Expanded Post Quench Ductility (PQD) Empirical Database

Introduction:

Based on internal discussions and comments received from public stakeholders, the staff identified three areas where further effort was needed to enhance the existing technical basis documented in NUREG/CR-6967 (ML082130389) and Research Information Letter (RIL) 0801 (ML081350225). One of these areas was testing of irradiated cladding with intermediate hydrogen levels. The need for additional testing was described in a memorandum to the Commission dated December 19, 2008 (ADAMS ML083440156):

> *The current PQD empirical database does not include testing on irradiated cladding segments with hydrogen concentrations from 100–500 parts per million. Further PQD tests are needed in this intermediate range of hydrogen to develop high-confidence regulatory criteria.*

Technical Background:

Ring compression tests were conducted to measure ductility of defueled, high burnup cladding samples (Zircaloy-4, ZIRLO and M5) following high-temperature steam oxidation as part of the Office of Nuclear Regulatory Research (RES) high burnup Loss-of-Coolant Accident (LOCA) research program conducted at Argonne National Laboratory (ANL). Through the LOCA research program at ANL, it was discovered that the major burnup effect is caused by hydrogen, which is absorbed in the cladding during the burnup-related corrosion process. Because of this, the embrittlement thresholds were correlated directly with the pre-accident hydrogen concentration. In Figure 1 in RIL-0801 (shown below as Figure 1), a linear relationship is depicted in characterizing the sensitivity of hydrogen on PQD.

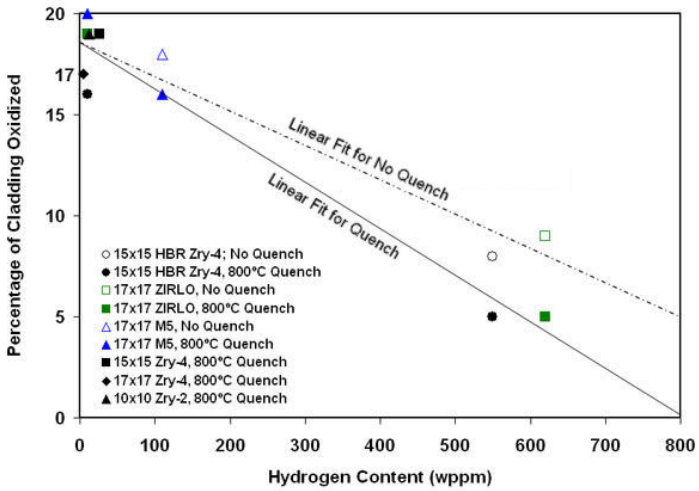

Figure 1 – Measured embrittlement threshold, expressed as a percentage of cladding oxidized and calculated with the Cathcart-Pawel equation, as a function of pre-test hydrogen content

The proposal for modifying rule language in Title 10 of the Code of Federal Regulations Part 50.46(b) is currently to specify the criteria for post quench ductility following a LOCA accident to decrease linearly with increasing hydrogen content (See Figure 2).

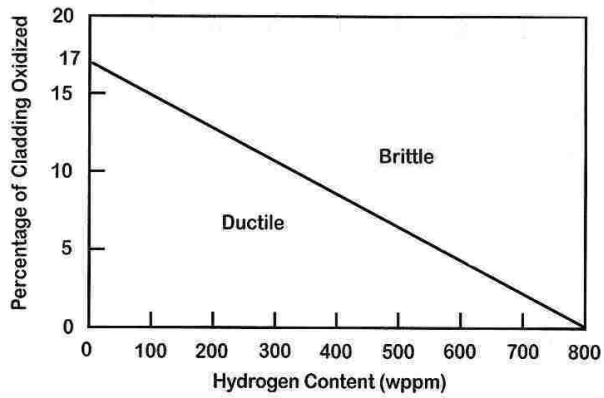

Figure 2 – Proposed linear variation in PQD criteria with hydrogen content

Because the data for the proposed linear variation of PQD with hydrogen content were derived from an empirical database of irradiated cladding with a limited number of hydrogen concentrations, specifically ≈10 and 550 weight parts per million (wppm) for Zircaloy-4, ≈10 and 100 wppm for M5™, and ≈10 and 600 wppm for ZIRLO™, additional tests were run with irradiated cladding at intermediate hydrogen concentrations (e.g., between 150 and 450 wppm) to confirm linear variation.

