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Oxidation, Embrittlement, and Growth of TREAT Zircaloy-3 Cladding

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Additional information is available at the end of the chapter

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Abstract

This chapter analyzes the effects of oxidation, embrittlement, and cladding growth on the Zircaloy-3 alloy used for 25 mil thick TREAT fuel assembly cladding. The fuel cladding is a protective shell which is used to prevent damage to the enclosed fuel. Therefore, its integrity is important to guarantee this protection. The above three factors which can affect the Zircaloy-3 cladding are considered in this chapter and investigated. Limits to operation are determined. The oxidation of Zircaloy-3 in air is of interest to air-cooled reactors and Zircaloy-2 and 4 for accidents in fuel storage pools. The temperature range of interest is from room temperature where the fuel is stored for long periods of time, through the temperature range encountered in normal operation (400 to 600°C) to the highest temperatures which are possible in extreme accident situations. This temperature range is considered in this chapter to be from room temperature to 1200°C.

Keywords: cladding, zircaloy, oxidation, embrittlement, metal growth

1. Introduction

This chapter describes the corrosion rate of Zirconium-2, 3, and 4 in air. Zircaloy-2 and 4 are used to clad fuel for all commercial power reactors. The Kendall Zircaloy-2 oxidation correlation is derived based on the well-known physically justified Arrhenius equation using legacy rate data at 500, 600, and 700°C. Additional data obtained by several other authors have shown that this correlation can be extended so that it adequately covers the range of 200 to 1100°C. This correlation also bounds the oxidation rate of Zircaloy-3, which is used to clad the fuel in the TREAT reactor. Zircaloy-4 rates are seen to be higher than the Zircaloy-2 correlation. Zircaloy-3 rates are seen to be lower than the Zircaloy-2 correlation.

loy-2 rates are higher than the Zircaloy-3 rates. The Zircaloy-2 correlation is verified for Zircaloy-3 by comparison to oxide thickness measurement on Zircaloy-3 coupons oxidized in air for different time periods in the temperature range of 500 to 1100°C: many coupons proceeded to disintegration. Although the latter samples still had a metal layer, oxygen incursion into the metal grain boundaries caused the metal to become brittle and crack like rust. The Kendall correlation is shown to adequately describe the behavior of these samples over the entire range 500 to 1100°C. Maximum oxide limit of 15.52 mils growth for TREAT cladding was determined from these data to ensure that the fuel assemblies could still be removed without disintegration.

The TREAT reactor, a graphite-moderated thermal reactor, is designed primarily for operation in the transient or pulsed mode for destructive testing of prototypic fast reactor fuel pins. It is designed conservatively to produce a pulse with a thermal neutron fluence of at least 3.5×10^{15} neutrons/cm² averaged over the core. The operating TREAT core temperature limit at the peak is 600°C.

The standard TREAT fuel assembly consists of upper and lower graphite reflector sections and a central section of uranium oxide-bearing graphite fuel. The fuel section is 4 ft long and contains six fuel blocks, each 8 in. long and 3.96 in. square with chamfered corners. The reactor fuel blocks consist of small particles (mean size, 10 microns) of fully enriched ²³⁵U dispersed in a graphite-carbon matrix. The carbon-to-uranium U²³⁵ atom ratio is nominally 10,000:1. The graphite-carbon-uranium blocks are sealed within evacuated Zircaloy-3 cans.

Zirconium alloys are used for cladding in all commercial power thermal reactors because of the high corrosion resistance, low cross section for thermal neutrons, and high temperature capability. As shown later in this chapter, Zircaloy-3 (Zr-3) is more corrosion resistant in air than either Zr-2 or Zr-4 and was used to clad the TREAT fuel. In low-temperature reactors such as TRIGAs, aluminum can be used. Since TREAT has a very thermalized spectrum, the low cross section and high temperature capability were the reasons Zr-3 was used.

The compositions of the common zirconium alloys are listed in **Table 1** (Gibbons [1], Blanchard [2] for Zr-2, Zr-4, and Alloy Digest [3] for Zr-3). Zr-3 has much less zinc than either Zr-2 or Zr-4.

Alloy	Zr	Sn	Fe	Cr	Ni	Nb	O	C	N	Hf
Zr-2	98.20	1.50	0.12	0.10	0.05	–	0.13	–	–	–
Zr-4	98.20	1.30	0.22	0.10	–	–	0.13	–	–	–
Zr-3	99.42–99.22	0.2–0.3	0.2–0.3	0.05	0.05	–	–	0.05	0.01	0.02

Table 1. Composition percentages of commercial Zirconium alloys (w/o).

A considerable amount of research has been carried out in investigating the oxidation of zirconium alloys used in different environments. The early research was carried out on Zircaloy-2 and the later work was carried out on Zircaloy-4. The recent oxidation research has been carried out because of concern about loss of cooling water from spent fuel pools where

temperatures range from 300 to 600°C. Natesan [4] in 2004 conducted air oxidation tests on unirradiated Zircaloy-4 cladding starting with a 25 to 30 μm (1 mil) oxide layer representative of the current inventory of spent fuel discharged after a medium or high level of fuel burnup. Temperatures were in the range of 300–600°C, which is representative of cladding heat up in the event of a partial or full draining of spent fuel pool coolant. Ji Min Lee [5] in 2012 investigated the oxidation of Zircaloy-4 under transient conditions from 500 to 800°C. Duriez [6] in 2009 summarized results of several studies comparing them in terms of kinetics and oxide scale structure and composition. Steinbrück [7] in 2009 studied the mechanism of the reaction between Zircaloy-4 and air at temperatures from 800 to 1500°C. Both of these studies considered pre-oxidized metal. Beuzet [8] in 2009 used existing correlations to simulate the zirconia scale growth under air atmosphere in the MAAP4.07 Severe Accident code. Duriez [9] in 2008 studied the degradation of Zircaloy-4 and M5 cladding tubes in air at high temperature by thermo-gravimetric analysis, in isothermal conditions, from 600 to 1200°C. Steinbrück [10] in 2007 conducted experiments on the reaction between Zircaloy-4 and air under mixed air (nitrogen) steam atmospheres and pre-oxidation conditions for severe nuclear reactor accident temperatures 800–1500°C. The earlier Zircaloy-2 and 3 work is described in the next section.

2. Oxidation characteristics of Zircaloy-3 cladding

The temperature range which might be encountered for the evaluation of the effects of oxidation on the Zircaloy-3 cladding for the TREAT fuel is from room temperature, approximately 25°C, to 1200°C. Extremely unlikely accidents cause temperature to approach 1200°C. Normal reactor operation restricts the maximum temperature to 600°C. The design basis reactivity insertion accident must not cause the cladding to exceed an equilibrium temperature of 820°C. During typical reactor operations, the cladding is below 600°C in a transient and near room temperature the rest of the time. So, the corrosion which occurs in all these temperature range is of interest.

Oxidation rate data in air have been obtained on zirconium, Zircaloy-2, and Zircaloy-4. Limited rates have been measured for Zircaloy-3, but rates are lower than Zircaloy-2. Conservatively, the data obtained by Kendall [11] on Zircaloy-2 are used to represent the rates of Zircaloy-3. Zircaloy-4 rates are higher. The following discussion presents the characteristics of the oxidation of zirconium and the above alloys in the temperature range of interest (25 to 820°C).

2.1. Zirconium oxidation

Lustman [12] summarized the oxidation rates of zirconium in air, oxygen, and nitrogen. The reaction rate of zirconium is higher with air than with oxygen or nitrogen. Lustman explains this by postulating that nitrogen dissolves in ZrO_2 ; since nitrogen is quadrivalent, defects would be created in the oxygen ion lattice, thus permitting a higher rate of diffusion of oxygen through ZrO_2 .

Phalnikar [13] studied the oxidation behavior of graphite-melted Bureau of Mines zirconium in air from 400 to 1200°C. Both oxygen and nitrogen enter into the reaction, and for tempera-

tures below 1050°C an outer white or buff monoclinic scale of ZrO_2 forms in addition to an inner black scale of monoclinic and tetragonal ZrO_2 , cubic ZrN , voids, and possibly dissolved nitrogen in the metal [12]. The outer white layer does not form immediately, but requires a definite time to nucleate. At 400°C, this time is 100 hours, whereas at 1300°C only 5 min is required [13]. The appearance of the white scale layer is an indication of an increased rate of reaction at low, but not at, high temperatures. A parabolic relation between weight gain and time occurs before the formation of the white outer scale.

The oxidation buildup is nearly linear with time on a log log plot, indicating a power relation between weight gain and time. The curves for 800°C and below all have a significant bend in them, indicating a change from a low reaction rate regime to a much higher one at later time. The change is referred to as the regime transition. The post-transition regime is a linear relation and the reaction rate is much higher than the pre-transition regime. Reactions at temperatures of 900°C and above do not exhibit this bend because of a change in the zirconium crystal structure from the alpha phase to the beta phase which occurs at 862°C [14].

2.2. Oxidation rates of Zircaloy-2

Kendall [11] measured the corrosion rates of sponge zirconium and Zircaloy-2 in dry air at 500, 600, and 700°C. Consistent with the previous discussion, he states that the reaction proceeds in two stages: initially the rate decreases with exposure time, approximating a cubic relationship. After sufficient time of exposure (after transition), the rate becomes a constant independent of time.

TREAT fuel was built in 1958 and its cladding oxidation rate estimates were based on the alloy research of Kendall [11]. Kendall measured the reaction rates on many different samples for different air flow rates, metal geometries, cold working, annealing, and at three different temperatures, 500, 600, and 700°C. He concluded temperature and metal composition are the important parameters which determine the reaction rate. **Figure 1** illustrates the uncertainty in the measurements [11].

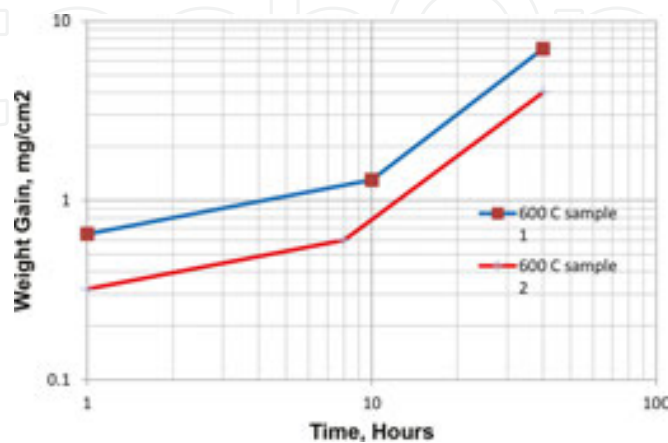


Figure 1. Weight gain of Zircaloy-2 at 600°C.

The two oxide growth measurements in **Figure 1** are for two samples cut from the same sheet and exposed to the same environment at 600°C. Oxidation growth for the other samples run at 600°C fell within these two extremes. Since the curves are almost parallel, the data obtained for each temperature were averaged to produce a single curve for each temperature. The averaged results are included in **Table 2** for Zircaloy-2 for the three different temperatures.

500°C		600°C		700°C	
Time	Wt. Gain	Time	Wt. Gain	Time	Wt. Gain
10	0.36	2	0.59	Not measured	
30	0.56	6	0.93	Not measured	
200	2.64	10	1.29	4	3.68
500	5.92	40	5.32	9	8.24

Time at Temperature (hours), Weight Gain (mg/cm²).

