



COMPARISON BETWEEN ZIRCALOY OXIDATION IN STEAM AND AIR SURROUNDINGS

M.E. Shawkat¹, H. Hasanein¹, M. Ali², Y. Parlattan², and H. Albasha³

¹ Fuel and Fuel Channel Safety Analysis, AMEC-NSS, Toronto, Ontario, Canada

² Safety Analysis Improvement Projects, Ontario Power Generation, Pickering, Ontario, Canada

³ Nuclear Safety & Support, Bruce Power, Toronto, Ontario, Canada

ABSTRACT – The available experimental data for Zircaloy oxidation in air were reviewed. The behavior of the oxidation kinetics at different temperature ranges was described. It was shown that maintaining the oxidation kinetics within the oxide pre-breakaway region can prevent elevated sheath temperatures due to the oxidation process during postulated accidents. The available correlations to model the oxidation kinetics for pre-breakaway region were reviewed and assessed. Zircaloy-air oxidation correlation based on Leistikow-Berg data was determined to be the most suitable correlation to model pre-breakaway kinetics and it was compared to Urbanic-Heidrick correlation which is widely used for Zircaloy oxidation in steam environment. The results showed that the energy release due to the Zircaloy-steam oxidation bounds the energy released due to Zircaloy-air oxidation up to a sheath temperature referred as the “crossover temperature”. Below this temperature, the impact of Zircaloy-air oxidation on fuel sheath temperature transient can be predicted conservatively using the Urbanic-Heidrick steam correlation. The crossover temperature was calculated for isothermal sheath heating as well as transient sheath heat-up assuming three linear heating rates of 0.6, 1.0, and 1.3 K/s.

Introduction

There are many events in a nuclear power plant where the hot fuel sheath can be exposed to air such as hot-leg failure with subsequent failure of the lower head of the vessel in a Pressurized Water Reactors (PWR), fuel handling failure accidents in CANDU¹ reactors, and accidental loss of cooling in spent fuel ponds in both PWR and CANDU reactors. In these events, an exothermic reaction will take place due to Zircaloy oxidation in air leading to higher sheath temperatures.

In general, Zircaloy oxidation kinetics in air was not extensively investigated compared to the oxidation kinetics in steam. The oxidation kinetics of Zircaloy is different in air and steam surroundings. The main two differences are:

- 1- Depends on the sheath temperature, the reaction rate of Zircaloy-air oxidation can be higher than the reaction rate of Zircaloy-steam depending on the reaction kinetics, which in turn is impacted by the oxide thickness and sheath temperature (as will be discussed later).
- 2- The exothermic heat released from Zircaloy-air oxidation is about 80% higher than the heat released from Zircaloy-steam oxidation which is about 6500 kJ/kg_{Zr} (References [1] and [2]).

¹ CANDU is a registered trademark of Atomic Energy Canada Limited (AECL).

Modelling Zircaloy oxidation is important in estimating the sheath temperature transient during postulated accident. For fuel bundle heat-up in air surrounding, the total heat generated due to sheath oxidation is function of the multiplication of the above two factors. Depends on the sheath temperature, the oxidation kinetics in steam could be much faster than air so that the total heat generated from steam oxidation is larger than air oxidation although the latter has higher reaction heat. Hence, in safety analysis, if conservative results are required, depends on the expected maximum sheath temperature, Zircaloy-air oxidation may be modelled using Zircaloy-steam oxidation correlation.

The objectives of this paper is to review the available correlations for Zircaloy-air oxidation and to compare the Zircaloy oxidation kinetics in air and steam surroundings to determine the sheath temperature where up to it modelling Zircaloy-air oxidation using Zircaloy-steam oxidation correlation is conservative. This temperature is referred here as the “crossover temperature”

1. Zircaloy-air Oxidation Kinetics and Modelling Efforts

Many experimental programs have been initiated worldwide to investigate the Zircaloy-air reaction since 1949. The detailed oxidation experiments were performed under isothermal conditions where the specimens were oxidized at constant temperature for a pre-determined time. The early experimental work of Hayes and Roberson [3] used pure zirconium samples under isothermal conditions. However, Zircaloy-4 cladding samples obtained from PWR were then used in the majority of the research work starting from the work of White [4] and Leistikow et al. [5]. Air oxidation for CANDU fuel specimens (with and without appendages) were also examined experimentally at relatively low temperatures of 600 to 850°C for long oxidation times (minimum of 24 to 72 hr at 600 to 650°C and 1 to 8 hr at 700 to 850°C) [6]. Air oxidation of steam pre-oxidized CANDU samples was tested in the Institute of Nuclear Research (INR) in Romania as described in Reference [7]. Leistikow and Berg [8], Natesan and Sobbet [9], Steinbruck et al. [10], and Duriez et al. [1] investigated air oxidation of bare and pre-oxidized Zircaloy-4 PWR cladding samples where the samples were kept at constant temperatures in the range from 400°C to 1500°C. Pre-oxidation was performed in an oxygen or steam environment to create an initial oxide thickness of about 15.2 to 81.8 μm , with most of the experiments having an initial oxide thickness in the range from 20 μm to 30 μm . The kinetics of Zircaloy-air oxidation was found to be different for bare and pre-oxidized samples. In CANDU reactors, the fuel bundles are placed in the reactor core at relatively low temperature during normal operating conditions and remain well cooled inside the fuelling machine, hence, under these conditions, the initial oxide thickness at the beginning of the fuel handling accidents is small (i.e., few micrometers) which is less than the range investigated in the pre-oxidation experiments. Therefore, the oxidation kinetics of bare Zircaloy samples is more representative for Zircaloy-air oxidation of CANDU fuel elements than pre-oxidized samples.

