

# ARGONNE NATIONAL LABORATORY

9700 SOUTH CASS AVENUE, ARGONNE, ILLINOIS 60439

TELEPHONE: (630) 252-7146

FAX: (630) 252-9232

E-Mail: billone@anl.gov

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Mr. Harold H. Scott  
Office of Nuclear Regulatory Research  
Division of Systems Technology  
U.S. Nuclear Regulatory Commission  
Washington, D.C. 20555-0001

Dear Harold:

At your request we have reviewed the steam oxidation kinetics data for zirconium alloys: Zircaloy-4, Zircaloy-2, E110, M5, and ZIRLO. We have also reviewed and compared oxidation kinetics correlations and models used to predict exothermic heat generation rate and weight gain.

Enclosed is our report "Steam Oxidation Kinetics of Zirconium Alloys," by M.C. Billone, H.M. Chung, and Y. Yan. If you have any further questions or requests, please contact me.

Sincerely,



M. C. Billone  
Irradiation Performance Section  
Energy Technology Division

cc: R.O. Meyer, USNRC/RES

# STEAM OXIDATION KINETICS OF ZIRCONIUM ALLOYS

M.C. Billone, H.M. Chung and Y. Yan  
Argonne National Laboratory  
June 4, 2002

## SUMMARY

High-temperature oxidation kinetics data for zirconium alloys exposed to steam and water are reviewed. The alloys (composition in wt. %) include Zr, Zr-1.3Cr-0.1Fe, Zircaloy-2, Zircaloy-4, Zr-1Sn-1Nb, Zr-1Nb and Zr-2.5Nb. The purpose of the review is to provide background data and interpretation relevant to ECCS Acceptance Criteria for LWR fuel rod cladding alloys. Based on the data review, it is concluded that all relevant LWR zirconium alloys exhibit about the same weight gain kinetics in the temperature range of 1100-1500 C, particularly at  $\approx 1200$  C. The differences in reported data and correlations appear to be due more to differences in temperature ramp rates, in absolute uncertainties in the steady oxidation temperature, in cooling rates and in measurement techniques (weight gain vs. metallography), than to alloy composition. Although most correlations are based on Zircaloy-4 data, recent data for Zircaloy-2 and advanced alloys -- ZIRLO (Zr-1Sn-1Nb), M5 (Zr-1Nb) and E110 (Zr-1Nb) -- suggest the same steam oxidation kinetics as for Zircaloy-4 in the range 1100 T 1500 C.

The Baker-Just correlation is specified in Appendix K of 10CFR50.46 for calculation of the heating rate due to oxidation, hydrogen generation and the Effective Cladding Reacted (ECR) because it was available in 1973. However, this correlation has the least significant database and justification of all those reviewed. Oxidation kinetics studies on a variety of zirconium alloys conducted since 1962 -- particularly in the 1970s -- have demonstrated that the Baker-Just correlation over-predicts weight gain and zirconium consumed by as much as 30% at the peak cladding temperature (1204 C) allowed by 10CFR50.46. USNRC Regulatory Guide 1.157 (May 1989) allows the use of a best-estimate correlation (e.g., Cathcart-Pawel) for temperatures greater than 1078 C. For temperatures below 1078 C, correlations must be checked against relevant data that include the effects of steam pressure and pre-oxidation of the cladding.

Based on this review and many past reviews, the oxidation kinetics of relevant zirconium alloys appears to be parabolic (e.g., weight gain  $w$  defined by  $w^2 = kt$ , where  $t$  is time) in the temperature range of 1000-1500 C for Zr-1.5 $\pm$ 0.3Sn, Zr-1Sn-1Nb, and Zr-(1-2.5)Nb alloys. Above 1577 C, the oxide layer transforms from tetragonal-to-cubic and the oxidation rate increases. Below 1000 C, the weight gain deviates from parabolic behavior as the alloys transform from the  $\beta$ -phase to the mixed ( $\beta+\alpha$ )-phase to the  $\alpha$ -phase. Phase transformation temperatures depend on alloy type and pre-test oxygen and hydrogen concentrations.

The implications of using the Cathcart-Pawel weight gain correlation, rather than the Baker-Just correlation, are discussed with respect to heat-of-reaction rate and ECR. Recommendations are made regarding the weight gain correlations in the USNRC-sponsored FRAPTRAN code, the algorithm for calculating ECR, and the relationship between ECR and ductility during ECCS quench and post-quench loading.