Table 2. Oxidation gains Zircaloy-2

Although it appears from the table that very few data points were obtained and only two data points at 700°C, there was a large amount of data obtained for each data point presented and then they were averaged to produce the few results shown. In fact, the two 700°C points represent the average of about 10 data points each. Plots of these data are shown in **Figure 2** in log-log coordinates. As stated previously, the bend in the 500 and 600°C curves is referred to as the transition point between the initial (parabolic to cubic) reaction regime and the post transition linear reaction rate regime.

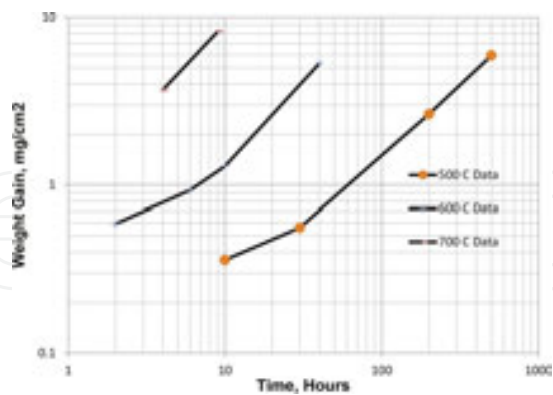


Figure 2. Averaged weight gain of Zircaloy-2, specimens at 500, 600, and 700°C [11].

Since the data appear as straight lines in each regime, the weight gain, M , in each section can be represented by the product of the rate constant k and the time t .

$$M^n = kt \tag{1}$$

The values of n and k for each straight line section of a plot can be determined by first taking the log of this equation and evaluating it at two data points and subtracting one from the other to obtain

$$n * (\log(M_2) - \log(M_1)) = (\log(t_2) - \log(t_1)); \text{is rearranged to;}$$
$$n * \log(M_2 / M_1) = \log(t_2 / t_1)$$

(2)

so that

$$n = \frac{\log(t_2 / t_1)}{\log(M_2 / M_1)} \text{ and } k = \frac{M_1^n}{t_1}$$

(3)

Kendall’s Zirconium constants [11] and this work’s slightly improved constants for Zircaloy-2 are presented in Table 2. Kendall [11] states that, “From the shapes of the curves and the calculated values of n_1 and n_2 above, it is evident that the same reactions control the rates at the different temperatures and that the reaction of Zircaloy-2 and zirconium are determined by the same mechanism. Variations in the values of n and k are then due to experimental error. A major source of error results from spalling of the reaction products. The reaction products of Zircaloy-2 are adherent and tough while those of zirconium are fragile and flaky.” Kendall concludes that the exponents for the pre-transition regime are $n_1 = 2.58$ and linear, $n_2 = 1$, for the post-transition regime (**Table 3**).

Initial Reaction		After Transition		
Temperature, °C	k_1 (mg/cm ²) ⁿ /hour	n_2	k_2 (mg/cm ²) ⁿ /hour	n_2
<u>Zircaloy-2</u>				
500	7.43×10^{-3}	2.49	1.25×10^{-2}	1.13
600	1.34×10^{-1}	2.41	1.31×10^{-1}	0.98
700	Not determined	–	9.18×10^{-1}	1.01
<u>Zirconium</u>				
500	3.34×10^{-3}	2.64	3.52×10^{-3}	1.14
600	5.62×10^{-2}	2.41	(2.57×10^{-2})	1.11*
700	8.93×10^{-1}	2.82	1.57×10^{-1}	1.07

*Average of values at 500 and 700°C; data at 600°C inadequate for direct determination because of sample failure. k_2 calculated from this average value. (Units of w are mg/cm² and unit of t is hours for these values of k_1 and k_2 .)

Table 3. Reaction constants.

The rate coefficients for Zircaloy-2 are plotted in **Figure 3** and the logarithms are seen to be linear with $1/T$, which shows that an Arrhenius equation can be used to fit these data.

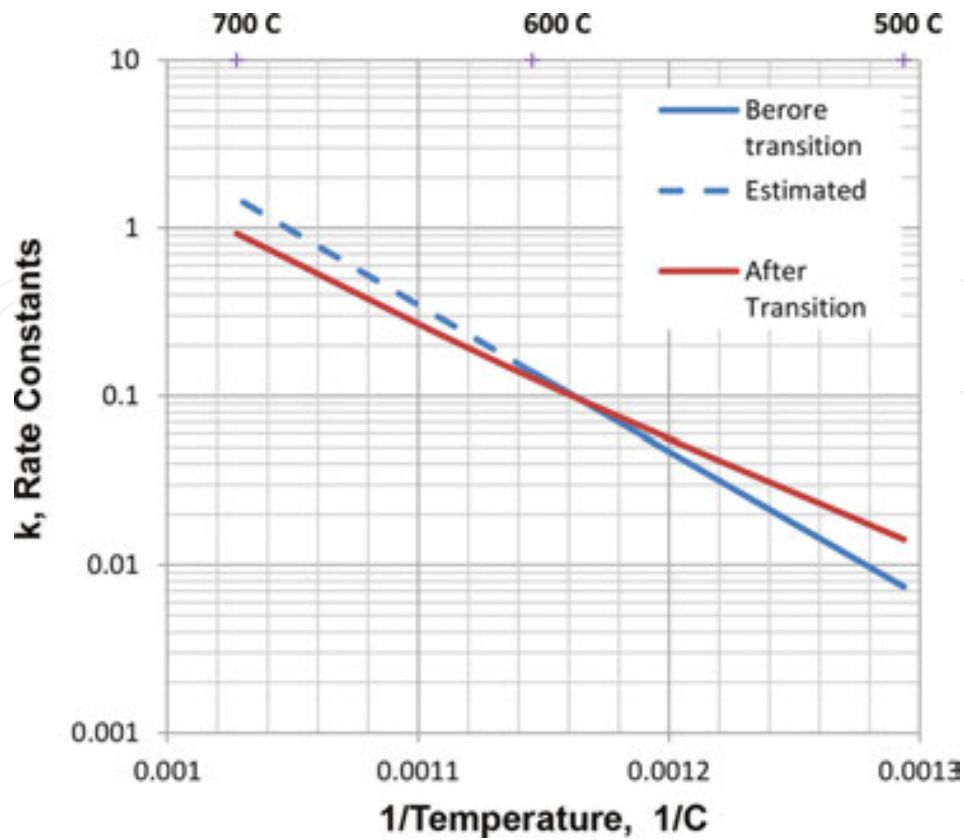


Figure 3. Rate constants for Zircaloy-2.

The rate constants in **Figure 3** are fit with the Arrhenius equation of the form

$$k = A * e^{\left(\frac{-Q}{RT}\right)} \quad (4)$$

where k is the rate coefficient, A is the “frequency factor”, Q is the activation energy, R is the gas constant = 1.9872 cal/(g-mole°K), and T is the absolute temperature, °K.

The activation energy, Q , is determined by taking the logarithm of both sides of the Arrhenius expression, evaluating at two data points, subtracting and solving for Q and A

$$\ln k = \ln A - \frac{Q}{RT} \quad Q = R \frac{\ln \frac{k_1}{k_2}}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \quad A = k_1 e^{+\frac{Q}{RT_1}} \quad (5)$$

Constants for both the pre-transition and post-transition regions were determined by Kendall [11]. The calculated values of A and Q that he reported for his data for both the pre-transition and the post-transition regions for both Zirconium and Zircaloy-2 are listed in Table 4.

	Before Transition			After Transition		
	A_1 (mg/cm ²) ^{2.58} /hour	Q_1 cal/mole	n_1	A_2 (mg/cm ²)/hour	Q_2 cal/mole	n_2
Zircaloy-2	1.1×10^9	3.94×10^4	2.58	8.5×10^6	3.10×10^4	1
Zirconium	1.8×10^9	4.14×10^4	2.58	7.9×10^5	2.98×10^4	1

Table 4. Values of A and Q in the Arrhenius equation for Zircaloy-2 and Zirconium in dry air [11].

The final equation is obtained by substituting the Arrhenius expression into Equation 1

$$M_{\text{gain}} = \left\{ A * t * e^{\left(\frac{-Q}{RT} \right)} \right\}^{\frac{1}{n}} \tag{6}$$

So, for example, the predicted amount of the oxide deposit after 10 hours at 500°C obtained from the above equation is calculated to be

$$M_{\text{gain}} = \left\{ 1.1 \times 10^9 * 10 * e^{\left(\frac{-3.94 \times 10^4}{2 * (500 + 273)} \right)} \right\}^{\frac{1}{2.58}} = 0.400011 \text{ mg / cm} \tag{7}$$

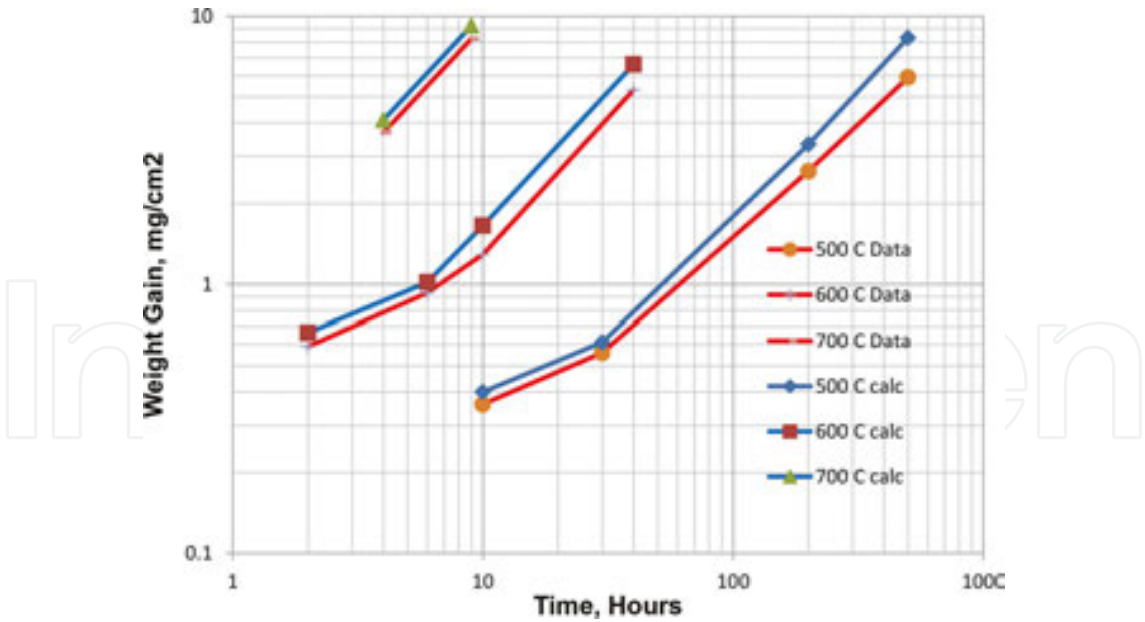


Figure 4. Comparison of final equations to original data.

The calculated results from the above correlation are compared in **Figure 4** to the original averaged data of **Figure 2**. It is seen the correlation values are all greater than the experimental values. So the constants in Table 4 will be used since they overestimate the total oxidation.

Equation 3, the above table, and graph list the weight gain per unit area from the reaction. The quantities of interest are: (1) the oxide thickness and (2) the loss of Zircaloy metal. These are obtained from Equation 3 for weight gain per unit area with the following relations.