Objective of additional testing:

Additional tests were conducted at ANL to verify if a linear relationship of PQD to hydrogen content, as depicted in RIL-0801 and in the proposed rule revision's embrittlement criteria, persisted at intermediate hydrogen concentrations. This was done by performing ring compression tests on short samples (25-mm long) of irradiated ZIRLO™ cladding, following high-temperature steam oxidation, which were sectioned from two 80-mm-long segments with a pre-transient corrosion layer of 26 μm and approximately 300 wppm hydrogen (H).

Quick Look Results:

Determining the value of PQD corresponding to a specific hydrogen level requires multiple steam oxidations and ring compression tests. A cladding sample is exposed to high temperature steam oxidation and the time and temperature is used to determine the amount of oxidation, as calculated with the Cathcart-Pawel equation[1]. This calculated value of oxidation is termed the Equivalent Cladding Reacted (ECR). Oxidized cladding samples are then sectioned into rings appropriate for ring compression tests. Ring compression tests are run until a load drop of >30% is detected, indicating failure (e.g., at least one through-wall crack along the length of the ring. For rings that fail with a single, tight through-wall crack, the measured decrease in cladding outer diameter in the loading direction is used to determine residual ductility (≥1% implies ductile behavior). For rings that fail with multiple cracks or with a wide single crack, the measured offset displacement is used as an indication of residual ductility (≥2% implies ductile behavior). In the determination of residual ductility for the samples oxidized in this test campaign, two ring compression tests for each oxidized sample were used to determine the residual ductility for a given ECR. Depending on the residual ductility of the first oxidized sample, additional cladding samples are oxidized to a higher or lower value of ECR (i.e. if the

[1] J. V. Cathcart, R. E. Pawel, R. A. McKee, R. E. Druscel, G. J. Yurek, J. J. Cambell and S. H. Jury, "Zirconium Metal-Water Oxidation Kinetics IV. Reaction Rate Studies," ORNL/NUREG-17, Aug. 1977.

first sample tested is ductile after oxidation to 10% ECR, then a second sample would be oxidized to a higher ECR to try to identify the ECR which produces brittle behavior). A sample plot illustrating ductility values (i.e. offset strains) as a function of ECR is show below in Figure 3.

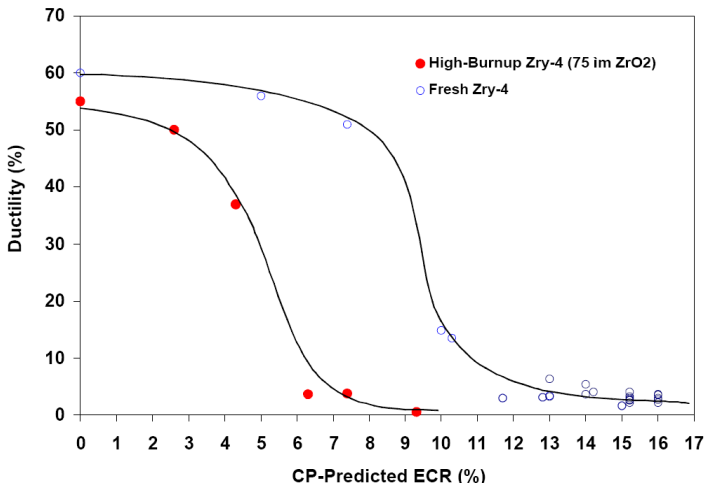

Figure 3 – Ductility after oxidation in steam at 1200°C (~2200 °F) and cooled slowly for irradiated and unirradiated Zircaloy-4 cladding; embrittlement occurs at about 2% ductility on this plot

Figure 3 illustrates how ductility values measured at a range of ECRs can be used to determine the value of ECR at which the transition from ductile to brittle behavior occurs. In this plot, values <2% ductility indicate brittle behavior. The value of ECR at which the ductility as measured by offset strain is equal to 2% is used to identify the ECR at which the transition from ductile to brittle behavior occurs for the hydrogen content of the sample tested.

In this test campaign, high burnup cladding samples of ZIRLO™ with approximately 300 wppm H were oxidized to two levels of ECR. The first sample was oxidized to an ECR of 10% and quenched at 800°C. The sample was sectioned to create two ring compression samples. The measured offset strains were 0.7% and 2.1%. Based on the 1.4% average offset strain, it was determined that these test conditions lead to brittle cladding behavior.