## 1. Introduction

The open literature contains numerous reports of data and correlations for the weight gain kinetics of zirconium alloys. Only a few references are cited here. However, the papers and reports cited contain long reference lists documenting the extensive steam oxidation kinetics database for zirconium alloys. Baker and Just [1] and Lemmon [2] studied the weight gain of zirconium in water at temperatures in the range of 1000 C to the melting point of Zr (1852 C). White (1967-68) {as reported by Urbanic and Heidrick [3]} performed his studies on Valoy (Zr-1.3Cr-0.1Fe). Urbanic [3,4] investigated the weight gain kinetics of Zircaloy-2, Zircaloy-4 and Zr-2.5Nb and concluded that there was no significant effect of alloy type on high-temperature steam oxidation behavior. Carthcart et al. [5] did an extensive study of the weight gain and oxidation kinetics of Zircaloy-4 in the temperature range of 900-1500 C. They found that the weight gain, oxide layer growth and (oxide +  $\alpha$ ) layer growth all exhibited parabolic kinetics for 1000 C  $\leq$  T  $\leq$  1500 C. These studies, along with a number of other investigations, were conducted prior to 1980 and are reviewed by Ocken [6]. Chung and Kassner [7] conducted an extensive investigation of the oxidation kinetics and phase boundary evolution of Zircaloy-4. In the 1990s, Grandjean et al. [8,9] investigated the oxidation kinetics of unirradiated, unirradiated/hydrided, and irradiated Zircaloy-4. More recently, Yan et al. [10] performed one-sided oxidation experiments at 1000-1200 C using unirradiated (archival) and highly irradiated Zircaloy-2 (recrystallized-annealed with inner-surface Zr liner), Waeckel and Jacques [11] performed two-sided oxidation experiments at 1050 and 1200 C on the same unirradiated Zircaloy-2 used by Yan et al., and Yegorova et al. [12] report oxidation data for the Russian Zr-1Nb alloy (E110) in the temperature range of 900-1300 C. The Waeckel and Jacques data agree well with the Leistokow correlation [13], while the Yan et al. data agree better with the Cathcart-Pawel correlations. Bourhis [14] found the steam oxidation kinetics of M5 to be close to that of Zircaloy-4 in the temperature range of 1100-1400 C. Leech [15] reported that the weight gain of ZIRLO is comparable to Zircaloy 4 in the temperature range of 1000-1200 C.

With the exception of the Moalem and Olander data [16], the experimental data and analyses confirm the following:

- a. The Baker-Just correlation over-predicts weight gain for T = 1000-1500 C.
- b. Weight gain kinetics are parabolic for T = 1000-1500 C  
 $w_o \, dw_o/dt = (k/2) t$  -- for isothermal conditions with no pre-steam oxide ( $w_o$ )<sup>2</sup> = kt, where  $w_o$  = weight-gain/surface-area due to oxygen pickup and t = time;  
below 1000 C kinetics are not parabolic due to  $\beta$  to ( $\beta+\alpha$ ) to  $\alpha$  phase transformations;  
above 1577 C (tetragonal-to-cubic oxide transformation) oxidation rate increases.
- c. High temperature steam oxidation behavior appears to be independent of alloy type.
- d. Within the scatter of the very limited data, the in-reactor-induced oxide layer appears to be "transparent" to steam [8-10]; however, more studies are needed to confirm this.
- e. The effective thickness of the oxygen-stabilized  $\alpha$  layer increases and the  $\beta$ -layer thickness decreases as the cool-down temperature ramp rate decreases.

The rate constant  $k$ , normalized to the Cathcart-Pawel rate constant  $k_{cp}$ , is shown in Fig. 1 for several correlations (Baker-Just, Leistikow, and Urbanic), along with normalized rate constants deduced from more recent Zircaloy-2, E110, and M5 data. The rate constant is needed to determine the heat generation rate for the exothermic steam-metal reaction. The standard semi-log plot of  $k$  vs.  $1/T$  is used in Fig. 1. At 1200 C, the Leistikow and Urbanic rate constants are  $\approx 15\%$  and  $3\%$ , respectively, lower than the Cathcart-Pawel rate constant, while the Baker-Just rate constant is  $69\%$  higher. For weight gain ( $w_o$ ) and ECR calculations, it is the square root of  $k$  that is important. Figure 2 shows the temperature variation of the normalized weight gain ( $w_o/w_{ocp}$ ) vs.  $T$  for the three correlations, along with recent test data, normalized to the Cathcart-Pawel predictions. At 1200 C, the Leistikow and Urbanic weight-gain predictions are  $9\%$  and  $2\%$  lower than the Cathcart-Pawel predictions, while the Baker-Just prediction is  $30\%$  higher.