The mass gain per unit area, $M_{\text{gain}}(\text{mg}/\text{cm}^2)$, due to Zr being oxidized to ZrO_2 , is given by

$$M_{\text{gain}} = M_{\text{ZrO}_2} - M_{\text{Zr}} \quad (8)$$

M_{ZrO_2} = mass per unit area of the oxide gained and M_{Zr} = mass per unit area of the metal lost.

M_{ZrO_2} and M_{Zr} to be related by the ratio of molecular weights as

$$M_{\text{ZrO}_2} = M_{\text{Zr}} \left(\frac{mw_{\text{ZrO}_2}}{mw_{\text{Zr}}} \right) \text{ or transposing } M_{\text{Zr}} = M_{\text{ZrO}_2} \left(\frac{mw_{\text{Zr}}}{mw_{\text{ZrO}_2}} \right) \quad (9)$$

Substituting in gives

$$M_{\text{gain}} = M_{\text{ZrO}_2} - M_{\text{Zr}} = M_{\text{Zr}} * \left(\frac{mw_{\text{ZrO}_2}}{mw_{\text{Zr}}} - 1 \right) = M_{\text{ZrO}_2} \left(1 - \frac{mw_{\text{Zr}}}{mw_{\text{ZrO}_2}} \right) \quad (10)$$

Solving for M_{Zr} and M_{ZrO_2} from these equations and dividing by the densities $\rho_{\text{Zr}} = 6.52 \text{ gm}/\text{cm}^3$ $\rho_{\text{ZrO}_2} = 6.0 \text{ gm}/\text{cm}^3$, the thickness of metal lost and oxide gained are obtained.

The thickness of metal loss, T_{Zr} , in mils is given as

$$T_{\text{Zr}} = \frac{M_{\text{Zr}}}{\rho_{\text{Zr}}} = \frac{M_{\text{gain}} \left\{ \frac{\text{mg}}{\text{cm}^2} \right\}}{6.52 \frac{\text{g}}{\text{cm}^3} * 2.54 \frac{\text{cm}}{\text{in}} * \left(\frac{123.224}{91.224} - 1 \right)} \frac{1 \text{ gm}}{10^3 \text{ mg}} \frac{10^3 \text{ mils}}{\text{in}} = 0.172 * M_{\text{gain}} \quad (11)$$

Similarly, the thickness of the oxide layer is

$$T_{\text{ZrO}_2} = \frac{M_{\text{ZrO}_2}}{\rho_{\text{ZrO}_2}} = \frac{M_{\text{gain}} \left\{ \frac{\text{mg}}{\text{cm}^2} \right\}}{6.0 * 2.54 * \left(1 - \frac{91.224}{123.224} \right)} = 0.253 * M_{\text{gain}} \quad (12)$$

So in summary, the thickness of the oxide layer in mils is 0.253 times the weight gain in mg/cm^2 . The reduction in metal thickness in mils is 0.172 times the weight gain in mg/cm^2 .

Figure 4 shows the post-transition period produces the highest rate of oxidation (i.e., slope or derivative, mg/cm²/hr) so that use of the post-transition equation to estimate the oxidation rate, the oxide accumulation, and metal loss will overestimate these quantities. Since the weight gain post-transition is linear with time, this conservative oxidation rate is constant for a given temperature.

The oxidation rate in the post-transition region is the derivative of correlation equation (2a) or

$$R = \frac{dM}{dt} = A * e^{\left(\frac{-Q}{RT}\right)} \quad (13)$$

Kendall [11] used the values of A and Q from Table 4 to extrapolate the reaction rates to temperatures below 500°C without the benefit of additional data but based on the applicability of the Arrhenius expression. Kendall's post-transition correlation is used in this document to conservatively estimate the oxidation rate over the range of interest from room temperature to 820°C. Additional data are referenced in the following discussion to show that use of his correlation conservatively bounds the Zircaloy-3 data obtained by Argonne at 600, 700, and 800°C and that his correlation conservatively bounds literature values of on Zircaloy-2 below 500°C even though his data were limited to the 500 to 700°C range.

2.3. Oxidation rates of Zircaloy-3 and low temperature data on Zircaloy-2

Boland [15] states that, "Data from the literature, (Kendall [11]; Lustman [12] and Tipton [16]) indicate that zirconium is more resistant to oxidation in air than Zircaloy-2, but no directly comparable data were found on the oxidation of Zircaloy-3 so that experimental data were obtained to supply the missing information. Since Zircaloy-3 contains less tin and more iron than Zircaloy-2, information in the literature would indicate that it should be more resistant to oxidation in air than Zircaloy-2. The published experimental data on oxidation has a scatter of about 50% and can be used only as a guide in estimating how fast oxidation occurs in alloys or environments that differ from those actually tested.

To obtain Zircaloy-3 oxidation data under temperature conditions similar to those expected in the reactor, samples of the cladding, which were removed from a fuel element after 805 transients, were tested in a furnace in the TREAT reactor building. Samples were cycled from room temperature to 600°C thirty-five times with a total time at 600°C of 69 hours. One of these samples was then heated to 800°C for 2 hours to simulate the cladding temperature that might follow an accident. The sample heated to 800°C showed an oxide penetration of about 2 mils while the other sample showed an oxide penetration of less than 0.5 mils." Boland did not translate the above into rates at 600 and 800°C, but instead reported corrosion rates for 600, 700, and 800°C.

Zirconium and Zircaloy-2 corrosion rates were computed at 500, 600, and 700°C using Kendall's constants substituted in Equation 2a. These and the Zircaloy-3 corrosion rates at 600, 700, and 800°C reported by Boland [15] are shown in **Table 5**. Boland did not include any details about the measurement or about whether they were based on the post-transition

kinetics or simply the total corrosion weight divided by the time at temperature. The 0.5 mils at 600°C corresponds to 2.07 mg/cm² and if divided by 69 hours to a rate of 0.029 mg/cm²/hour which is less than the 600°C value in Table 5. The 2.0 mils corresponds to 8.26 mg/cm² and if divided by 2 hours to a rate of 4.13 mg/cm²/hr. The latter value is higher than the data in Table 5. A value of 0.21 mg/cm²/hour reported by Freund [17] (converted from 0.9 mil/day) at 700°C is also included in the table and is close to the Boland number. The table values of Zircaloy-3 are less than those of Zircaloy-2 and slightly greater than zirconium.

Temperature, °C	Zirconium	Zircaloy-2	Zircaloy-3	Zircaloy-3*
500	0.003	0.015		
600	0.026	0.148	0.041	
700	0.150	0.926	0.24	0.21*
800			2	

*Converted value of 0.9 mil/day for Zircaloy-3 at 700°C P. 85 of Freund [17].

Table 5. Comparison of corrosion rates (mg/cm²/hour).

Causey [18] of Sandia reports that a considerable amount of data on Zircaloy-2 have been obtained since the work of Kendall [11]. He states: "There are a substantial number of reports dealing with the oxidation of Zircaloy at temperatures of 527°C and below. Regardless of the type of oxidant (oxygen, water, water vapor, CO, etc.) to which zirconium or its alloys such as Zircaloy-2 and 4 are exposed, the general behavior of the process is more or less the same. The reaction rate depends more on the pressure of the gas than the composition and that it applies to air as well. Oxidation occurs at the same rate in air or in water and proceeds in ambient condition or in high vacuum. He reports the dependence of the post-transition oxidation rate R on temperature and pressure as

$$R = 13.9 P^{1/6} \exp\left(\frac{1.47}{k_B T}\right) \quad (14)$$

where R is oxidation rate gram/(cm²-second); P is the pressure in atmospheres (note the factor $P^{1/6} = 1$ at ambient pressure; the activation energy is 1.47 eV; k_B is the Boltzmann constant (8.617×10^{-5} eV/°K).

This correlation is plotted in **Figure 5** along with Kendall's Zr-2 extrapolated correlation down to 200°C. It agrees well with the Kendall Zircaloy-2 correlation over the temperature range of 200 to 800°C. It is lower below 500°C than the Kendall Zircaloy-2 correlation extrapolated below 500°C, which means the Kendall correlation conservatively overestimates the rates below 500°C. And the Kendall correlation fits the Zircaloy-2 data in the medium temperature range of 500 to 700°C range where Kendall took his data. The Kendall correlation (extrapolated to 800°C) is also higher than the Argonne 600 to 800°C Zircaloy-3 data. Therefore, the Kendall

correlation which is used by TREAT to estimate the amount of oxide which has formed on the fuel does so conservatively. Note no transients performed so far have brought the fuel or cladding above 600°C.

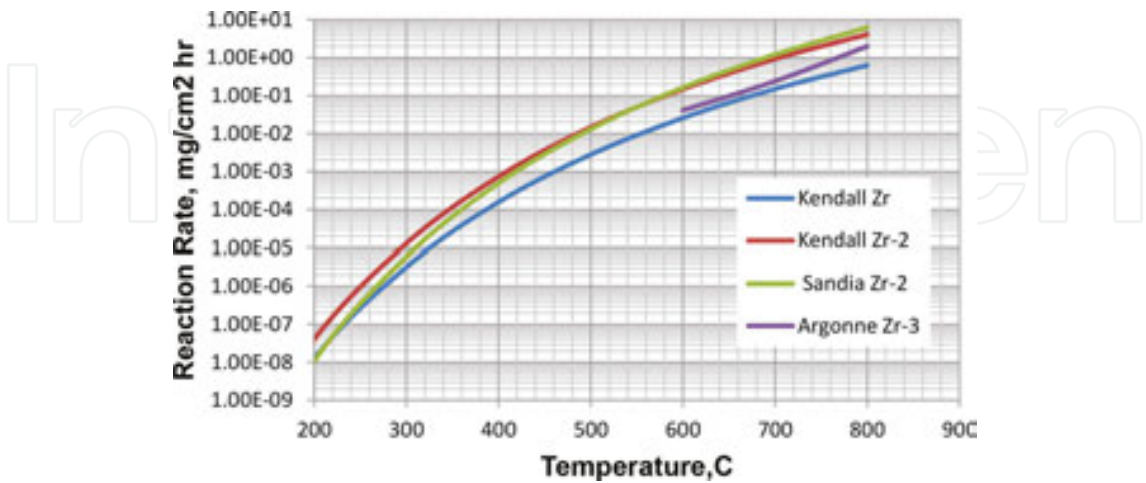


Figure 5. Comparison of the Kendall and Sandia correlations and Argonne Zircaloy-3 values.

2.4. Oxidation rates at higher temperatures and Zircaloy-4

Although the TREAT design basis accident shows that the cladding temperature does not exceed 820°C, higher temperature data are also of interest. The above three correlations were extrapolated to 900°C and are shown in Figure 6 along with other data.