Figure 1 shows the oxidation kinetics obtained by several researchers using initially bare Zircaloy-4 sheath samples in air at different isothermal sheath temperatures. The figure shows that the oxidation kinetics changes from slow parabolic kinetics to the faster linear kinetics due to the oxide breakaway. This transition was not observed at all sheath temperatures. In general, the Zircaloy-air oxidation kinetics can be summarized as follows:

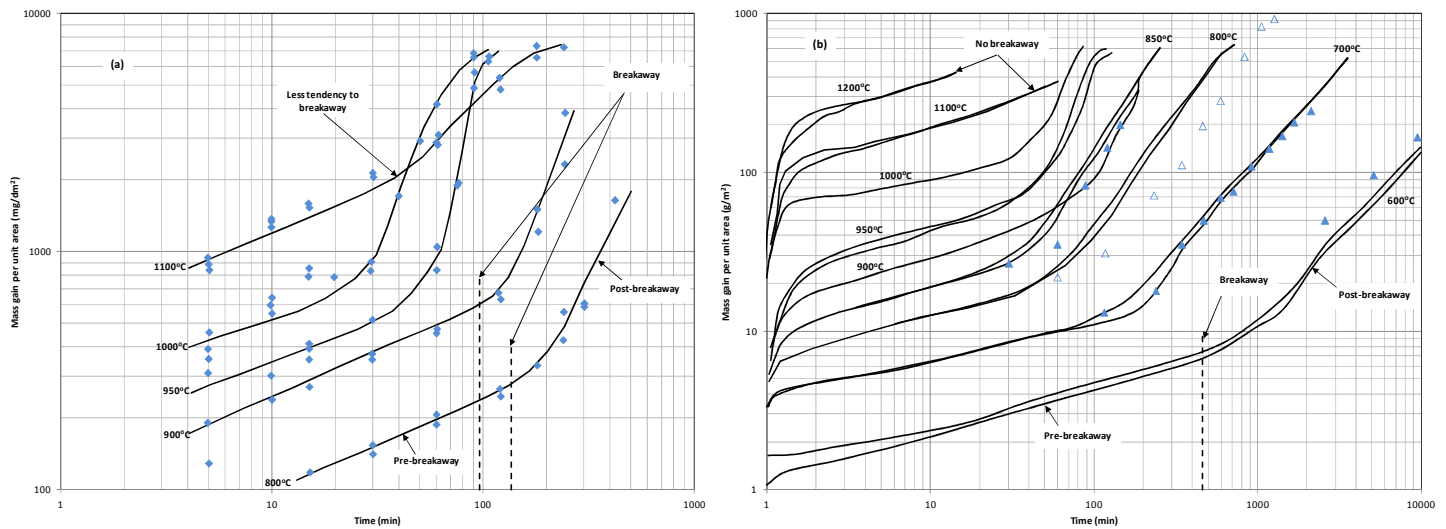


Figure 1: Experimental Zircaloy-air Oxidation Kinetics for Bare Zircaloy-4 PWR Cladding samples (a) Leistikow and Berg [8] and (b) Duriez et al. [1] (the experimental points are from ANL [9])

(a) For sheath temperatures less than about 1100 to 1200°C:

(i) Pre-breakaway region: This is the region where the oxidation reaction results in the formation of a dense columnar oxide which grows to form a protective oxide layer that decreases the rate of oxidation. This region is usually modelled using parabolic kinetics correlations.

(ii) Transition or breakaway region: As the oxide thickness grows, compressive stresses in the oxide build up, and are finally relieved by formation of cracks. Cracking occurs in the radial direction, giving direct access for the air to the metal and hence more reaction. In this reaction, the oxygen is consumed first, creating microscopic oxygen starvation. The pure nitrogen atmosphere remains, which is then able to react either with the Zircaloy itself or the alpha-Zr(O) phase or the sub-stoichiometric oxide layers forming ZrN. The transition time is a function of the sheath temperature and the oxide thickness. There are no extensive direct measurements for the ZrO₂ thickness or weight gain at breakaway. Duriez et al. [1] derived the ZrO₂ thickness at breakaway from the measured times to breakaway assuming fully dense zirconia. Duriez et al. verified his calculations by post-test metallographic where the thickness of the dense zirconia was measured at different temperatures. The verification showed that the metallography values are close to the minimum value of the calculated break-away thickness up to 900°C. For higher temperatures, the calculated thicknesses were higher than the measurements. There is still no definitive correlation form for this region; however, Coindreau et al. [11] presented a model to calculate the Zircaloy-4 weight gains per unit surface area at breakaway based on assuming that breakaway is linked with the tetragonal to monoclinic zirconia transformation. The weight gain per unit area required for transition was modelled as a function of the sheath temperature, the transformation temperature from monoclinic to tetragonal ZrO₂, and the transformation enthalpy. However, the hypothesis used to develop the above model was discarded by other researchers (Barberis [12] and Pétigny et al. [13]).

(iii) **Post-breakaway region:** As the oxide scales further grow, the already formed nitride migrates outwards where it is re-oxidized by fresh air. Due to the lower density of ZrO_2 (~5.8 g/cm³) in comparison to ZrN (~7.1 g/cm³) this reaction is associated with a significant volume mismatch leading to high compressive stresses that result in more cracks leading to self-sustained reaction. This region may be modelled using linear kinetics which is faster than the parabolic kinetics.