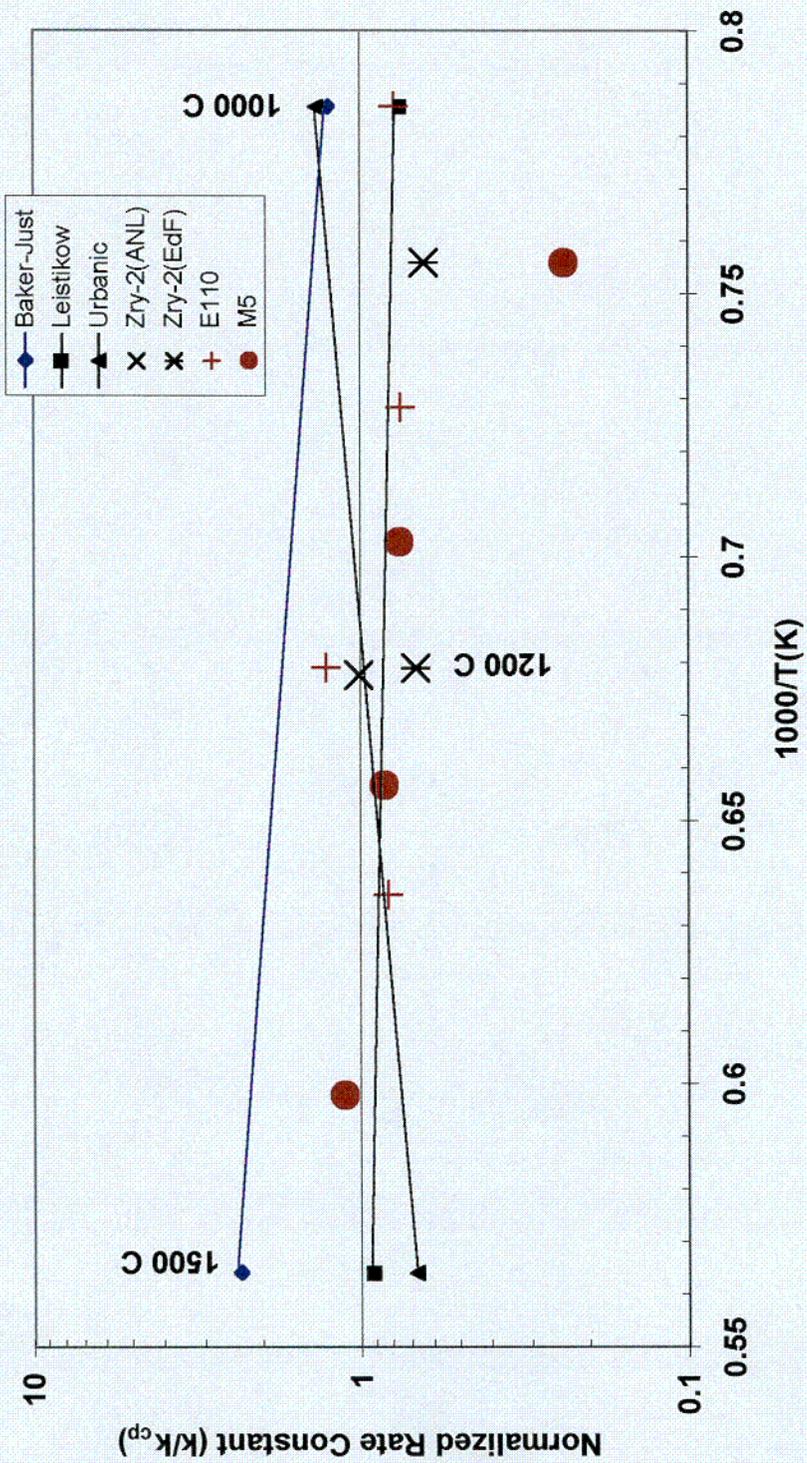


Fig. 1. Comparison of correlations and data for steam-oxidation rate constant ( $k$ ) normalized to the Cathcart-Pawel Correlation.