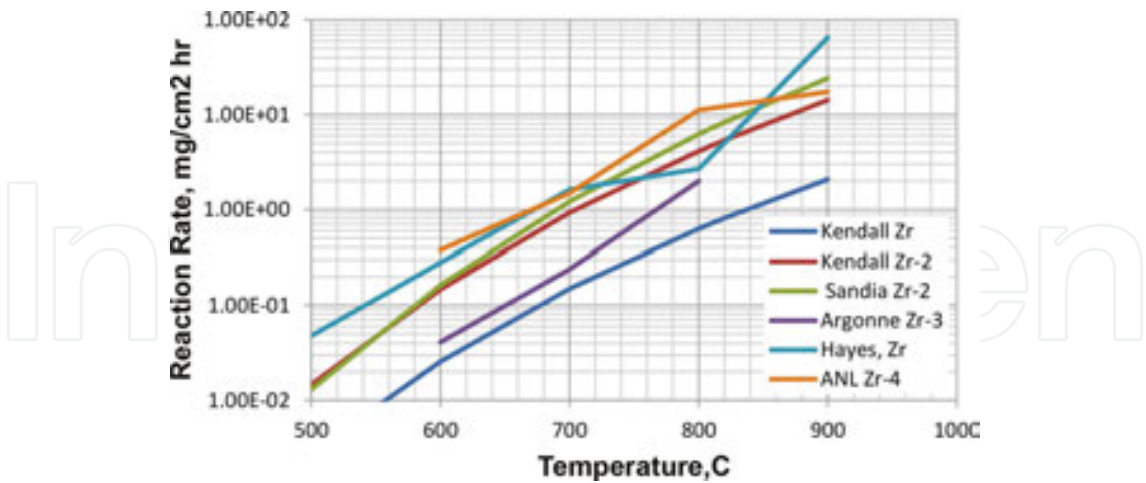


Figure 6. Comparison of correlations and data in the high temperature range.

Hayes [19] made measurements on zirconium in moist air up to and including 900°C. Hayes was only able to obtain oxidation data at 900°C for 1 hour whereas his 500 to 800°C data were gathered over a 24 hour period. As shown in Figure 6, except for the 800°C data point, the oxidation rate was higher for zirconium oxidation in moist air than the Zircaloy-2 rates of

Kendall. Other 900°C data include measurements at Argonne reported by Natesan [4] on bare Zircaloy-4 up to 900°C, which is also shown in **Figure 6**. Again, this is higher than the Zircaloy-2 data.

Hayes [19] concluded that the increase in the oxidation rate at 900°C is due to the change from alpha phase zirconium to beta phase zirconium at 862°C. He states “Microscopic examination of all specimens shows that there is no evidence of oxygen or nitrogen penetration into the body of the metal below 700°C. Short time exposures of less than 1 hour at 800°C produced only oxide surface layers and showed no evidences of further penetration. The specimens exposed for 1 hour and longer showed the intragranular rods and coarsened grain boundaries found in the oxygen series. In the 900°C series, it was found that the diffusion was extremely rapid. In one test with a thicker section, oxides were observed at the center of a quarter-inch (6.3 mm) sheet, which had been held at this temperature only 30 min. It appears probable that this sudden vulnerability to oxygen penetration can be ascribed to the change in volume that takes place at 862°C when the close-packed, hexagonal, alpha phase transforms to the body-centered, cubic beta form.”

This large increase in the rate is not seen for Zircaloy-4, but perhaps this one metal sample was not representative. The design basis reactivity insertion accident maximum temperature is 820°C and this is below the zirconium phase change of 862°C. Although zirconium data in moist air and the Zircaloy-4 data are higher than the 1955 Kendall Zircaloy-2 correlation, the experience with the TREAT cladding is that the Kendall correlation in the dry climate of the INL and the less reactive Zircaloy-3 cladding has conservatively bounded the oxide growth. If there has been any oxide growth so far on the fuel, it is less than the uncertainty in the measurements of 0.5 mils [20]. Based on the continued low oxide buildup reported in Mouring [21] and Kramer [20], the conservative method of estimating oxide buildup is sufficient with visual observation if the computed buildup is greater than 3 mils or if the temperature of a transient exceeds 600°C.

2.5. Corrosion rate summary

In summary, to conservatively calculate oxide buildup on Zircaloy-3, use the oxide buildup rate equation for Zircaloy-2 which is

$$M_{\text{gain}} = 8.5 \times 10^6 * t * e^{\left(\frac{-3.1 \times 10^4}{1.9872 * (T + 273)} \right)} \quad (15)$$

Where M_{gain} is in mg/cm² and T is temperature in °C and t in hours.

The relations between the weight gain due to oxide buildup, M_{gain} , the metal loss thickness, and the oxide thickness, T_{ZrO_2} , are:

$$T_{Zr} = 0.172 * \bar{M}_{\text{gain}} \quad T_{ZrO_2} = 0.253 * \bar{M}_{\text{gain}} \quad T_{Zr} = 0.680 * T_{ZrO_2} \quad (16)$$

$$\frac{\text{Zirc Lost}}{\text{Oxide Thickness}} = 0.680$$

3. Maximum recommended operating temperature for Zirconium-3

The maximum cladding oxidation which is allowed in a light water reactor (LWR) is 0.17 times the total cladding thickness. This limit is imposed to prevent the cladding from becoming brittle, which occurs due to the incursion of hydrogen and oxygen into the grain boundaries in the unreacted Zircaloy-2 cladding. Oxygen incursion into the remaining metal is also a problem with the oxidation of Zircaloy-3. This problem is circumvented by limiting the maximum cladding temperature. Lustman [12] states that: “below 900°C no evidence was found for the penetration of oxygen or nitrogen into zirconium. Above the alpha-to-beta phase transformation the diffusion of oxygen into the metal was rapid.” Alpha zirconium transforms to beta zirconium above 862°C as reported in Hayes, 1949. Both confirm that oxygen does not diffuse into zirconium below 862°C. So, the zirconium which remains under the oxidation layer will not become brittle as long as it remains below 862°C. Note, there is some variation in the literature on the alpha-to-beta temperature (for example, Lyman [22] reports 872°C). All, however, are equal to or above 862°C.

The zirconium transformation temperature is changed when it is alloyed into Zircaloy-3. The major additives in Zircaloy-3 are reported in Gibbons [1] as 0.2–0.3% Sn and 0.2–0.3% Fe. The only other trace element is a maximum of 0.05%. Lyman [22] and Hanson [23] report an increase in the transformation temperature with tin (Sn) concentration so that the tin addition does not lower this temperature. Hanson [23] shows a decrease in this temperature when Fe is added. A portion of the phase diagram boundary is shown and magnified in **Figure 7**. It is seen that with 0.3% addition of iron, the transformation temperature remains above 857°C.

Therefore, the transformation temperature for Zircaloy-3 is 857°C or above. Since Lustman [5] states that no penetration of oxygen or nitrogen was observed below 900°C for exposure up to 6 hours, this penetration is assumed to be very small between 850 and 900°C. Taking all of the above information into account leads to the conclusion that as long as the maximum limiting temperature is selected at or below 900°C, the disintegration of the metal due to nil ductility will not be a problem nor will there be a rapid increase in oxidation rate over that described above.

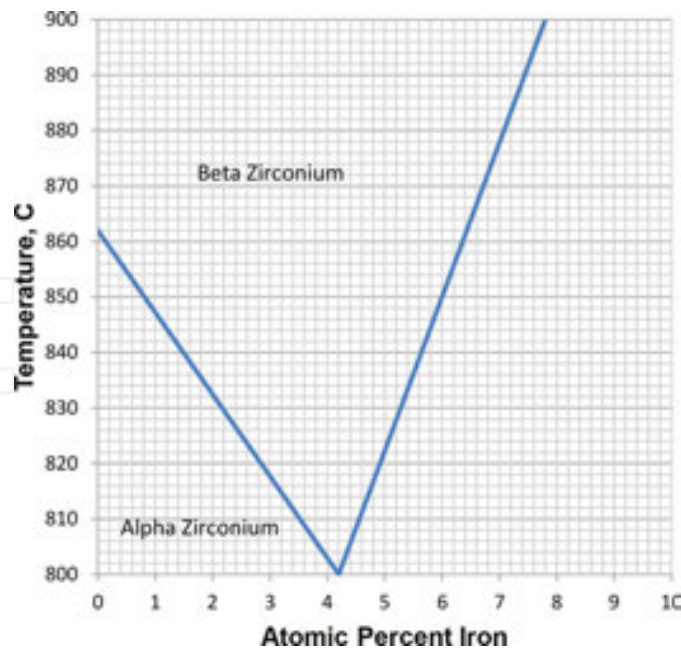


Figure 7. Partial phase diagram for the Zr-Fe binary alloy.

The brittleness of the cladding material was also investigated experimentally. The approach to nil ductility is accompanied by an increase in hardness. Microhardness tests on a control sample and on each of the above samples showed an average hardness increase of about 45 Knoop hardness points for the heated samples. There was no clear pattern established between the center and the edges of the samples. If oxygen had diffused into the surface metal, one would expect a significantly harder material at the edge than in the center [15].

The weld material was also tested to determine if there was any preferential oxide formation in this area. A section of a sample that contained a weld was bent on a 3/8-in. diameter mandrel after the 600°C thermal cycling test without cracking the weld or the oxide layer over the weld. Metallographic examination of the welded area of a sample heated at 600°C did not show any greater oxide penetration than in the adjacent areas of the base metal [15].

The value of 820°C is recommended as the safety limit based on the above discussion and data. This value is sufficient to allow margin for operation, but is below the zirconium phase change of 862°C. This is a temperature limit at which further accident analysis would predict to not be exceeded with a large degree of certainty. Data for highly oxidized samples at 800°C do exhibit embrittlement and these are discussed in the next section.

4. Comparison oxidation correlation to experimental data on Zircaloy-3 samples

Zircaloy-3 samples approximately 1 in. square were oxidized in air for a range of temperatures for various times. The thickness of the oxide layer has been measured by an eddy current

instrument. A color picture of the resulting sample set was taken and included in this chapter. The measured oxide layer is compared to the conservative equation (Equation 3) developed earlier. A best estimate correlation for cladding thickness was developed from the results. The sample pictures are placed on an excel spread sheet as a function of temperature and oxide thickness. The metal thickness remaining is estimated for those samples.

4.1. Comparison of conservative oxide calculation and measured data

Figure 8 shows a palette of 25 mil thick, 1 in. square samples of legacy Zircaloy-3 oxidized at specific temperatures for fixed periods of time (time listed is in hours(h)) starting at 500°C up to 1100°C. Two samples of the un-oxidized metal are also included in the top row. According to personnel observations, these samples, (photo, 2014) have the same appearance as when originally placed on the chart (circa, 1983). This provides evidence that the TREAT Zircaloy-3 cladding does not oxidize while in storage or in the inactive reactor.

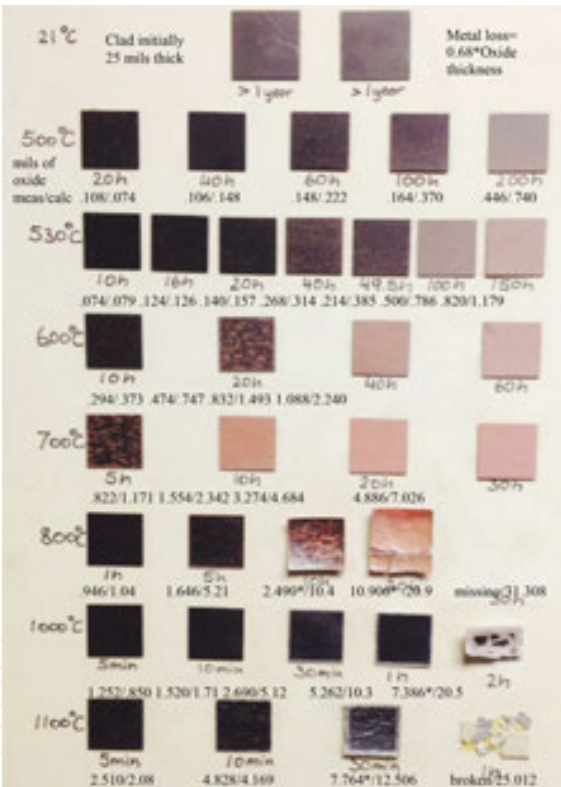


Figure 8. Photograph of Zircaloy-3 oxidation chart (Photo taken 10/1/2014).