(b) For sheath temperatures equal to or higher than about 1100 to 1200°C:

In this temperature range, the oxidation kinetics becomes very close to the pre-breakaway region. A possible explanation is that the compressive stresses created in the oxide layer may be relieved through higher plasticity of the oxide layer or the faster creep of the metal and none or a smaller number of cracks will be formed [7]. Therefore, parabolic kinetics may be used to model the whole oxidation process in this temperature range [14].

The above review indicates that during any postulated accident that involves fuel bundles exposure to air surrounding, it would be preferable (if possible) to maintain Zircaloy-air oxidation in the pre-breakaway region where the oxidation rate is not relatively high. As the critical thickness (or weight gain) for breakaway is exceeded, the oxidation kinetics becomes linear and occurs in much faster rate which releases high oxidation energy that may result in elevated fuel and fuel sheath temperatures.

2. Time to Breakaway and Modelling Pre-breakaway Region

Since there are no definitive models to determine the critical oxide thickness for the onset of breakaway, the sheath temperature and the time to breakaway could both used as metrics to determine if Zircaloy-air oxidation is in pre- or post-breakaway regions. Table 1 summarizes the times to breakaway as obtained from different experimental datasets. The shortest time to breakaway for each examined sheath temperature was associated with Duriez et al. [1] that presents one of the most up-to-date extensive Zircaloy-air oxidation measurements. In the temperature range where the oxidation phenomenon is observable (>800°C) up to 1100°C, Table 1 shows that the average of the shortest times to breakaway is 21.2 minutes. For temperatures higher than 1100°C, the breakaway phenomenon was not observed. Hence, in sheath temperature range of 800 to 1100°C it can be concluded that Zircaloy-air oxidation is in the pre-breakaway region as long as the oxidation time did not exceed 21.2 minutes. This conclusion is conservative as it is based on isothermal temperature measurements. During accidents sheath temperature will vary with time and longer breakaway times will be needed if the sheath temperature is ramped up to any of the temperatures shown in Table 1.

Most of the available correlations that model Zircaloy-air oxidation during pre-breakaway follow the parabolic kinetics form:

$$W_{O_2} (kg_{O_2} / m^2) = K_{pO_2} (kg_{O_2} / m^2 s^{0.5}) * \sqrt{t} \quad (1)$$

where, t is the oxidation time in seconds and K_{PO_2} is the parabolic constant ($= A e^{-\frac{E/R}{T+273.15}}$), and T is the sheath temperature in Kelvin. Different values for A and E were proposed for each correlation.

Table 1: Breakaway Time for Zircaloy-air Isothermal Oxidation Experiments using Bare Zircaloy Specimens

Sheath Temperature (°C)	Breakaway time from Leistikow & Berg 1987 [8] (min.)	Breakaway time from ANL-2004 [9] (min.)	Breakaway time from Duriez et al. 2008 [1] (min.)	Shortest breakaway time (min.)
600	Not Applicable	~4133.4	460.7	460.7
700	Not Applicable	~394.8	97.7	97.7
800	~136	~359.3	27.2	27.2
850	Not Applicable	Not Applicable	17.2	17.2
900	~96.1	~96.9	19.2	19.2
950	~26	Not Applicable	18.7	18.7
1000	~22	Not Applicable	14.9	14.9
1100	~30	Not Applicable	Breakaway was not observed	30
Average breakaway time (min) from 800°C to 1100°C				21.2

The applicable temperature range of the L-B correlation is relatively wide compared to other correlations that are based on Zircaloy-4 cylindrical sheath samples.

The parabolic constant for L-B correlation was modeled by Duriez et al. [1] as:

$$K_{PO_2}(L - B) = 75.9 e^{\frac{13333.65}{T+273.15}} \quad \text{for } 700^\circ\text{C} < T < 1250^\circ\text{C} \quad (2)$$

Table 2 lists the parabolic constant models for pre-breakaway Zircaloy-Air oxidation correlations available in literature and the corresponding applicable sheath temperature ranges. The correlation based on Leistikow and Berg (L-B) data [8] is determined to be the most suitable correlation to represent Zircaloy-air oxidation in the pre-breakaway region for the following main reasons:

- 1- Experimental data of Leistikow and Berg were carefully collected using a special procedure to suppress the temperature peaking that arises when the specimens are first subjected to air flow and hence causes additional weight.
- 2- The specimens used by Leistikow and Berg were not pre-heated in argon (or helium) atmosphere up to the nominal temperature which eliminates any weight gain due to argon diffusion at elevated temperatures or the moisture that may present in the argon.
- 3- The applicable temperature range of the L-B correlation is relatively wide compared to other correlations that are based on Zircaloy-4 cylindrical cladding samples.

The parabolic constant for L-B correlation was modeled by Duriez et al. [1] as:

$$K_{PO_2}(L - B) = 75.9 e^{\frac{13333.65}{T+273.15}} \quad \text{for } 700^\circ\text{C} < T < 1250^\circ\text{C} \quad (2)$$

3. Comparison between Pre-breakaway Zircaloy-air Oxidation and Zircaloy-steam Oxidation Kinetics

In this section the Zircaloy-air oxidation correlations listed in Table 2 (including L-B) are compared to Urbanic -Heidrick oxidation correlation (U-H) [15] that is widely used to model Zircaloy-steam oxidation.