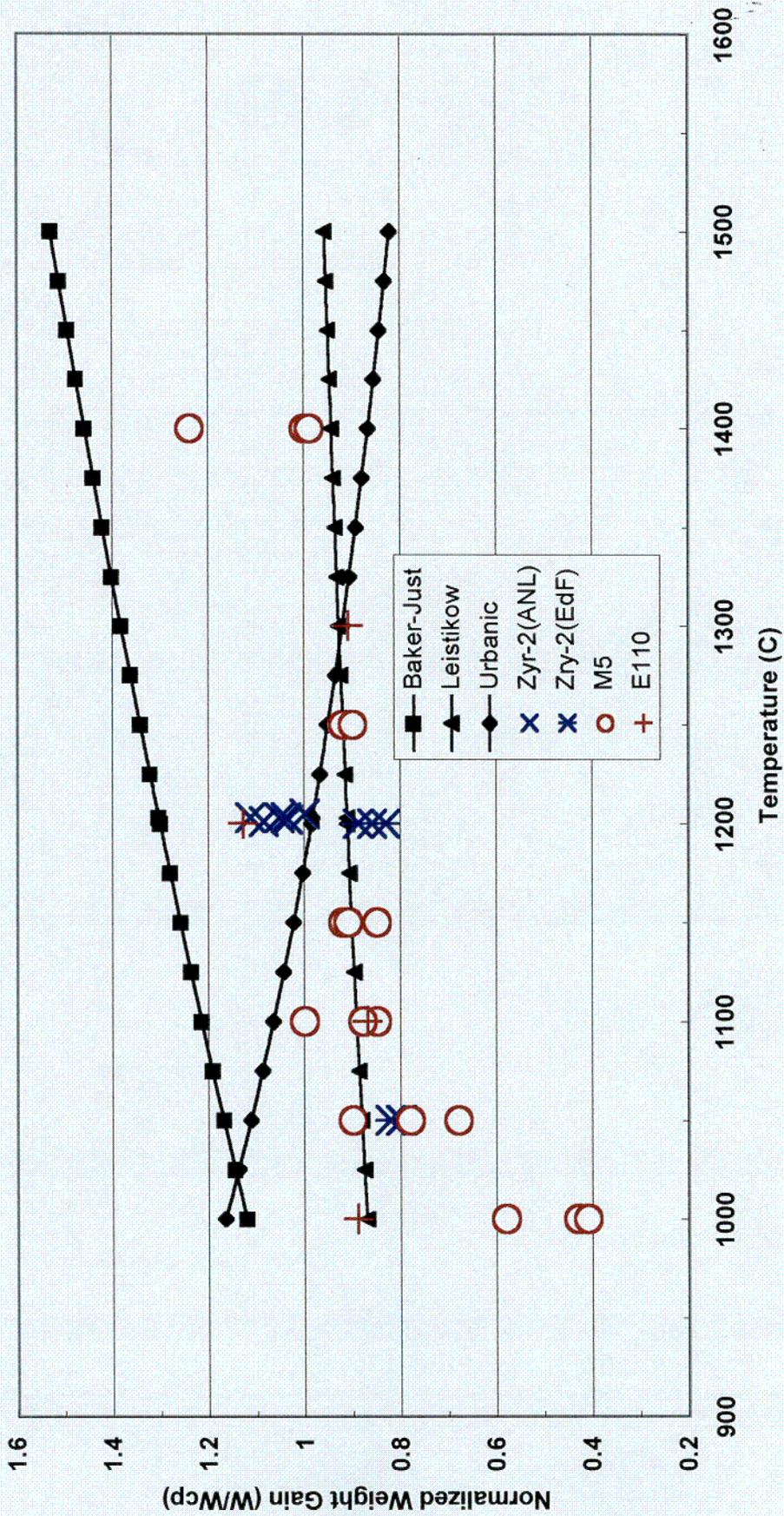


Fig. 2. Comparison of steam-oxidation-kinetics weight gain correlations and data normalized to the Cathcart-Pawel correlation.

The work of Moalem and Olander [16] is very interesting in that weight gain is measured dynamically as a function of time by a continuously recording microbalance, and steam is not introduced into the system until the sample is stabilized at temperature in flowing argon. This differs from almost all previous experiments in which steam is introduced prior to the temperature ramp and weight gain is measured and/or deduced after completion of the test. Given the sophistication of the Moalem and Olander experimental setup and the large number of data points generated per test, it is a remarkable coincidence that their data matches the Baker-Just correlation. The Baker-Just correlation was developed based on only one test temperature – the melting point of zirconium ( $\approx 1850$  C) – and four “adjusted” data points from Lemmon in the temperature range of 1000-1300 C. However, no metallographic analysis is available to support the weight-gain data of Moalem and Olander. Yan et al. [17] initially generated weight gain data that fit better with the Baker-Just correlation than the Cathcart-Pawel correlation. However, this was due to an experimental artifact resulting in low steam flow rates that were spatially and temporally nonuniform. Metallographic analysis revealed highly irregular oxide-alpha and alpha-beta boundaries with regions of locally enhanced oxide growth. These irregularities disappeared when the apparatus was redesigned to isolate the specimen environment in the test chamber and to force all of the steam generated to flow within that chamber. As the Moalem and Olander study was conducted in a mode not relevant to LOCA – in a LOCA there is ample steam during the cladding heat-up phase – and as it is not supported by metallography, their “data” should not be included in the LOCA-relevant database at this time until they can be confirmed by metallographic analysis.

The current LOCA cladding temperature limit (PCT) is 1204 C based on using the Baker-Just correlation to calculate heat generation and ECR. The consequences on this limit of using a best-estimate oxidation correlation vs. the Baker-Just (BJ) correlation are explored in this work. The three factors considered are: temperature for breakaway oxidation due self-heating; failure threshold temperature at 17% ECR based on fragmentation during thermal quench, and nil-ductility limit following quench under these conditions. The Cathcart-Pawel (CP) correlation and models are chosen as “best-estimate” for this comparison because:

- a. The Cathcart et al. data are considered acceptable to NRC (Reg. Guide 1.157). The correlations based on these data are also used in the NRC-sponsored code FRAPTRAN and are documented in MATPRO (Version 11, Revision 2, 1981).
- b. The CP correlations for weight gain, oxide layer thickness and (oxide +  $\alpha$ ) layer thickness are based on extensive metallographic analyses.
- c. The ANL [10] weight gain and oxide-layer-thickness data for unirradiated and highly irradiated Zircaloy-2 are in good agreement with model predictions.
- d. Both the Cathcart et al. and the ANL data are based on detailed metallographic analysis of one-sided oxidation tests; as ANL is also testing highly irradiated cladding with in-reactor-induced, outer-surface oxide layers of 10-100  $\mu\text{m}$ , the one-sided approach is desirable because it allows isolation of the effects of the outer-surface oxide layer on the oxidation kinetics.

