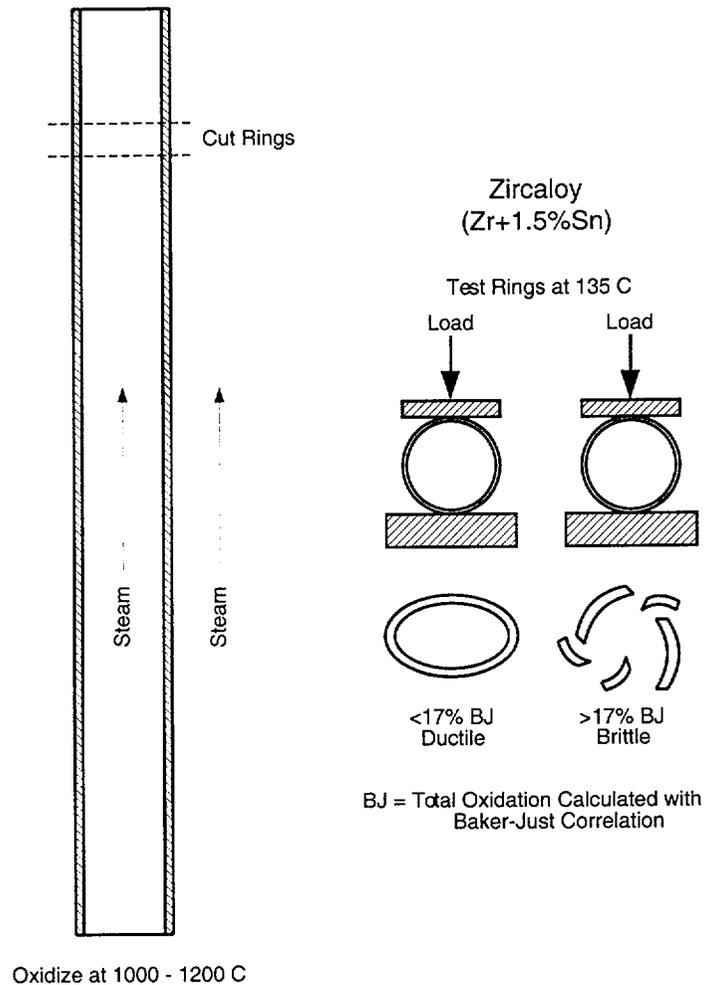


Fig. 1. Illustration of ring-compression tests

However, in those tests in the early 1980s, enhanced hydrogen absorption was found in the ruptured region. This was related to the stagnant steam environment inside the ballooned region because this stagnant environment was not removing hydrogen that was released in the disassociation of water molecules. Thus, extra hydrogen was being absorbed from the inside. Consequently, when rings were cut from this location, they were found to have been embrittled by the excess hydrogen even when the total oxidation was well below 17%. This situation is illustrated in Fig. 2.