Table 2: Zircaloy-air Oxidation Correlations for the Pre-Breakaway Region

Experimental program	K_{PO_2} in ($\text{kg}_{O_2}/\text{m}^2.\text{s}^{0.5}$) [T is the temp. in Kelvin]	Experimental sheath temperature range ($^{\circ}\text{C}$)	Notes
Hayes & Roberson 1949 [3]	$0.3391 \exp(-6879.15/T)$	425 to 900	The correlation is given in Reference [1]
Benjamin et al. 1979 [16]	$0.3391 \exp(-6879.718/T)$ for $T \leq 1193$ K $75.895 \exp(-13334.17/T)$ for $1193 < T \leq 1428$ K $2.49 \exp(-7316.81/T)$ for $T > 1428$ K	~ 510 to 1610	The correlation was based on the data given in References [3], [4], and [5], which can be observed by comparing the low and intermediate temp. correlations to Hayes & Roberson and Leistikow & Berg, respectively.
Sailor et al. 1987 [17] (NUREG-2)	$175.784 \exp(-14242.577/T)$	~810 to 1160	
Leistikow & Berg 1987 [8]	$75.9 \exp(-13333.65/T)$	800 to 1100	The correlation is given in Reference [1], where it was indicated that the correlation can be used in temperature range of 700°C to 1250°C . However, the Leistikow and Berg experiments [8] were performed over a temperature range of 800°C to 1100°C .
Powers et al. 1994 [18] (NUREG-1) as implemented in ATHLET-CD code (as inferred from Reference [14])	$1.1367 \exp(-7815/T)$ for $T < 1300$ K $9907227.991 \exp(-28590/T)$ for $1300 \leq T \leq 1400$ K $2.49 \exp(-7315/T)$ for $T > 1400$ K	~ 510 to 1610	The correlation was based on the data given in References [16] and [4]. The interpolation was obtained from Table 1 in Reference [14].
Natesan and Soppet [9] (ANL-2004)	$2.84605 \exp(-9310/T)$	400 to 900	
Duriez et al. 2008 [1]	$9.916 \exp(-10752.79/T)$ for $873 < T \leq 1273$ K $30000 \exp(-20723.68/T)$ for $1273 < T < 1473$ K	600 to 1200	A factor of 2 was multiplied to the presented correlations as compared to Ref. [1] (i.e., Equations 8 and 9 in [1]). The corresponding author of Ref. [1] confirmed that factor of 2 was missed in the original equations.

U-H correlation is based on several isothermal experiments using CANDU type fuel sheaths. In U-H correlation, the mass gain per unit surface area due to oxygen diffusion (W_{O_2}) can be modelled using parabolic kinetics with parabolic reaction rate constant of²:

$$K_{p_{O_2}}(U - H) = \begin{cases} 0.532 e^{\frac{6796.5}{T+273.15}} & \text{for } T \leq 1580^{\circ}\text{C} \\ 2.0894 e^{\frac{8011}{T+273.15}} & \text{for } 1580^{\circ}\text{C} < T \leq 1850^{\circ}\text{C} \end{cases} \quad (3)$$

The comparison is shown in Figure 2 where some of correlations were extended beyond their experimental range until they intersect with the U-H correlation. The figure shows that the parabolic constant of the U-H correlation bounds all the air oxidation correlations up to a temperature range

² In Urbanic and Heidrick [15] the correlation is presented for the ZrO_2 thickness and was converted to weight gain using Equation (6)

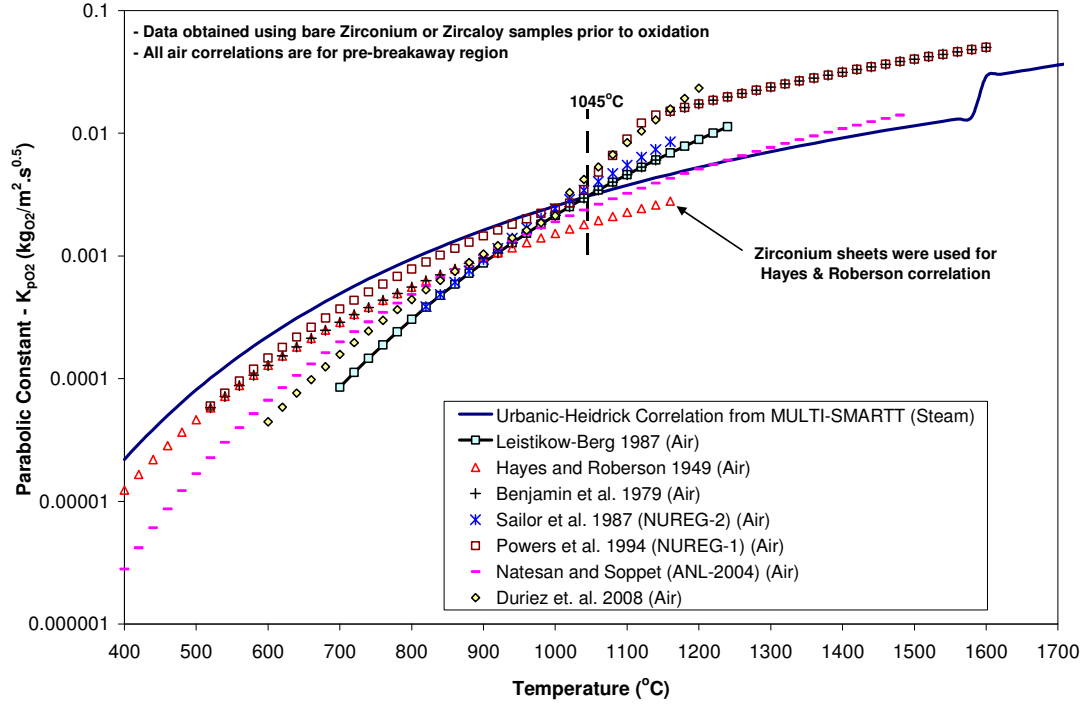


Figure 2: Comparison between the Parabolic Constant of U-H and L-B Correlations

from about 1000°C to 1200°C. L-B and U-H correlation intersects at 1045°C. Beyond this temperature, the oxidation kinetics based on L-B Zircaloy-Air correlation is faster than that based on U-H Zircaloy-Steam oxidation. The most recent correlation of Duriez et al. [1] developed in 2008 is close to L-B.