## 2. Baker-Just Correlation for Weight of Zirconium Consumed during Steam Oxidation

The integrated form of the Baker-Just (BJ) correlation for weight/surface-area ( $w$ ) of zirconium consumed during steam oxidation is given in Ref. 1 as:

$$w^2 = 33.3 \times 10^6 t \exp(-45500/RT), (\text{mg}/\text{cm}^2)^2 \quad (1)$$

where  $t$  is time in seconds,  $T$  is temperature in K and  $R = 1.987$ . This equation applies to isothermal oxidation in steam for fresh cladding with no protective, pre-transient oxide layer. The units for  $w$  are converted to  $\text{g}/\text{cm}^2$  for the purposes of the current work:

$$w^2 = 33.3 t \exp(-45500/RT), (\text{g}/\text{cm}^2)^2 \quad (2)$$

The weight of Zr consumed (per surface area) is obtained by taking the square root of Eq. 2:

$$w = 5.7706 t^{0.5} \exp(-22750/RT), \text{g}/\text{cm}^2 \quad (3)$$

For comparison purposes, it is also important to express Eq. 3 as weight-gain/surface area due to oxygen pick up ( $w_o = 32/91.2 w = [1/2.85] w$ ):

$$w_o = 2.0248 t^{0.5} \exp(-22750/RT), \text{g}/\text{cm}^2 \quad (4)$$

In order to calculate heat generation rate, as well as to follow the LOCA temperature transient, the rate form of Eq. 2 is required:

$$w (dw/dt) = 16.65 \exp(-45500/RT), (\text{g}/\text{cm}^2)^2/\text{s} \quad (5)$$

As is typical of parabolic rate equations, the rate goes mathematically to infinity at  $t = 0$ . This is physically unrealistic as the steam supply and rate of dissociation of  $\text{H}_2\text{O}$  molecules are rate limiting as  $t \rightarrow 0$ . This mathematical artifact can be overcome in finite difference numerical schemes by assuming an initial ( $t=0$ ), small oxide layer [e.g.,  $w(t=0) = 4 \times 10^{-4} \text{g}/\text{cm}^2$ , the weight gain associated with a 1  $\mu\text{m}$  oxide layer].

The associated ECR can be calculated by dividing  $w$  by the density of zirconium ( $\rho_z = 6.50 \text{g}/\text{cm}^3$ ) and the reference cladding thickness ( $h_r$  in cm) defined in 10CFR50.46:

$$\text{ECR (fraction)} = w/(\rho_z h_r) \quad (6)$$

Equation 6 applies to one-sided oxidation. For double-sided oxidation following burst, the right-hand side of Eq. 6 is simply multiplied by 2.

For irradiated cladding, the weight gain due to in-reactor-induced oxidation is  $> 0$ . However, the limited data to date suggest that the oxide layer associated with this weight gain is non-protective. The preliminary recommendation is that this layer be retained for heat transfer purposes, but that it be "disregarded" for calculating transient heat generation rate, oxidation rate, weight gain and ECR.

### 3. Cathcart-Pawel Correlation for Weight Gain (Oxygen Pickup) during Steam Oxidation

The integrated form of the Cathcart-Pawel (CP) correlation for weight-gain/surface-area ( $w_o$ ) due to oxygen pickup is given in Ref. 5 as:

$$(w_o)^2 = 0.3622 t \exp (-39940/RT), (\text{g/cm}^2)^2 \quad (7)$$

where  $t$ ,  $T$  and  $R$  are in the same units as in Eq. 1. The equation is considered valid in the temperature range of 1000-1500 C for isothermal oxidation in steam and for fresh cladding with no protective pre-transient oxide layer. Taking the square root of Eq. 7 gives:

$$w_o = 0.60183 t^{0.5} \exp (-19970/RT), \text{g/cm}^2 \quad (8)$$

In order to calculate heat generation rate, as well as to follow the LOCA temperature transient, the rate form of Eq. 7 is required, along the conversion  $w = 2.85 w_o$ :

$$w (dw/dt) = 1.471 \exp (-39940/RT), (\text{g/cm}^2)^2/\text{s} \quad (9)$$

The conversion to ECR is similar to the one given in Eq. 6 except for the added conversion factor for zirconium consumed ( $91.2/32 = 2.85$ ) vs. oxygen weight gain.

$$\text{ECR (fraction)} = 2.85 w_o/(\rho_z h_r) = w/(\rho_z h_r) \quad (10)$$

For double-side oxidation following burst, the right-hand side of Eq. 10 is multiplied by 2.