Wachs [24] recently measured the oxide thickness of these 1 in. square coupons. The oxide thickness was also calculated using the conservative technique (Equation 3). Both the measured and the conservative values are included in Figure 8. The reaction products of Zircaloy-2 are adherent and tough, while those of zirconium are fragile and flaky [11]. The samples of Zircaloy-3 also are tough and none of the oxide has scaled off.

The conservative equation for calculating the oxide thickness discussed earlier is:

$$\bar{M}_{\text{gain}} = t * 8500000 * e^{\left(\frac{-31000}{1.9872 * (T + 273)}\right)} \quad (17)$$

The deposition in mg/cm² of each sample is converted to mils (Equation 4) as

$$T_{\text{ZrO}_2} = 0.253 * M_{\text{gain}} \quad (18)$$

For a few cases (very thin oxide layers), the measured values appear larger than the calculated values, but surface roughness and imperfections cause measured values to be at least 0.1 mils. In those cases, the conservative calculation is more accurate than the measured and the conservative values would be larger than the actual. A correlation which describes the actual thickness will be derived using the measurements and the conservative equation. For the highest temperature 1100°C, the measured values were slightly greater than the calculated values, which is probably due to the sample distortion.

All samples with measured oxide thicknesses less than 5 mils show color change due to oxidation and the samples are flat and undeformed. The largest oxide thickness measured on samples held at 700°C and lower was 4.9 mils (equivalent to 3.33 mils of metal loss) for 30 hours at 700°C. The oxidation occurs on both sides of these 25 mil thick samples, but for this subset of samples the backside oxidation has not affected the top side. Due to the TREAT fuel cladding cans being evacuated during fabrication, these samples with a metal loss of 3.33 mils or less on a side are representative of the TREAT cladding which only is exposed to air on one side.

This sample chart is reproduced in black and white, so colors have not been preserved. The five samples that appear in 500, 530, and 600°C are grey. The dots on the samples are light pink. All of the colors for samples 700 and 800°C that appear grey are actually a light pink. The grey colors in 1000 and 1100°C are really grey.

Figure 9 is a more detailed look gradual transition from a black oxide through pink dots to all grey for the samples at 530°C illustrating the color change as oxide thickness increase to 0.5 mils.



Figure 9. Expanded view of the 530°C gradual transition from black to grey oxide.

4.2. Correlation between the oxide measured and calculated thicknesses

A plot of the measured data versus calculated values from **Figure 8** is shown in **Figure 10**. An identity line is also shown. Data points below this line indicate that the calculated values are

larger than the measured values. Points above are non-conservative. Three points are above the line which means they are non-conservative, one is for 1000°C and the other two are for 1100°C. Using all the data points to fit a straight line which goes through the origin gives a relation between measured and calculated of

$$T_{\text{ZrO}_2}^M = 0.4794 * T_{\text{ZrO}_2}^C \quad (19)$$

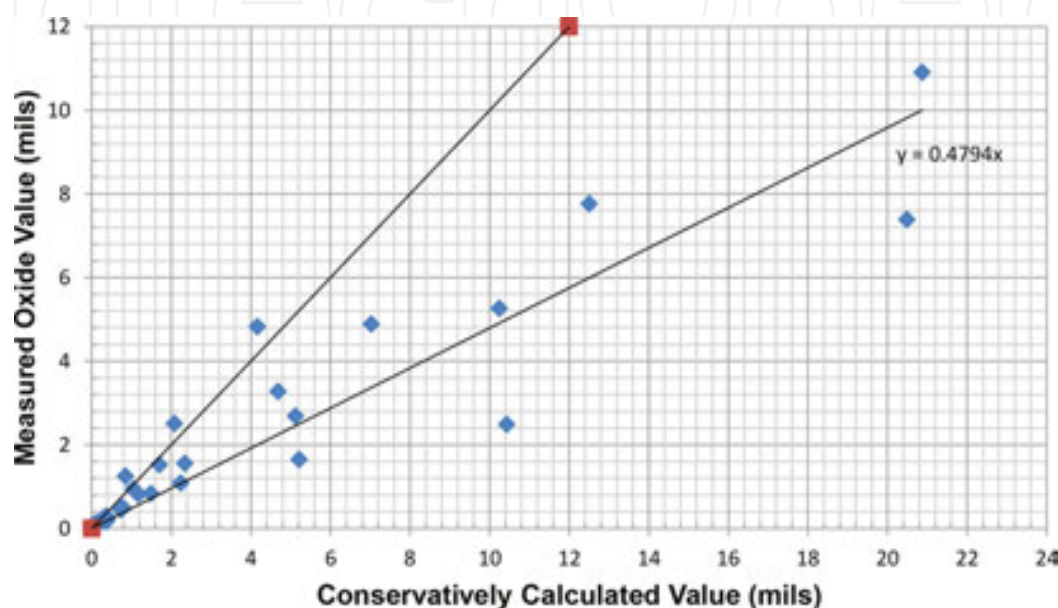


Figure 10. Measured versus conservative oxide values.

Combining this with the previous equation gives a correlation which predicts the actual oxide thickness.

$$T_{\text{ZrO}_2}^M = t * 1030949.7 * \text{EXP}\left(\frac{-31000}{1.9872 * (T + 273)}\right) \quad (20)$$

4.3. Oxide color as a tool for estimating oxide thickness

A qualitative evaluation may be made of oxide thickness by correlating color to oxide thickness. The surface color change to black occurs almost immediately with the start of oxidation (0.1 mils), but then remains the same for a certain amount of oxidation until it gets spots of pink. This occurs at slightly different amounts of oxidation for different temperatures. To see this more clearly, the samples have been placed on a grid in order of ascending oxidation as shown in **Figure 11**. The oxidation values used for plotting are the smoothed values from the above correlation, which are 0.4794 of the conservatively calculated values in **Figure 8**.

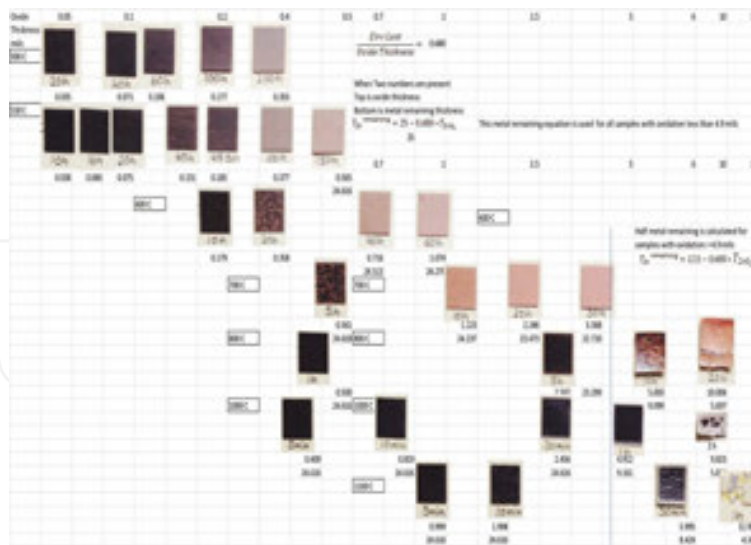


Figure 11. Samples placed according to oxide thickness and temperature.

Pink dots start to appear with about 0.2 mils of oxide for 500, 530, and 600°C. But this does not represent higher temperature oxidation, since the 5 hours 800°C is still black with an oxide thickness of 3.2 mils, and the 1 hour 1000°C is still black with an oxide thickness of 6.3 mils. The 500, 530, and 600°C start to turn grey at a thickness of 0.45 mils, although the grey in the 600°C samples appear to start at slightly larger thicknesses.

As a result of the above observation, it may be concluded that the oxide thickness transition between black oxide and grey oxide increases with temperature, so that a single color does not indicate a unique thickness of the oxide, but it does if the temperature history is known as it is in TREAT.

Figure 12 reproduces the 500, 530, and 600°C data, which is the expected region of interest in oxidation of the TREAT cladding since none of past transients have exceeded 600°C. As long as TREAT reactor excursions remain in the temperature range of 600°C and below, then the

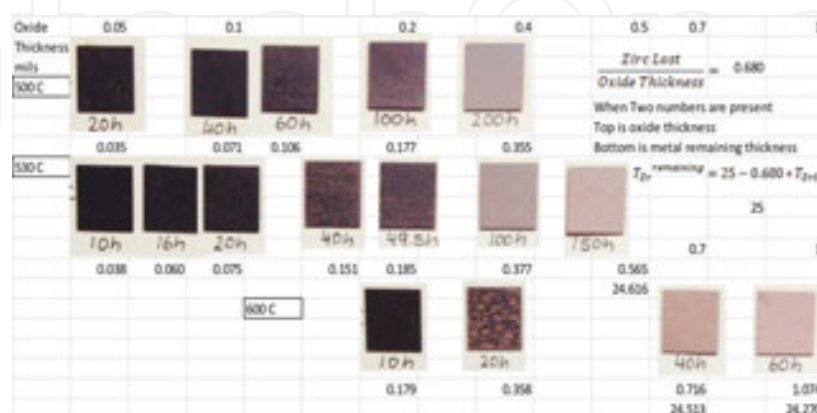


Figure 12. Color chart of concern to TREAT operation.

start of a grey color oxide layer would be evidence of an oxide between 0.35 and 0.75 mils thick. Black oxide would indicate an oxide thickness of 0.18 or less.

Since Equation 7 yields an estimate of the actual oxide thickness, the metal remaining in each sample is calculated by subtracting the metal loss from the original 25 mils. The metal loss is obtained from the ratio of oxide growth to metal loss, which is shown below as 0.680.

$$T_{Zr} = 0.172 * \bar{M}_{\text{gain}} T_{ZrO_2} = 0.253 * \bar{M}_{\text{gain}}, \text{ so } \frac{\text{Zirc Lost}}{\text{Oxide growth}} = \frac{T_{Zr}}{T_{ZrO_2}} = \frac{0.172}{0.253} = 0.680 \quad (21)$$

For the 500, 530, and 600°C samples, the oxidation on the back side of the samples has no effect on the remaining metal, so the oxidation characteristics would be the same as that which would occur on the TREAT cladding which only oxidizes on one side. Therefore, the remaining cladding thickness on TREAT cladding which looks like the color of these samples can be calculated by subtracting the metal loss from 25 mils as in the following

$$T_{Zr}^{\text{remaining}} = 25 - 0.680 * T_{ZrO_2} \quad (22)$$

These numbers have been included in **Figure 12** as the second number under some of the samples.

4.4. Determination of the minimum cladding thickness remaining

Although the TREAT cladding will probably never oxidize more than 2 mils, regulations require that a minimum undamaged metal (no oxygen incursion into the metal grain boundaries) remaining thickness limit be specified. This section determines the thickness of undamaged metal that is required for sufficient mechanical strength to be able to remove, insert, or handle a fuel assembly. This is then followed by a determination of the amount of oxidation that is acceptable to have the required thickness of the metal remaining.