4. Crossover Temperature between L-B and U-H Correlation

During fuel heatup in air or steam, the fuel element energy conservation equation shows that fuel temperature variation is mainly function of the integration of both; the bundle power (decay power) and the heat rate generated due to oxidation ($Q_{\text{oxidation}}$). The decay power is independent on the oxidation environment; therefore, the integration of $Q_{\text{oxidation}}$ marks the impact of oxidation environment on fuel temperature variation. To compare between the impact of steam and air oxidation on the fuel temperature, new parameter known as the “crossover temperature” was defined as the sheath temperature where the cumulative oxidation energy released ($E_{\text{oxidation}}$) due to Zircaloy-air oxidation estimated using L-B first exceeds that estimated from Zircaloy-steam oxidation using U-H. For all the sheath temperatures up to the crossover temperature, the fuel sheath temperature transient in air will be conservatively estimated if U-H steam oxidation correlation is used instead of a L-B oxidation correlation (or, in general, any adequate Zircaloy-air oxidation correlation). The cumulative oxidation energy released ($E_{\text{oxidation}}$) represents the integral of $Q_{\text{oxidation}}$ during the transient and is calculated by numerically integrating $Q_{\text{oxidation}}$ over the time using the trapezoidal approach as follows:

$$E_{\text{oxidation}} (kJ) = \int Q_{\text{oxidation}} dt = \sum \left(\frac{Q_{\text{oxidation}}|_t + Q_{\text{oxidation}}|_{t+\Delta t}}{2} \right) \Delta t \quad (4)$$

$E_{\text{oxidation}}$ is main term in the fuel element energy conservation equation that determines the contribution of the oxidation to the predicted sheath temperature during the transient. The heat rate generated by oxidation is modelled as:

$$Q_{\text{oxidation}} (kW) = RH * \left(\rho_{\text{ZrO}_2} A_s \frac{d\delta_{\text{ZrO}_2}}{dt} \right) * X_{\text{ZrO}_2 \rightarrow \text{Zr}} \quad (5)$$

where, RH= Reaction heat of Zircaloy oxidation = 1.8* 6500 kJ/kg_{Zr} (for air oxidation) [1] and 6500 kJ/kg_{Zr} (for steam oxidation) [2]

ρ_{ZrO_2} = ZrO₂ mass density = 5800 kg/m³ [19]

A_s = Bundle oxidation surface area = 0.73 m² (37-element fuel bundle was assumed)

$d\delta_{\text{ZrO}_2}/dt$ = Rate of ZrO₂ growth calculated numerically as= $\frac{\delta_{\text{ZrO}_2}|_{t+\Delta t} - \delta_{\text{ZrO}_2}|_t}{\Delta t}$

$X_{\text{ZrO}_2 \rightarrow \text{Zr}}$ = Mass conversion factor from ZrO₂ to Zr. This factor was calculated based on the Zircaloy oxidation chemical reaction (either in steam or air):



Hence,

$$X_{\text{ZrO}_2 \rightarrow \text{Zr}} = \frac{\text{Mass of Zr}}{\text{Mass of ZrO}_2} = \frac{\text{no. of Zr moles}}{\text{no. of ZrO}_2 \text{ moles}} \frac{\text{Molecular weight of Zr}}{\text{Molecular weight of ZrO}_2} = \frac{1 \times 91.224}{1 \times (32 + 91.224)} = 0.7403 \frac{\text{kg}_{\text{Zr}}}{\text{kg}_{\text{ZrO}_2}}$$

The ZrO₂ thickness (δ_{ZrO_2}) equivalent to W_{O_2} was obtained by converting the mass gain to reacted Zr thickness (δ_{Zr}) and then use the Pilling-Bedworth ratio to convert the Zr thickness to ZrO₂ thickness

$$\delta_{\text{ZrO}_2} = (\delta_{\text{Zr}})_{PB} = \left(\frac{W_{\text{O}_2} X_{\text{O}_2 \rightarrow \text{Zr}}}{\rho_{\text{Zr}}} \right)_{PB} \quad (6)$$

where, PB = Pilling-Bedworth ratio = $\delta_{\text{ZrO}_2}/\delta_{\text{Zr}} = 1.56$ (Reference [20])

$X_{\text{O}_2 \rightarrow \text{Zr}}$ = Mass conversion factor from O₂ to Zr = 2.85075 kg_{Zr}/kg_{O2} (obtained similar to $X_{\text{ZrO}_2 \rightarrow \text{Zr}}$)

ρ_{Zr} = 6570 kg/m³ [19]

L-B and U-H are both isothermal correlations and to be used for a known temperature transient the weight gain was discretized assuming constant temperature over each time step (Δt) as follows:

$$(W_{\text{O}_2})|_{t+\Delta t} = \sqrt{(W_{\text{O}_2})^2|_t + K_{\text{PO}_2}^2 \Delta t} \quad (7)$$

where, $W_{\text{O}_2}|_t$ and $W_{\text{O}_2}|_{t+\Delta t}$ are the mass gain per unit surface area at the beginning and the end of the time step, respectively. Equation (7) is applicable for isothermal conditions as well as temperature transient conditions. Small time step of 0.1 seconds was used in this analysis.