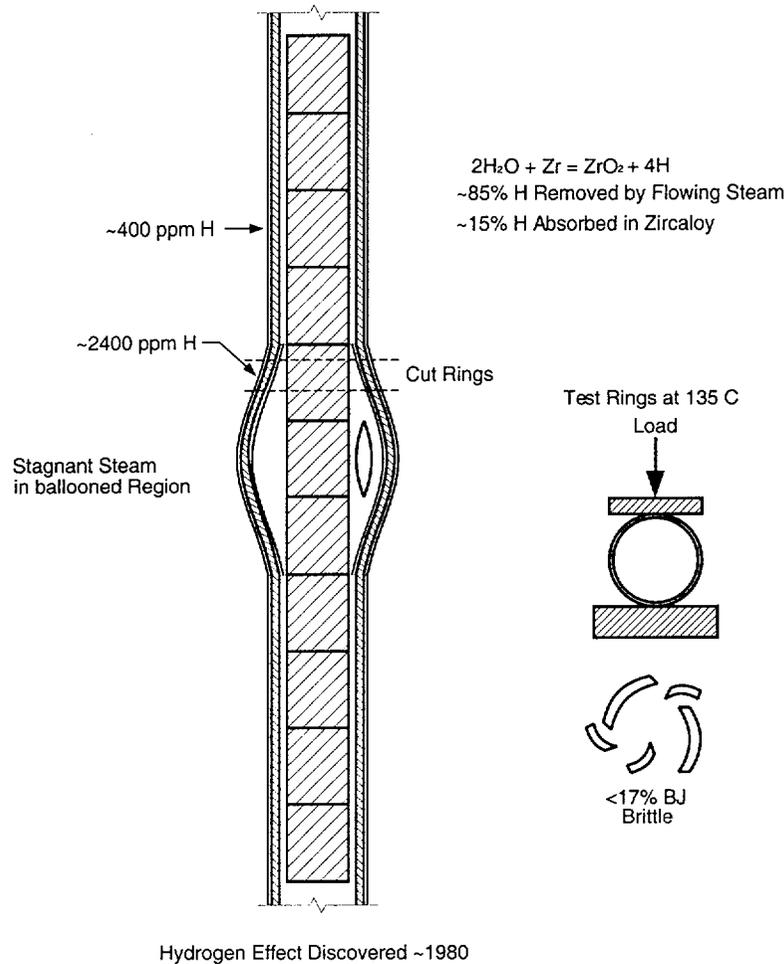


Fig. 2. Illustration of enhanced hydrogen absorption in ruptured region

It was known that resistance to fragmentation was the underlying objective of the Commissioners in 1973, and resistance to fragmentation can also be characterized by toughness. Therefore, a toughness test was devised that consisted of a pendulum impactor that would strike the fuel rod in the ruptured region, precisely where the hydrogen absorption was worst. This test apparatus is illustrated in Fig. 3.

Heavily oxidized rods would fail during thermal shock, before being tested with the impactor. Rods that survived the quenching with little margin were fragile and would fracture with a low impact energy of about 0.03 J at room temperature. A factor of 10 in impact energy was chosen as a measure of robustness, and rods with a measured total 17% oxidation or less were found to survive the 0.3 J impact at room temperature, provided the oxidation did not take place much above 2300°F. There was a defacto acceptance of these tests in 1981 as confirmation that the §50.46 embrittlement criteria were conservative.

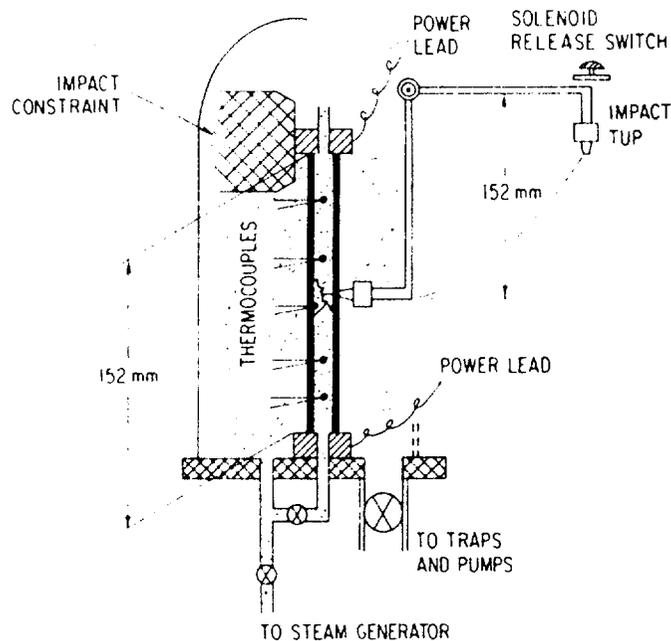


Fig. 3. Diagram of test facility with impactor for toughness tests reported in Ref. 3

Restating the above historical account, (a) peak cladding temperature and maximum oxidation limits were based on ductility tests on undeformed tubing, (b) tubing that had ballooned and ruptured was subsequently found to have reduced ductility, and (c) tests on ballooned and ruptured tubes showed that they still resisted fracturing thus confirming the adequacy of the temperature and oxidation limits.