### 4. Comparison of Baker-Just and Cathcart-Pawel Correlations

#### 4.1 Heat generation Rate

The Baker-Just correlation over-predicts the oxidation rate and, hence, over-predicts the heat generation rate. The LOCA peak temperature limit should protect against breakaway oxidation due to self-heating from the exothermic oxidation reaction. However, the Baker-Just correlation is conservative from two viewpoints: the rate constant in Eq. 5 is greater than the best-estimate rate constant in Eq. 9 and the assumption that all of the oxygen pickup forms zirconia ( $\text{ZrO}_2$ ). Another way to demonstrate this conservatism in rate constant is to calculate the Cathcart-Pawel temperature ( $T_{cp}$ ) that would give the same heat-generation rate as the Baker-Just correlation evaluated at a temperature  $T_{bj}$ . Setting Eq. 5 equal to Eq. 9 gives:

$$T_{cp} = 0.8778 T_{bj} (1 - 1.0596 \times 10^{-4} T_{bj})^{-1} \quad (11)$$

$$\Delta T = 0.8778 T_{bj} (1 - 1.0596 \times 10^{-4} T_{bj})^{-1} - T_{bj} \quad (12)$$

Table 1 lists values for  $T_{cp}$  and  $\Delta T$  vs.  $T_{bj}$ . Figure 3 shows  $\Delta T$  vs.  $T_{bj}$ .

Table 1 Comparison of Cathcart-Pawel (CP) and Baker-Just (BJ) Correlations in Terms of the CP Temperature ( $T_{cp}$ ) that would Predict the same Heat-Generation-Rate, Weight Gain and ECR as the BJ Correlation for an assumed BJ Temperature of  $T_{bj}$

$T_{bj}$ , C	$T_{cp}$ , C	$\Delta T$ , ° C
1300	1384.0	84.0
1290	1371.3	81.3
1280	1358.8	78.8
1270	1346.2	76.2
1260	1333.7	73.7
1250	1321.2	71.2
1240	1308.7	68.7
1230	1296.3	66.3
1220	1283.9	63.9
1210	1271.5	61.5
1204	1264.1	60.1
1200	1259.1	59.1
1150	1197.9	47.9
1100	1137.4	37.4

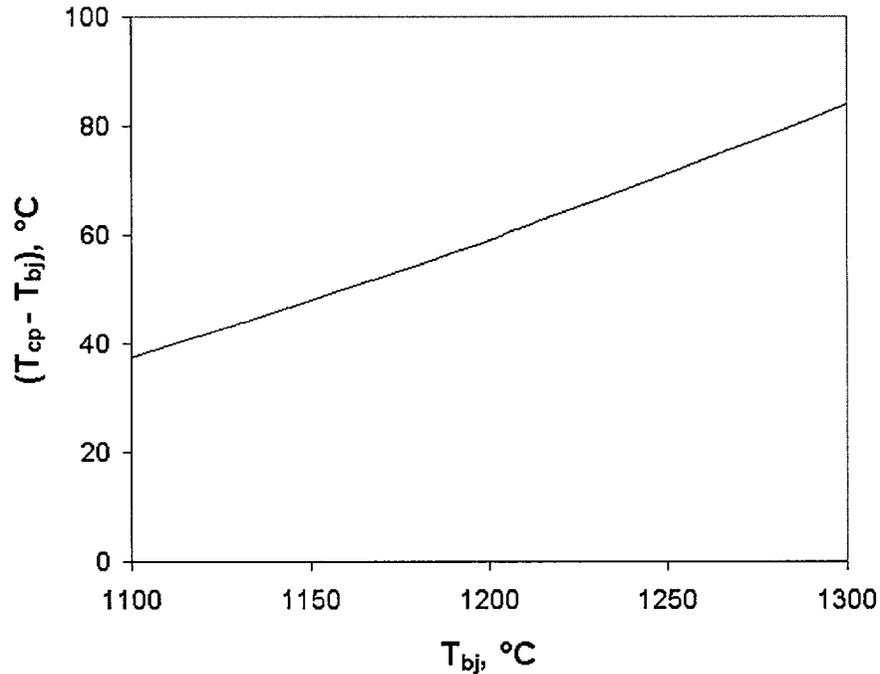


Fig. 3. Temperature increase required for the Cathcart-Pawel (CP) correlation to predict the same heat generation rate, weight gain and ECR as the Baker-Just (BJ) correlation.  $T_{bj}$  is the temperature used in the BJ correlation.  $T_{cp}$  is the resulting CP temperature needed to calculate the same results as predicted by the BJ correlation.