The crossover temperatures were calculated for isothermal conditions (0.0 K/s) as well as for three linear heating rates of 0.6, 1.0, and 1.3 K/s starting from an initial sheath temperature of 100°C assuming an initial ZrO₂ thickness of 2 µm.

Figure 3 shows $E_{\text{oxidation}}$ as a function of time for the three constant temperatures of 800°C, 908°C, and 1100°C. In general, at constant temperature, $E_{\text{oxidation}}$ rapidly increases at the beginning of oxidation

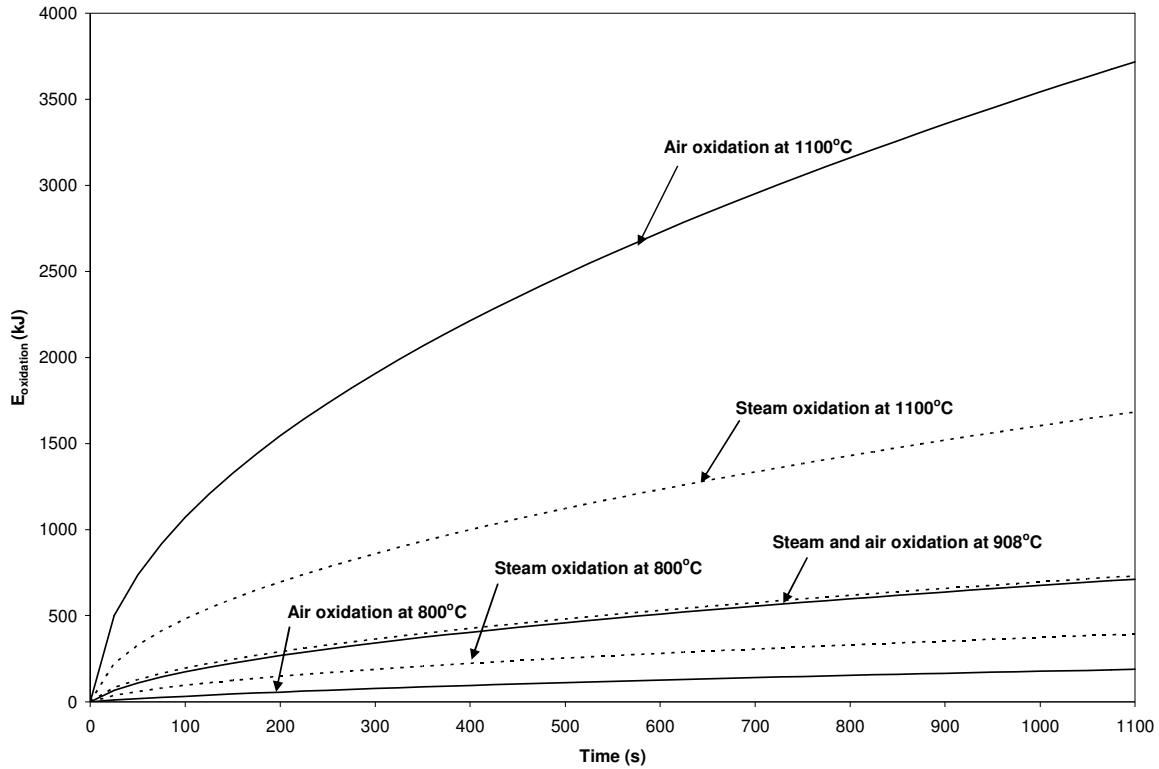


Figure 3: Comparison between the Cumulative Oxidation Energy using L-B and U-H under Isothermal Temperatures

and then the slope of the curve decreases with time due to the formation of the protective oxide layer. For a sheath temperature of 800°C, $E_{\text{oxidation}}$ due to steam oxidation is higher than that due to air oxidation. As the sheath temperature is increased to 908°C, $E_{\text{oxidation}}$ due to steam oxidation becomes almost equal to that for air oxidation. For further increase in the sheath temperature, $E_{\text{oxidation}}$ due to air oxidation becomes higher than that due to steam oxidation. Therefore, 908°C is considered the crossover temperature under isothermal heating.

Figure 4 shows the variation of $E_{\text{oxidation}}$ with the sheath temperature under temperature ramping conditions for heating rate of 1.0 K/s. Similar trends were obtained for heating rates of 0.6 K/s and 1.3 K/s. Figure 5 shows the estimated crossover temperatures as function of the heating rate for all the investigated cases. In general, the crossover temperature increases as the heating rate is increased. Under the examined temperature ramping conditions, the increase in the crossover temperature is relatively small (from 988°C at 0.6 K/s to 994°C at 1.3 K/s).

5. Conclusions

The available experimental data and correlations for Zircaloy oxidation in air surrounding were reviewed. The majority of the available experiments were conducted under isothermal conditions. The kinetics of the Zircaloy-air oxidation was found to go through three stages for sheath temperatures less than about 1200°C: (i) pre-breakaway oxidation, (ii) breakaway transition, and (iii) post-breakaway oxidation. For sheath temperatures higher than about 1200°C, no breakaway