A second sample was oxidized to an ECR of 8% and quenched at 800°C. The sample was sectioned to create three ring compression samples: two for data generation and one to confirm that 2% offset strain corresponded to about 1% permanent strain and ductile behavior. The two rings compressed for ductility determination exhibited ductile behavior with offset strain measurements greater than 2%, specifically 2.9% and 4.6%. Both of these rings failed with two cracks, so no meaningful permanent strain based on diameter decrease could be determined. Compression of the third ring was terminated prior to cracking to allow determination of the post-test diameter for an intact ring. The results – 2.0% offset strain and 1.2% permanent strain – confirmed the use of the 2% offset strain ductility criterion. Additional information on ductility measurements will be contained in a forth coming ANL letter report.

The results of additional tests run on other ZIRLO™ segments with approximately 300 wppm H are given in Appendix A (additional details for all tests run in this test campaign are available in Appendix A as well, including hydrogen measurements). This includes samples which were oxidized and slow cooled, rather than quenched at 800°C. For the purpose of determining the

value of PQD for cladding with 300 wppm H, the values of offset strain from ring compression tests for samples oxidized to 8% and 10% ECR and quenched at 800°C are plotted below in Figure 4. From this figure, it can be determined that the segments of high burnup ZIRLO™ with approximately 300 wppm H are ductile following oxidation to 8% ECR and brittle following oxidation to 10% ECR. From these data, it is determined that the ductile to brittle transition for zirconium cladding with 300 wppm H takes place at 9% ECR.

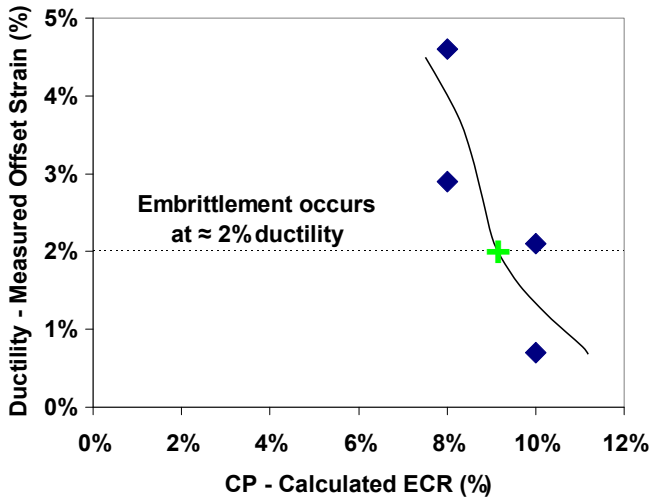

Figure 4 – Ductility measurements from High Burnup ZIRLO™ with approximately 300 wppm H

Since RIL-0801 was written and issued, additional tests have been run at ANL. Figure 5 below includes the current database of results for both high burnup and prehydrided cladding which was quenched at 800°C. The value of 9% ECR at 300 wppm H for material that has been quenched at 800°C is in fact in line with the previous results, as shown in Figure 5 below. In addition to the new high burnup ZIRLO data point at 9% ECR at 300 wppm H, there are a few other differences between the data in Figure 5 and the data used in plotting Figure 1 in RIL-0801. First, pre-hydrided data are plotted together with high burnup data. Second, the ZIRLO sample which transitioned from ductile to brittle behavior at 5% ECR is now plotted against the value of its post-transient hydrogen content, rather than the pre-test hydrogen content. Since the publication of RIL-0801, it was understood that the hydrogen of consequence is in the base metal. Pre-test hydrogen contents account for hydrogen in the oxide as well, and for ZIRLO, the hydrogen content in the oxide was significant. Finally, additional tests were run on the M5 cladding sample with ≈ 100 wppm H, which indicated that the PQD was slightly lower than the value plotted in Figure 1 of RIL-0801. Further details on the information obtained at ANL since the publication of RIL-0801 are contained in NUREG/CR-6967 and will be contained in a forthcoming ANL letter report.