## 4.2 ECR

The BJ correlation predicts a higher weight gain, and hence ECR, at a given temperature than the CP model. For example, the BJ correlation predicts weight gains that are 38%, 30%, 21% and 12% higher than the CP predictions at 1300 C, 1200 C, 1100 C and 1000 C, respectively. Another way to compare the two correlations is to set Eq. 4 equal to Eq. 8 and calculate the CP temperature ( $T_{cp}$ ) corresponding to the BJ weight gain prediction at the BJ temperature ( $T_{bj}$ ). The resulting equations for  $T_{cp}$  vs.  $T_{bj}$  and  $\Delta T = T_{cp} - T_{bj}$  vs.  $T_{bj}$  are the same as those given in Eqs. 11 and 12. This should be obvious because if the two correlations have the same rate constant, they will result in the same weight gain and ECR values. Thus, Table 1 and Fig. 3 also apply to weight gain and ECR.

## 4.3 Cladding failure thresholds for quench and post-quench vs. ECR and PCT

For rod-averaged burnups  $\leq 62$  GWd/MTU, the following factors must be considered:

### a. The effect of burnup on cladding ballooning, burst and fuel relocation

As the burnup increases, the moles of gas within the rod increases due to fission gas release, the void space within the rod decreases, and the gas pressure within the rod increases. Concurrently, the gas communication (i.e., fuel permeability) decreases and fuel-cladding bonding (mechanical and/or chemical) increases. The net effect of these phenomena on ballooning, burst and fuel relocation, as well as their effects on oxidation and ECR, needs to be determined experimentally through hot-cell and in-reactor LOCA Integral Tests using fueled rod segments.

### b. The effect of hydrogen increase with burnup

The presence of hydrogen will lower the  $\alpha$ -to- $\beta$  (during heating) and  $\beta$ -to- $\alpha$ -prime (during cooling) phase transformation temperatures. It also lowers the ECR failure thresholds for quench with axial loading and post-quench loading. The hydrogen-embrittlement effect has been demonstrated for unirradiated cladding samples [18].

### c. The effect of tight fuel-cladding contact on the ECR failure threshold during quench

Failure during quench can result from stresses due to differential thermal contraction within the cladding, differential thermal contraction between the fuel and cladding, axial loads on the cladding (e.g., due to grid-spacer constraints), and/or radial loads due to rod-to-rod contact. The effect of tight fuel-cladding contact either due to bonding during normal reactor operation or fuel relocation following ballooning needs to be determined experimentally. The presence of the fuel can reduce the ECR threshold for fragmentation during quench. However, as Nagase and Uetsuka [18] performed LOCA oxidation and quench experiments on unirradiated Zircaloy tubing under conditions ranging from no axial constraint to full axial constraint, one would expect the axial-constraint effects of the fuel to be within the range of the test conditions for their as-received and pre-hydrided samples.

d. Cooling rate effects on the ECR failure threshold during quench and post-quench

Most oxidation kinetics studies (e.g., Cathcart et al. [5]) are conducted under “near-isothermal” conditions for relatively short periods of time, resulting in small weight gains and ECR values. Very fast heat-up and cool-down rates are used. Cathcart et al. and others recognized that slow cooling (e.g., 1-5 C/s) results in enhanced growth of the alpha layer at the expense of the beta layer. These alpha “incursions” occur because of the diffusion of oxygen within the beta layer to form additional oxygen-stabilized alpha both at the alpha-beta interface and within the beta phase. Although this phenomenon does not impact weight gain, it does reduce the effective beta layer thickness. As the weight gain increases to approach an ECR of 17% at 1204 C, the oxygen concentration in the beta phase increases to its saturation limit of  $\approx 0.6$  wt. %, and the alpha-incursions increase in magnitude. The situation becomes even more interesting in the presence of hydrogen. Given enough time for diffusion, oxygen migrates from beta-to-alpha and hydrogen migrates from alpha-to-beta during cooling from high temperature to  $\approx 800$  C. The hydrogen has an embrittling effect on the reduced beta layer region [16], particularly as it precipitates out into hydrides at T 550 C – more significant for post-quench failure threshold than for quench threshold.

The oxidation-kinetics database for the best-estimate correlations consists mainly of short-time tests with low ECR values and high heat-up and cool-down rates. For example, the CP correlations [5] are based on data at 1203 C for oxidation times 280 s (< 5 min.) with corresponding ECR values < 8%. In a special test, Cathcart et al. oxidized at 1200 C for 120 seconds and cooled down at  $\approx 4$  C/s. Their measured alpha layer thickness was  $\approx 20\%$  higher than predicted. As oxidation temperature and/or time increases, the alpha layer can grow 40-50% higher than predicted by the correlation. Attempts to model these alpha incursions using rate constants developed to fit the isothermal data have been generally unsuccessful.