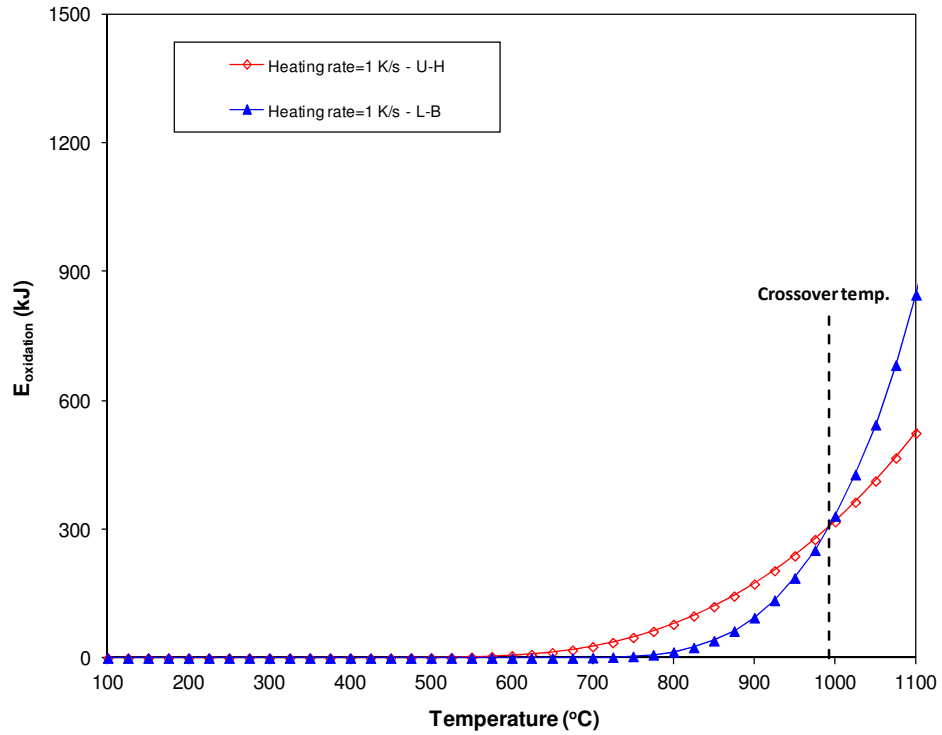


Figure 4: Comparison between the Cumulative Oxidation Energy using L-B and U-H for Heating Rate 1.0 K/s

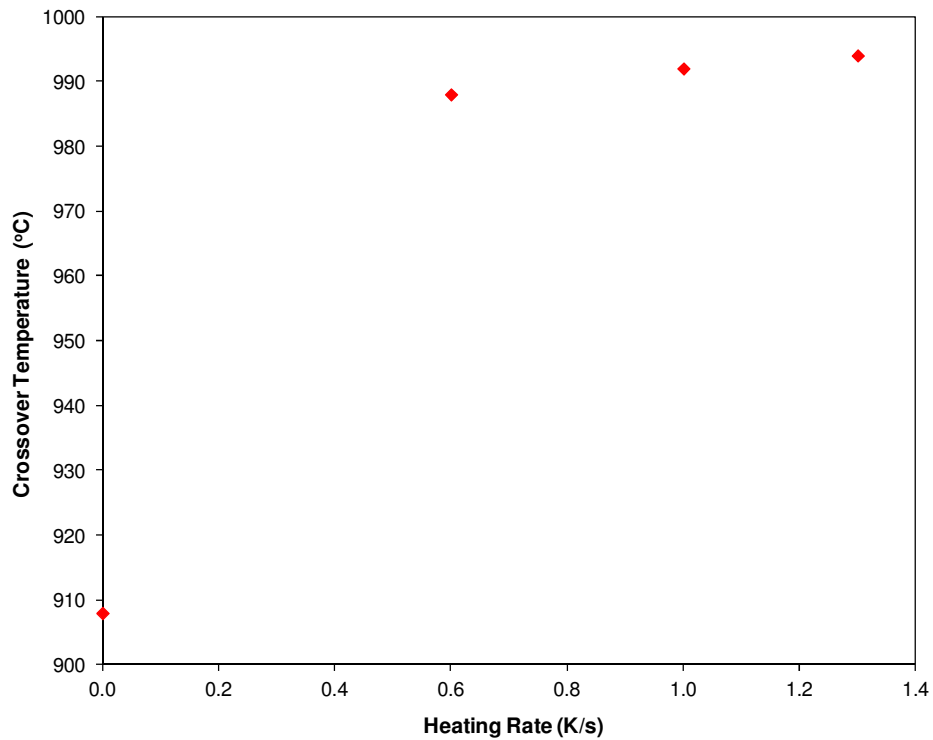


Figure 5: Crossover Temperature Variation with the Examined Heating Rates

transition was observed. Examination of the Zircaloy-air experimental data revealed that the best estimate of the shortest time required for the oxide breakaway is about 21.2 minutes considering available isothermal data below 1200°C. During postulated accidents where fuel bundles are exposed to air, it is preferred to maintain Zircaloy-air oxidation within the pre-breakaway region to avoid elevated fuel sheath temperatures relative to post-breakaway region. The correlation based on Leistikow-Berg data was determined to be the most suitable correlation among the reviewed correlations and it was compared to the Urbanic-Heidrick correlation that is widely used in assessing Zircaloy-steam oxidation. For each correlation, the cumulative oxidation energy was estimated as a function of the sheath temperature. Cumulative oxidation energy is the main term in the fuel element energy conservation equation that determines the contribution of the oxidation to the predicted sheath temperature during the transient. The comparison was conducted under isothermal and transient conditions (i.e., heating rates of 0.0, 0.6, 1.0, and 1.3 K/s). The comparison results showed that the cumulative oxidation energy from Zircaloy-steam oxidation bounds Zircaloy-air oxidation under isothermal and transient conditions up to a specific sheath temperature referred here as the “crossover temperature”. Below this temperature, the impact of Zircaloy-air oxidation on fuel sheath temperature transient can be predicted conservatively using the Urbanic-Heidrick steam correlation. The crossover temperature is function of the heating rate and it generally increases as the heating rate is increased. For the examined heating rates, the crossover temperature varied from 908°C at 0.0 K/s to 994°C at 1.3 K/s.