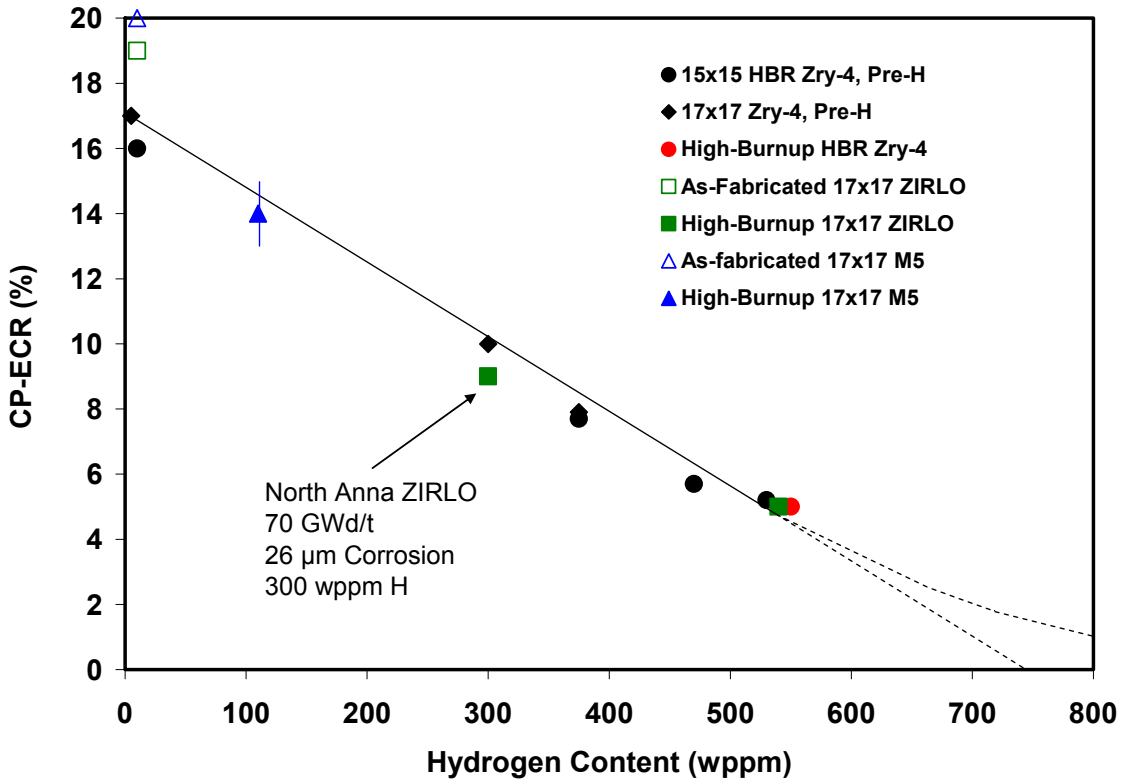

Figure 5 – Current Database for Ductile-to-brittle Transition Oxidation Level (CP-ECR) as a Function of Hydrogen Content for As-fabricated, Pre-hydrided, and High-burnup Cladding Alloys.

Conclusion:

The data that were available through the ANL program at the time RIL-0801 was published were obtained from cladding samples with low range hydrogen contents and cladding samples with relatively high range hydrogen contents. The data from those tests were used to depict a linear decrease in ECR with increasing hydrogen content. Because the relationship of ECR to hydrogen content is an integral component in the proposed rule revision's embrittlement criteria, it was necessary to confirm this linear relationship with at least one data point at an intermediate hydrogen level. With this test campaign, a series of measurements were made to confirm that the value of PQD at intermediate hydrogen levels fell in line with the linear trend depicted in RIL-0801 and in the proposed rule.

Appendix A – Data from all Tests run in this campaign of High Burnup ZIRLO

Cladding	Oxidation Test	ECR	Sample	Cooling	Pre-Test Hydrogen (wppm ± ≈ 30 wppm)	Approximate Metal Hydrogen Content (wppm ± ≈ 30 wppm)	Offset Strain	Permanent Strain	Behavior
High Burn Up ZIRLO	ZLI#7 Test	10%	648B2B	Without Quench	365	300	9.9%	5% (1 crack)	Ductile
High Burn Up ZIRLO	ZLI#7 Test	10%	648B2D	Without Quench	365	300	13.7%	9.4% (1 crack)	Ductile
High Burn Up ZIRLO	ZLI#8 Test	10%	648A3B	800°C Quench	306	300	0.7%	(2 cracks)	Brittle
High Burn Up ZIRLO	ZLI#8 Test	10%	648A3C	800°C Quench	306	300	2.1%	(2 cracks)	Ductile (borderline)
High Burn Up ZIRLO	ZLI#9 Test	8%	648A6B	800°C Quench	318	300	2.9%	(2 cracks)	Ductile
High Burn Up ZIRLO	ZLI#9 Test	8%	648A6C	800°C Quench	318	300	4.6%	(2 cracks)	Ductile
High Burn Up ZIRLO	ZLI#9 Test	8%	648A6D	800°C Quench	318	300	> 2.0%	> 1.2% (No cracks)	Ductile