In the ANL test conducted by Yan et al. [10], oxidation times of 5, 10 and 20 minutes were used. For these tests at  $\approx 1203$  C using irradiated Limerick Zry-2 samples, the measured weight gains correspond to ECR values (8.6-15.3%) that are  $\approx 6\%$  higher than the CP-predictions. However, the measured effective beta layer thicknesses (541-430  $\mu\text{m}$ ) for these tests are  $> 8\%$  smaller than the CP-predictions. The “ $> 8\%$ ” reflects the fact that the sum of the oxide and continuous alpha layers were subtracted from the total cladding thickness to calculate the effective beta layer thickness. Additional work is required to also subtract the oxygen-stabilized alpha regions within the beta layer.

The solubility of oxygen in the beta layer increases with temperature. In the absence of hydrogen, the solubility is  $\approx 0.6$  wt.% at 1204 C and  $\approx 0.8$  wt.% at 1300 C. These temperatures can shift downward by as much as 80 C in the presence of the significant hydrogen contents found in high burnup PWR rods. As discussed by Chung and Kassner [7], the quench and post-quench failure thresholds decrease as the oxygen level in the beta phase increases, with  $\approx 0.7$  wt. % being a limit for ductility.

Chung and Kassner [7] showed that for unirradiated cladding slow-cooling (5 C/s) led to a higher ECR quench, post-quench ring-compression and post-quench impact failure thresholds than for fast cooling ( $\approx 100$  C/s). However, their ERC values are derived from very careful metallographic analysis that include the enhanced alpha layer growth and the oxygen-stabilized alpha regions within the prior beta regions. It would be interesting to compare fast vs. slow cooling failure thresholds based on “calculated” ECR values to see if the same trend holds true. The calculated (e.g., by CP correlations) ECR values would be lower and the beta layer predictions would be higher than measured.

Hache and Chung [19] give an excellent summary of the logic and database that were used to establish the 1204 C PCT and 17% ECR limits that appear in 10CFR50.46. In particular, the imposed limits reflect the need to maintain cladding ductility following quench to allow for the load uncertainties (e.g., due to assembly restraint and rod-to-rod interaction) during quench and to maintain a coolable core geometry following quench in the presence of hydraulic, seismic, handling and transport forces. Although the results of tests demonstrating thermal-quench survival for higher PCT and ECR values were comforting, the criteria were actually established based on post-quench ductility tests.

For all experimental studies reviewed by Hache and Chung [19] with hydrogen contents  $< 700$  wppm, the 1204 C PCT and 17% ECR criteria (as calculated by Baker-Just) proved to be conservative with respect to quench and post-quench failure thresholds. However, for unirradiated cladding with no pre-transient oxide, local regions of high hydrogen concentrations ( $\approx 2000$  wppm) were found near the necks of ballooned and burst regions. These regions were found to be brittle for ECR values  $< 17\%$ . Chung and Kassner [7] suggested that  $< 0.7$  wt. % average oxygen content in the beta layer,  $< 800$  wppm hydrogen in the beta layer and a beta layer thickness of  $300 \mu\text{m}$  would be sufficient to ensure quench and post-quench ductility. They reasoned that the cladding temperature limit corresponding to the 0.7-wt.-% oxygen would be in the range of 1200-1250 C.

## 5. Summary of Issues Regarding LOCA PCT and ECR Limits

### 5.1 Breakaway oxidation due to self-heating

Based on a comparison of the best-estimate Cathcart-Pawel and the conservative Baker-Just weight gain correlations, it appears as if the PCT limit could be raised from 1204 C to 1264 C without losing any significant safety margin with regard to breakaway oxidation.

### 5.2 Failure threshold for surviving thermal quench without fragmentation

Based on unconstrained thermal shock tests, it appears that there may be some justification for raising the PCT and/or ECR limits without risking thermal shock fragmentation during the ECCS quench. However, uncertainties regarding loads on the cladding beyond the thermal stress loads due to differential cladding contraction, suggest that one should be cautious in taking this approach. Also, criteria based on the effective beta layer thickness and oxide content of that layer (e.g., <0.7 wt. %) should be evaluated in terms of CP-calculated beta layer thickness rather than measured thickness. It is well recognized that the best-estimate models over-predict the beta layer thickness for slow-cooling (e.g.,  $\approx 5$  C/s) transients.

### 5.3 Failure threshold based on post-quench ring-compression and/or impact ductility

From the perspectives of surviving both ECCS quench and post-quench loading without the occurrence of cladding fragmentation, it is important to consider not only best-estimate calculations of weight gain and ECR, but also the effects of oxygen and hydrogen content in the effective beta layer. Based on previous studies, it appears that temperatures in the range of 1200-1250 C and ECR 17% may be adequate to ensure a reasonable safety margin to zero post-quench ductility for hydrogen contents 700 wppm. However, Zircaloy cladding regions with hydrogen contents >700 wppm may not exhibit sufficient post-quench ductility. Such high hydrogen content could be present in high burnup PWR Zircaloy-4 cladding prior to the LOCA transient; for fresh cladding it could be formed in the neck region of a ballooned and burst cladding due to steam/hydrogen that is trapped between the fuel pellets and the cladding.

## References

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