The minimum undamaged cladding thickness needed during handling operations is based on the strength of the cladding. The handling forces, F_H , that the assembly must withstand are primarily in the axial direction being the weight of the fuel being suspended, friction between assemblies during insertion or removal, and sticking forces between the assemblies and the bottom grid plate. These forces are assumed to be borne by the cladding horizontal cross section, A_c . This undamaged cladding cross section is modelled as a uniform layer of metal around the circumference of the fuel times the perimeter of the fuel cross section. This assumes that oxidation leaves a uniform thickness of undamaged metal. The stress, σ , which occurs during fuel handling, is then estimated by the equation:

$$\sigma = F_H / A_c \quad (23)$$

The minimum area, and hence the minimum thickness allowed, would be that area able to support the maximum stress which the metal can support without incurring damage. This stress is taken to be the yield stress of Zircaloy-3. From the Alloy Digest, the yield strength of Zircaloy-3 at room temperature is 44.2 ksi and 16.7 ksi at 500°F (260°C) for undamaged metal. The yield strength of 16.7 ksi will be used to calculate minimum cladding thickness. Using the yield strength at 260°C is conservative in two ways. First, the yield strength is the stress where proportional elongation ends and where plastic deformation begins. The ultimate yield strength is where the material breaks. The yield strength is approximately 58% lower than the ultimate yield strength. Second, the use of the yield strength at 260°C is conservative because fuel handling operations are normally done at room temperature, with no reason to attempt to remove fuel from the reactor at higher temperature.

The force used to calculate the minimum cladding thickness is 300 lbs. This includes the weight of the fuel assembly (95 lbs) and any friction forces associated with assembly removal. The value of 300 lbs has historically been used as the limit during fuel handling operations. The area of the cladding, A_c is obtained by solving Equation 12 for the area, by using the values of 300 lbs, and by requiring a safety factor of five times the area to account for non-uniformity in the oxide layer. The thickness of the cladding, T , is calculated by dividing the area required by the approximate circumference of the cladding.

$$A_c = 5 * \frac{300}{16700} = 0.090 \text{ in}^2 \quad T = 0.090 \frac{\text{in}^2}{16 \text{ in}} = 5.6 \text{ mils} \tag{24}$$

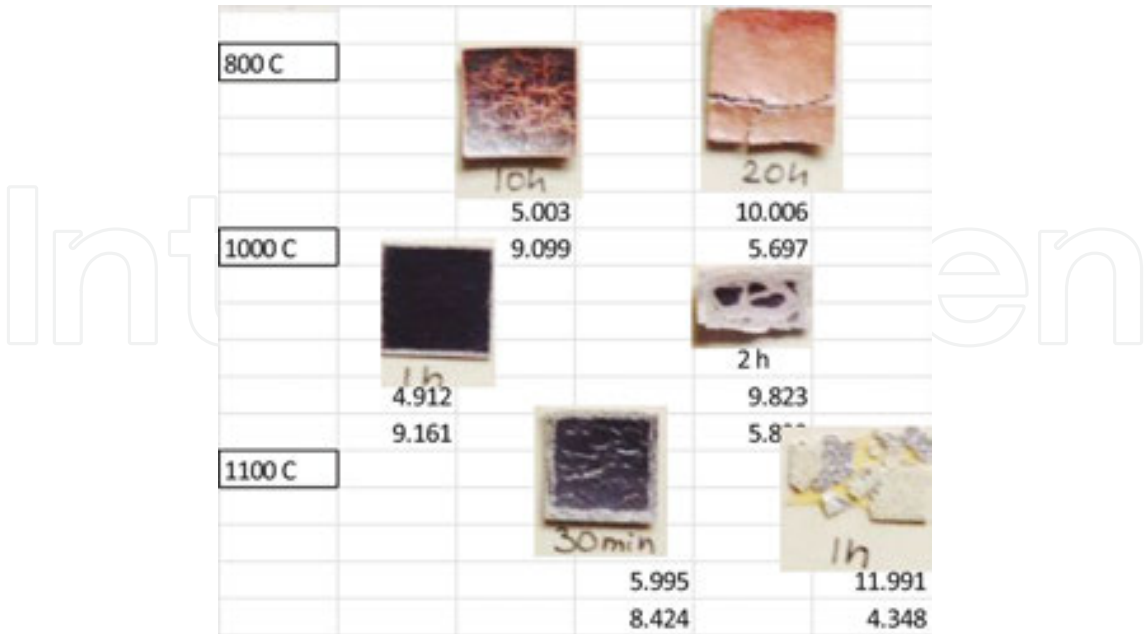


Figure 13. High temperature, high oxidation samples.

Since data are not available on 25 mils thick, one-sided Zircaloy-3 oxidized on one side, the minimum cladding thickness must be inferred from the data 25 mils samples oxidized on two sides. It is seen in **Figure 12** that the longer oxidation runs at 800, 1000, and 1100°C have experienced oxygen incursion and have become brittle. **Figure 13** shows this high temperature large oxidation part of Figure 12.

If a sample has become brittle, then oxygen incursion must have occurred from both the top and the bottom. Assuming symmetry, this would mean that the oxygen incursion reached half way through the 25 mils or 12.5 mils. A determination of half metal thickness remaining is calculated by the equation

$$T_{Zr}^{\text{remaining}} = 12.5 - 0.680 * T_{ZrO_2} \quad (25)$$

Even though the 20 hours 800°C sample is below the 862°C limit temperature mentioned in Section 14a, it has become brittle which is evidenced by the large crack. To be conservative, it is assumed that in addition to the temperature limit of 862°C, there is also a limit on the amount of oxidation which can occur before oxygen penetration of the grain boundaries occurs at temperatures below 862°C. For this sample, the effective thickness of 12.5 mils shows that 10 mils of oxide formed (a loss of 6.8 mils of metal) and that 5.7 mils of metal under it became brittle. Almost the same value is observed in the 1000°C sample. This result is applied to TREAT cladding that is 25 mils thick and protected on one side by realizing that if 10 mils of oxide forms (which is 6.8 mils of metal loss), then an additional 5.7 mils of cladding under it has been damaged (brittle) and could not support a load. This would leave a thickness of $25 - 6.8 - 5.7 = 12.5$ mils of undamaged metal left.

This is extended to other oxide thicknesses by assuming the damage thickness (embrittled) is proportional to the cladding thickness as

$$T_{\text{damaged}} = 5.7 * T_{\text{oxide}} / 10 \quad (26)$$

The amount of undamaged metal T_{Good} remaining is estimated by subtracting the metal loss due to the oxide layer $0.68 * T_{\text{oxide}}$ and the damaged metal layer $0.57 * T_{\text{oxide}}$ from the original metal thickness of 25 mils to obtain

$$T_{\text{Good}} = 25 \text{ mils} - 0.68 * T_{\text{oxide}} - 0.57 * T_{\text{oxide}} \quad (27)$$

Thus, the oxide thickness limit required to leave 5.6 mils of undamaged metal is determined by

$$5.6 \text{ mils} = 25 \text{ mils} - 0.68 * T_{\text{oxide}} - 0.57 * T_{\text{oxide}} \quad (28)$$

$$T_{\text{oxide}} = \frac{25 \text{ mils} - 5.6 \text{ mils}}{0.68 + 0.57} = 15.52 \text{ mils} \quad (29)$$

It must be remembered that the measurement technique measures oxide thickness and does not differentiate damage metal from undamaged metal. The remaining 5.6 mils of metal thickness remaining provides a factor of 5 safety factor to account for experimental uncertainties and non-uniformities in the oxide layer growth and excess.

The total remaining metal is $5.6 + 0.57 * 15.52 = 14.4464$ mils, which is the minimum allowable metal thickness. These three components, oxide, brittle metal, and undamaged metal add up to the original 25 mils $= 0.64 * 15.52 + 0.57 * 15.52 + 5.6$. In summary, the two limits are:

Maximum oxide thickness allowable = 15.52 mils

Minimum metal thickness allowable = 14.45 mils

The oxide thickness which leaves only damaged metal is

$$0 = 25 \text{ mils} - 0.68 * T_{\text{oxide}} - 0.57 * T_{\text{oxide}} T_{\text{oxide}} = \frac{25 \text{ mils}}{0.68 + 0.57} = 20 \text{ mils} \quad (30)$$

The metal converted to oxide $0.68 * T_{\text{oxide}} = 13.6$ mils. The damaged metal is $0.57 * T_{\text{oxide}} = 11.4$ mils. This remaining oxygen damaged metal layer would not provide a complete barrier to keep air from the graphite-carbon fuel which might burn if it is at temperature over 700°C.

4.5. Deductions about cladding oxidation

The calculation of the cladding remaining with the Zircaloy-2 reaction rate from Section 1 compared to the oxidation samples shows that this equation is conservative. The measured data and calculations also show that, after approximately 35 years of operation at recorded temperatures up to approximately 570°C, and an accumulated energy development of over 2.6×10^6 MJ, there is minimal measured cladding oxidation. A continued program of oxide growth tracking for fuel assembly temperatures that exceed 400°C is considered prudent, but is not of sufficient concern to be included as a technical specification surveillance. However, as discussed in the previous subsection, an evaluation of cladding oxidation should be made if fuel assembly temperatures exceed 600°C. Part of this recommended evaluation should be the requirement to remove any fuel element that has less than 14.45 mils of cladding remaining or an oxide layer greater than 15.52 Mils. These are sufficient criteria to ensure fuel elements can be removed from the core.

As long as TREAT reactor excursions remain in the temperature range of 600°C and below, then the start of a grey color oxide layer would be evidence of an oxide between 0.45 and 0.92 mils thick. Black oxide would indicate an oxide thickness of 0.23 mils or less.

4.6. Current oxidation of TREAT fuel

The current oxidation of the TREAT fuel is basically the same as measured in the report of Kramer [20] in 1983. In the report, he determined the average amount of oxidation at that time (0.76 mils) and pointed out that it was less than the average measurement of Mouring [21] in 1977 (0.83 mils). In fact, the accuracy of the measurement method used on the fuel assemblies seems to be about 0.5 mils because the measurement head is affected by surface irregularities [20]. This is about the same magnitude as the most recent oxide measurements. Although Kramer [20] measured the average thickness at 0.76 mils, he also said that the observation of color put it in the range of 0.4 to 0.6 mils. Observations made in 1981 showed that the color was black with a touch of pink. This corresponds to a thickness of about 0.4 mils. Thus, it seems that the oxidation is less than 0.76 mils and may be as small as 0.4 mils.

It should be pointed out that even though the average measurements in Mouring and Kramer are about 0.8 mils, some of the measurements were as high as 2 mils. But Kramer pointed out that several factors caused inaccuracies in the measurements made with the fuel assembly in motion and tended to increase the value so that these higher values are probably misleading. These factors included roughness of the surface due to oxidation, scratches on the surfaces with left ridges, weld seams, etc. Also, the fact that the oxidation did not increase over the time between the two measurements in 1977 and 1983 indicates that the oxidation rate has been small.

A conservative method described in the next section is in place to keep track of an upper limit on how much oxidation has occurred. This tracking method is based on the conservative method of estimating the oxide growth rate. Measurements may be required as part of the evaluation for any fuel assembly that exceeds 600°C. It should be noted that 151 transients were performed since the last measurement and the oxide buildup is estimated at 0.229 mils [26].