Performance-Based Embrittlement Criteria

To obtain performance-based embrittlement criteria, it would be possible to follow a procedure that is similar to the historical approach, but instead of specifying fixed temperature and oxidation limits in §50.46, specifying a ductility criterion that could be applied to any cladding alloy at any burnup level. The cladding temperature and oxidation limits that are needed for analysis might vary for different materials and different burnups, but those limits could be deduced from results of the ductility tests that met the ductility criterion. Methods for performing the ductility tests and for determining corresponding temperature and oxidation limits will be determined in ongoing research at Argonne National Laboratory and could be described in a regulatory guide. Ring-compression tests on undeformed cladding segments and four-point bend tests on ruptured segments of fuel rods are currently planned. Results from these tests should provide the deformation parameters that would be needed for the ductility criterion.

Metal-Water Reaction Correlations

Recent measurements of oxidation of irradiated and unirradiated Zircaloy-2 and Zircaloy-4 confirm the adequacy of the Cathcart-Pawel correlation as seen in Fig. 4 (Ref. 4, p. 369).

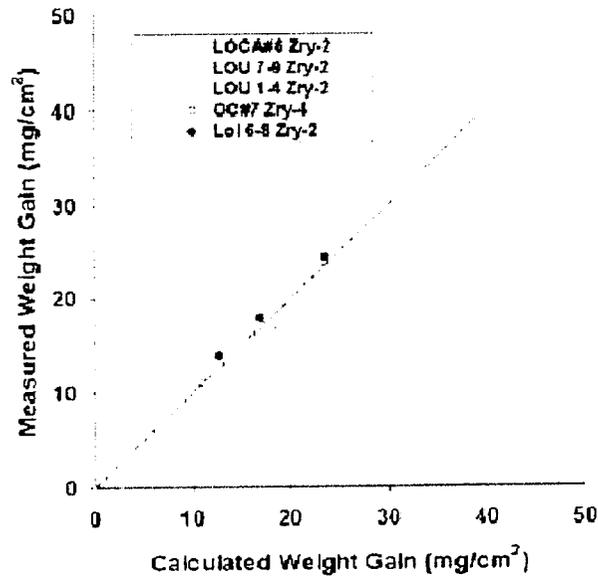


Fig.4. Comparison of Cathcart-Pawel model predictions and weight gain data deduced from metallographic analysis of unirradiated Zircaloy-2 (LOCA#6 and LOU) and Zircaloy-4 (OC#7) and irradiated Limerick Zircaloy-2 (Loi6-8) samples exposed to steam for 5-40 minutes at ~1200°F

Further, from the above discussion related to Table 1, it appears that the Cathcart-Pawel correlation could be used for all zirconium-based alloys, although modest improvements in accuracy might be achieved by using correlations determined for specific alloys. In any event, a rather strong enhancement of oxidation rate has been observed at elevated pressures (Ref. 5). Adjustments to the Cathcart-Pawel correlation or other correlations should be made for small-break LOCA calculations where the pressure is significantly above 1 bar. While the Cathcart-Pawel correlation appears adequate for most calculations, it should not be used for calculating maximum cladding oxidation for comparison with the existing 17% limit in §50.46. In deducing the 17% limit from Hobson's data, the amount of oxidation on the rings was not measured but was calculated with the Baker-Just correlation. Had the Cathcart-Pawel correlation -- which did not exist at that time -- been used, the cladding oxidation limit would have been about 13%. Therefore, the Baker-Just correlation must be used when comparing results with the old 17% limit.

Summary

Revisions could be made to §50.46 to permit performance-based testing of any zirconium-based cladding alloy at any burnup level for the purpose of determining alternate values of peak cladding temperature and maximum cladding oxidation to be used instead of the ones now specified in paragraphs (b)(1) and (2), respectively. This could be done while retaining an option to use the existing criteria of 2200°F peak cladding temperature and 17% maximum cladding oxidation for Zircaloy and ZIRLO. The performance-based tests would be conducted to find new temperature and oxidation limits below which fuel rods would retain an amount of ductility that would be specified in §50.46 or in a regulatory guide (instead of specifying the temperature and oxidation limits). The peak cladding temperature limit determined from these tests should not exceed 2300°F in order to preserve adequate margin against runaway temperature escalation. The Cathcart-Pawel metal-water reaction correlation could be used for most calculations except when making comparisons with the old 17% oxidation limit (Baker-Just must be used for that). All correlations should be adjusted for enhanced oxidation at elevated pressures when they are used in the analysis of small-break LOCAs.

References

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