6. References

- [1] C. Duriez, T. Dupont, B. Schmet, and F. Enoch, "Zircaloy-4 and M5 High Temperature Oxidation and Nitriding in Air", *Journal of Nuclear Materials*, Vol. 380, 2008, pp. 30-45.
- [2] “Phenomenology-Based Matrix of Tests for use in the Validation of Fuel and Fuel Channel Thermal-Mechanical Behaviour Codes Employed in CANDU Safety Analysis”, Ontario Hydro, FC09, N-06631.01-P965094, N-08131.02-P, also AECL RC-1773, Revision 01, 1998, July.
- [3] E.T. Hayes and A.H. Roberson, “Some Effects of Heating Zirconium in Air, oxygen, and Nitrogen”, *J. Electrochem. Soc.*, Vol. 96, 1949, pp. 142-151.
- [4] J.H. White, “Physico-Chemical studies of Clad UO₂ in Potential Meltdown Environments”, reported in AEC Fuels and Materials Development Program, Progress Report No. 67, GEMP-67, General Electric Co., 1967, pp. 151-165.
- [5] S. Leistikow, H.V. Berg, D. Jennert, R. Kraft, G. Schanz, “Study on High Temperature Steam Oxidation of Zircaloy-4 Cladding Tubes”, *Nuclear Safety Project Second Semi-annual Report*, KfK-2262, Karlsruhe, 1976, pp. 233-260.
- [6] E.T.C. Ho, “Oxidation and Biaxial Deformation Behaviour of CANDU Reactor Zircaloy-4 Fuel Sheathing in Air and Steam Environments in the Temperature Range 600 to 850°C”, *CANDU Owners Group*, Report No. COG-90-204, 1991, March.
- [7] C. Duriez, M. Steinbrück, D. Ohai, T. Meleg, J. Birchley, T. Haste, "Separate-Effect Tests on Zirconium Cladding Degradation in Air Ingress Situations", *Nuclear Engineering and Design*, Vol. 239, 2009, pp. 244-253.

- [8] S. Leistikow and H.V. Berg, "Investigation under Nuclear Safety Aspects of Zircaloy-4 Oxidation Kinetics at High temperatures in Air", Proceeding of the 2nd Workshop of German and Polish Research on High Temperature Corrosion of Metals, Julich, Germany, 1987 December 2-4.
- [9] K. Natesan and W.K. Soppet, "Air Oxidation Kinetics for Zr-Based Alloys", Argonne National Laboratory, ANL-03/32, NUREG/CR-6846, 2004, June.
- [10] M. Steinbrück, U. Stegmaier, and T. Ziegler, "Prototypical Experiments on Air Oxidation of Zircaloy-4 at High Temperatures", Forschungszentrum Karlsruhe, FZKA 7257, 2007, January.
- [11] O. Coindreau, C. Duriez, and S. Ederli, "Air oxidation of Zircaloy-4 in the 6000-1000°C temperature range: Modeling for ASTEC code application", *Journal of Nuclear Materials*, Vol. 405, 2010, pp. 207-215.
- [12] P. Barberis, "Zirconia Powders and Zircaloy oxide films: tetragonal phase evolution during 400°C autoclave tests", *Journal of Nuclear Materials*, Vol. 226, 1995, pp. 34-43.
- [13] N. Pétigny, P. Barberis, C. Lemaignan, C. Valot, and M. Lallemant, "In situ XRD analysis of the oxide layers formed by oxidation at 743 K on Zircaloy 4 and Zr-1Nb", *Journal of Nuclear Materials*, Vol. 280, 2000, pp. 318-330.
- [14] C. Bals, E. Beuzet, J. Birchley, O. Coindreau, S. Ederli, T. Haste, T. Hollands, M.K. Koch, J.-S. Iamy, and K. Tramauer, "Modelling of Accelerated Cladding Degradation in Air for Severe Accident Codes", Paper no. 2-4, 3rd European Review Meeting on Severe Accident Research (ERMSAR-2008), Nessebar, Bulgaria, 2008 September 23-25.
- [15] V.F. Urbanic and T.R. Heidrick, "High-Temperature Oxidation of Zircaloy-2 and Zircaloy-4 in Steam", *Journal of Nuclear Materials*, Vol. 75, 1978, pp.251-261.
- [16] A.S. Benjamin, D.J. McCloskey, D.A. Powers, and S.A. Dupree, "Spent Fuel Heatup Following Loss of Water During Storage", Sandia Laboratories SAND77-1371, NUREG/CR-0649, 1979, March.
- [17] V.L. Sailor, K.R. Perkins, and J.R. Weeks, "Sever Accidents in Spent Fuel Pools in Support of Generic Issue 82", Brookhaven National Laboratory, NUREG-4982, 1987, June.
- [18] D.A. Powers, L.N. Kmetyk, R.C. Schmidt, "Review of the Technical Issues of Air Ingression during Severe reactor Accidents", Sandia Laboratories, SAND94-0731, NUREG/CR-6218, 1994, September.
- [19] "VOLUME 4: MATPRO - A Library of Materials Properties for Light Water-Reactor Accident Analysis", Idaho National Engineering and International Laboratory, Volume 4, Revision 2.2, INEEL/EXT-02-00589, 2003, October.
- [20] K.E. Locke, "SMARTT: A Computer Code to Predict Transient Fuel and Pressure Tube Temperature Gradient under Asymmetric Coolant Conditions", Ontario Hydro, Design and development Division-Generation, Nuclear Studies & Safety Department, Report No. 86007, 1987, March.