The current number of transients on the fuel assemblies over 35 years of operation is 2880. The oxidation of the TREAT fuel has resulted in a loss of less than 1 mil of cladding loss over those transients. No more than an additional 1 mil cladding loss would be expected within the next 35 years of operation if the same type of transients and frequency as the original 35 years resulting in a minimum cladding thickness of 23 mils.

4.7 Predicted cladding losses during 10 years of operation

The section presents calculated results of temperature predictions in transients which are run in TREAT reactor and the amount of cladding oxidation which can be expected in each. **Figure 14** shows calculated temperatures for fuel and cladding following a transient where the hot spot fuel temperature reaches a maximum of 600°C.

It is assumed in the analysis that the reactor air flow rate is about 6000 cfm, which is the normal mode of operation during a transient. **Figure 14** shows temperatures for the case where the cladding has collapsed on the fuel. The control rods are pulled to their full out programmed location to begin a transient. The graphite carbon uranium fuel matrix heats up very fast (~1 sec). In this case, the cladding and fuel surface temperature equilibrate within 0.5 minutes.

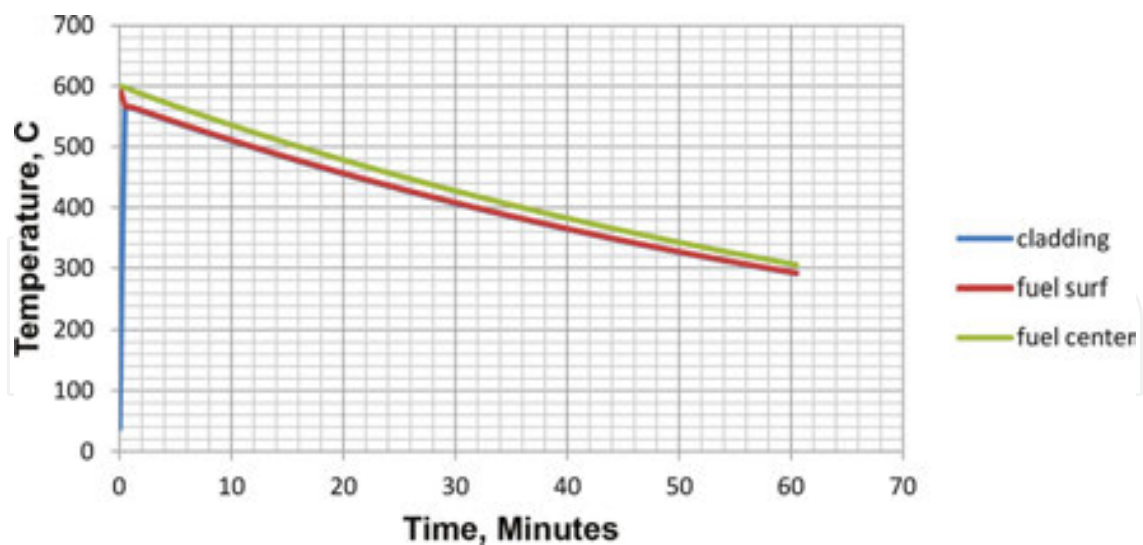


Figure 14. Cladding and fuel temperatures for the no cladding-fuel gap case.

Figure 15 shows the cladding loss during this transient, which is seen to reach 0.00152 mils. This value is less than 1/10 of one used by TREAT to estimate cladding oxidation, showing that the TREAT method is quite conservative.

Figure 16 shows the temperatures when it is assumed that the original 55 mil design gap still exists. The lower cladding temperature results in a cladding loss of only 0.000007 mils. The fuel assemblies in the outer regions of the core may retain their original gap, but the gap in assemblies in the inner region where the temperatures are highest have closed due to the weaker cladding at higher temperatures and the vacuum in the cladding can. Visual observation of the fuel (by technicians using binoculars) in the past has shown that the cladding has shrunk down on the higher temperature fuel because cladding indents were observed at the interfaces between the 8 in. long fuel blocks.

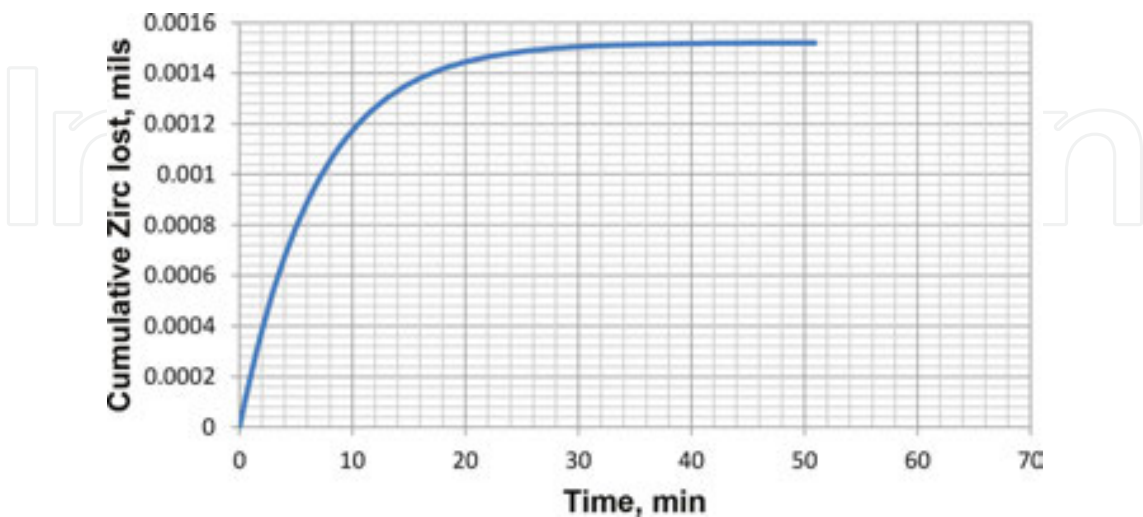


Figure 15. Cladding loss for the no cladding-fuel gap case.

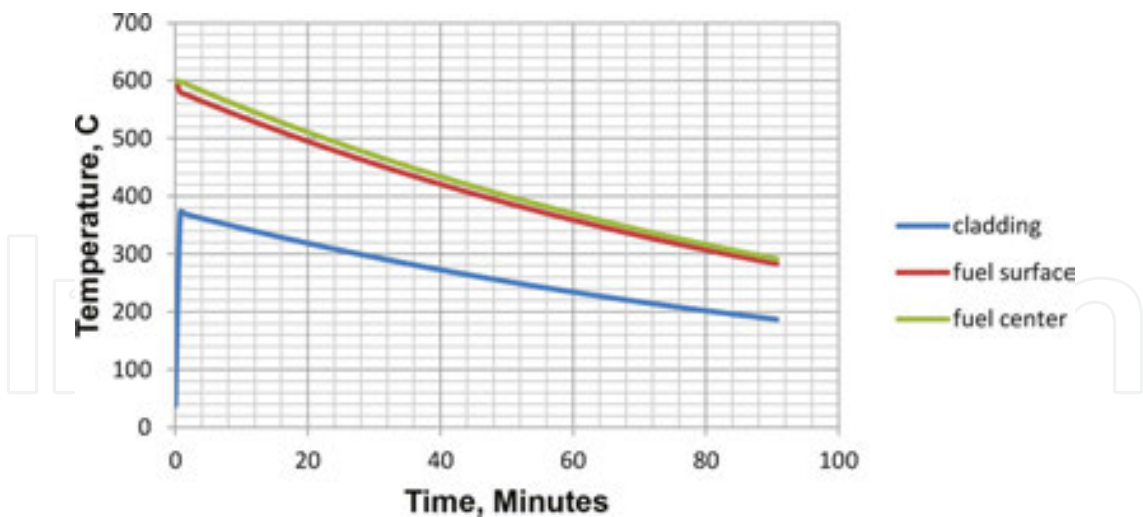


Figure 16. Cladding and fuel temperatures with a 55 mil gap.

Since the no-gap model of the fuel shows the most metal loss, it is conservatively used to estimate the cladding loss in other transients. The calculated amount of metal loss at the fuel hot spot for three temperature limited transients with no gap fuel is shown in **Table 6**. This calculation uses the conservative reaction rate described in the previous sections of this chapter.

Maximum Temperature of Transient	Metal Thickness Loss Calculated, mils	Metal Thickness Loss Used by TREAT, mils	Temperature Range Where the TREAT Metal Loss is Used.
600	0.00152	0.01693	500 to 600°C
500	0.00014	0.00153	400 to 500°C
400	0.000007	0	<400°C

Table 6. Comparison of calculated metal loss to loss used by TREAT.

The TREAT constants used to estimate cladding loss uses values [25, 26] also listed in Table 6. The metal loss for a 600 and 500°C transient that TREAT uses to estimate the total metal loss is seen to be over 10 times larger than the calculated value. Thus, the method used by TREAT is very conservative and estimates a metal loss more than 10 times larger than the conservative calculation presented here.

To be even more conservative, the TREAT method assumes that all the transients which have a maximum temperature between 500 and 600°C use the metal loss for a 600°C transient, and those which had a maximum temperature between 400 and 500°C use the metal loss calculated for 500°C. The metal loss for transients below 400°C is neglected.

As an example, the metal loss calculated with the TREAT method for an experimental program of 100 experiments in the 500 to 600°C range and 300 in the 400°C to 500°C range is

$$\text{Metal loss} = 100 * 0.01693 + 300 * 0.00154 = 2.17 \text{ mils} \quad (31)$$

which corresponds to a buildup of 3.19 mils of oxide. If 600 additional transients are assumed which reached 400°C, this would increase the calculated metal loss less than 1%. Thus, the metal will still be at least 22 mils thick after the above program assuming this conservative result. In fact, the smaller conservative values calculated after such a program is less than 0.2 mils.

$$\text{Metal loss} = 100 * 0.00152 + 300 * 0.00014 = 0.194 \text{ mils} \quad (32)$$

Even this later estimate is extremely conservative. Based upon the more realistic estimate of cladding oxidation, it is recommended that the TREAT values could be reduced by a factor of 10.

5. Cladding growth

Cladding oxidation also causes lateral growth of the cladding due to the increased specific volume of the oxide over that of the cladding. This growth could reduce cooling of the fuel assembly because it decreases the flow area between fuel assemblies. Such a decrease could also hamper fuel handling operations. When Zircaloy is oxidized in air, the oxide film is under lateral compression [11], and the growth of the base metal occurs from the tension the oxide puts on the base metal. Three measurements of growth were made: (1) A Zircaloy-3 fuel-element 48 in. long can exposed to air at 700°C for 48 hours exhibited longitudinal and transverse growth of 7/8 and 1/16 in., respectively [17]. (2) The growth observed in the 1 in. samples at 600°C for 69 hours was 3.2×10^{-3} in./in. (3) The sample heated to 800°C for 2 hours grew 2.5×10^{-3} in./in. Based on these tests, growth rate constants of 4.6×10^{-5} , 3.25×10^{-4} , and 1.2×10^{-3} in./in./h were obtained for temperatures of 600, 700, and 800°C, respectively.

An Arrhenius expression for the metal growth rate (MGR) has been used to describe the above data which is

$$\text{MGR} = 5000 * e^{\left(\frac{-32000}{RT}\right)} \quad (33)$$

where MGR is in (in./in./hour).

This expression is plotted for a range of temperatures in **Figure 17** and compared to the data. The expression is slightly larger than the above reported data so it is slightly conservative.

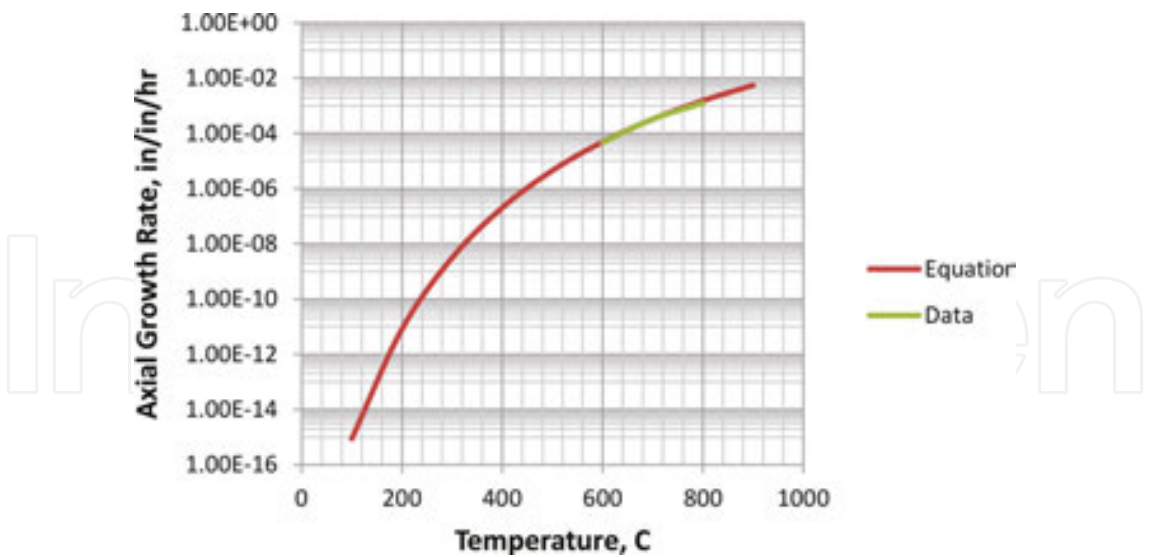


Figure 17. Growth rate of Zirconium-3.

The lateral growth for the TREAT 4 in. with fuel elements was calculated for 600°C transient presented in the previous section and the growth is shown in **Figure 18**. Similar calculations were done for 500 and 400°C. The resultant growth for each transient is shown in **Table 7**.

Maximum Temperature of Transient	Lateral Calculated Growth, mils	Temperature Range Where the TREAT Metal Loss is Used
600	0.011096	500–600°C
500	0.000949	400–500°C
400	0.000041	<400°C

Table 7. Calculated lateral growth of TREAT fuel elements.

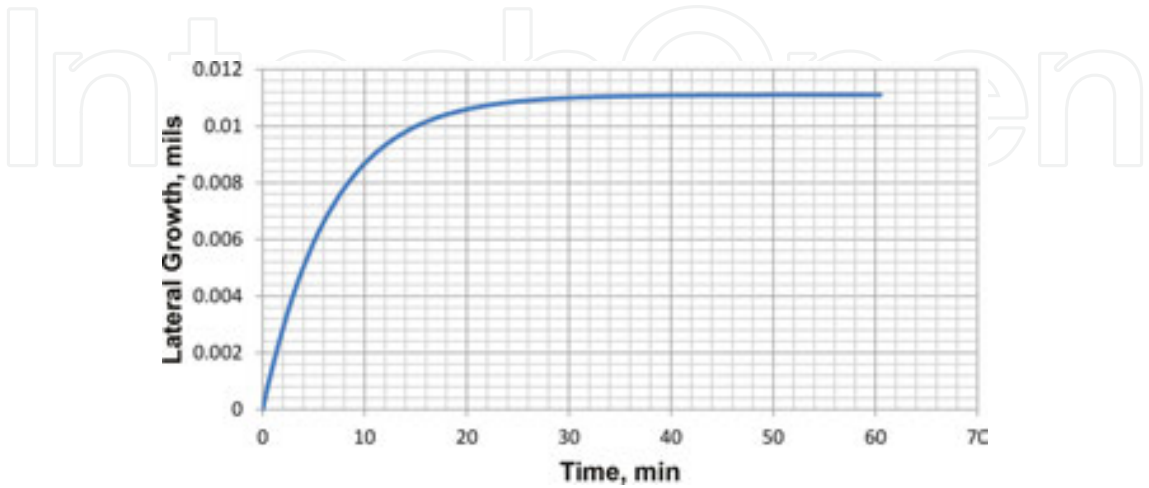


Figure 18. Lateral growth of fuel element during a 600°C transient.

Based on the conservative assumptions that the growth rate for transients above 500°C is equal to that at 600°C, growth rates for transients between 400 and 500°C are calculated at the 500°C rate, and transients 400°C or less at 400°C rate. The experimental program analyzed in the last section yields a total lateral increase of 1.15 mils.

$$\text{Cladding Growth} = 100 * 0.011096 + 300 * 0.000949 + 600 * 0.000041 = 1.15 \text{ mils} \quad (34)$$

This is a value which is too small to measure accurately due to the uncertainty of original width. The highest temperature elements would be the ones with the most growth, but these are the most likely to have the cladding collapsed on the fuel due to high temperatures and the evacuation of the fuel during manufacture. Fission gas production or any leakage into the cans would also change the geometry. The consequences of this possible growth are very small since the core is unclamped when fuel is to be moved and adjacent fuel elements can be moved to take out any elements which have grown.

A fuel element with 48 in. long fuel section could grow in the axial direction; but since the fuel elements are supported on a bottom grid and are free to grow longitudinally, a gradual change in length should not interfere in any way with reactor loading operations.

If temperatures in the fuel assemblies exceed 600°C during an off-normal event, an evaluation of the effect of oxidation on the cladding of a fuel assembly from the region of highest temperature shall be evaluated. If any unexpected oxidation or resulting growth of the cladding is detected during such an inspection, appropriate actions will be taken, such as removing all assemblies that have similar time-at-temperature histories or moving them to cooler areas in the core. Alternatively, reactor fuel temperatures could be limited to 400°C until a complete evaluation is made.

6. Summary of conclusions/recommendations

An equation based upon Zircaloy-2 oxidation rate is developed from the literature and compared to literature data that covers the range of temperatures from room temperature to 1100°C. This equation is shown to be conservative when predicting the oxidation rate of Zircaloy-3 based on the Zircaloy-3 data available. This equation is recommended to conservatively predict oxide growth, metal loss, and remaining Zircaloy metal.

An evaluation of the minimum temperature at which Zircaloy-3 transition between alpha and beta phase occurs concluded that 857°C is consistent and conservative with the data reported in the literature. The beta phase shows a rapid increase in oxygen inclusion in the grain boundaries with a corresponding increase in the brittleness of the Zircaloy-3. A safety limit of 820°C was chosen to avoid this undesirable behavior.

An equation was developed that expresses the relationship between the conservatively calculated oxide growth and measured data on 1 in. Zircaloy-3 samples. This equation was

used to predict the actual oxide growth. A chart is provided on the use of Zircaloy-3 color to estimate oxide thickness in the range of interest for operation ($<600^{\circ}\text{C}$).

A corroded cladding thickness of 14.45 mils is recommended as the limit below which fuel assemblies should be removed from service to ensure that fuel may be handled without damage. It was concluded that, based on historical data and conservative calculations, fuel assembly cladding would only develop another 1 mil of oxide for the next 35 years of operation if the cladding temperatures are maintained below 600°C . The total fuel growth was calculated for 150 transients conducted in TREAT. The total calculated growth was 0.36 mils. This is a value too small to measure accurately. It is recommended that the effects of cladding growth be evaluated if fuel assembly temperatures ever exceed 600°C .

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References

- [1] Gibbons, R. C., Woldman's Engineering Alloys, American Society for Materials, 1979.

- [2] Blanchard, J., Zirconium Cladding, *fti.neep.wisc.edu/neep423/FALL97/lecture9.pdf*, 1997.
- [3] Alloy Digest, Zircaloy-3: Corrosion & Heat Resistant Alloy, ZZR5, ASM International, Engineering Alloy Digest, May 1969.
- [4] Natesan, K., and Sopper, W. K., Air Oxidation Kinetics for Zr-Based Alloys, NUREG-CR-6846, University of Chicago; Argonne National Laboratory University of Chicago, U.S. NRC Division of Systems, June, 2004.
- [5] Lee, J. M., Kim, J. S., Kim, Y. S., Air oxidation behavior of Zircaloy-4 at transient condition, Transactions of the Korean Nuclear Society Spring Meeting Jeju, Korea, May 17–18, 2012.
- [6] Duriez, C., Steinbrück, M., Ohai, D., Meleg, T., Birchley, J., Hasted, T., Separate-effect tests on zirconium cladding degradation in air ingress situations, Nuclear Engineering and Design, 2009; 239: 244–253.
- [7] Steinbrück, M., Prototypical experiments relating to air oxidation of Zircaloy-4 at high temperatures, Journal of Nuclear Materials, 2009; 392: 531–544
- [8] Beuzet, E., Lamy, J. S., Simoni, E., Modelling of Zr-4 cladding oxidation by air under severe accident conditions using MAAP4 code, International Conference Nuclear Energy for New Europe, 2009, Bled/Slovenia/September 14-17.
- [9] Duriez, C., Dupont, T., Schmet, B., Enoch, F., Zircaloy-4 and M5 high temperature oxidation and nitriding in air, Journal of Nuclear Materials, 2008; 380: 30–45.
- [10] Steinbrück, U. Stegmaier, T., Prototypical Experiments on Air Oxidation of Zircaloy-4 at High Temperatures, report FZKA 7257, Institut für Materialforschung Forschungszentrum Karlsruhe, January 2007.
- [11] Kendall, L. F., Reaction kinetics of Zirconium and Zircaloy-2 in dry air at elevated temperatures, HW-39190, Hanford Atomic Products Division, GE, September 1955.
- [12] Lustman, B., Kerze, F., Jr., The Metallurgy of Zirconium, Chapter 11, First Edition, McGraw Hill Book Company, Inc., New York, 1955; 581–600.
- [13] Phalnikar, C. A., Baldwin, W. M., Jr., The scaling of zirconium in air, American Society Testing Materials, Proceedings, 1951; 51: 1038.
- [14] de Boer, J. H., Fast, J. D., The influence of oxygen and nitrogen on the α - β transition of zirconium, Recueil des Travaux Chimiques des Pays-Bas, 1936; 55: 461–468.
- [15] Boland, J. F., Safety analysis of the operation of treat with fuel temperatures up to 600°C, Addendum to ANL-5923, Hazards Summary Report on The Transient Reactor Test Facility (TREAT), Idaho Division, December 7, 1967.
- [16] Tipton, C. R., Jr., Editor, Reactor Handbook, Vol. 1, Materials, Interscience Publishers, Inc., New York, 1960, 726–738.

- [17] Freund, G. A., et al., Design Summary Report on the Transient Reactor Test Facility (TREAT), Argonne National Laboratory, ANL-6034, 1960.
- [18] Rion, A. C., Don, F. C., Bob, H. N., Review of the Oxidation Rate of Zirconium Alloys, Sandia National Laboratory, SAND2005-6006, November 2005.
- [19] Hayes, E. T., Roberson, A. H., Some effects of heating zirconium in air, oxygen, and nitrogen, *Journal of the Electrochemical Society*, 1949; 96 (3): 142–151.
- [20] Kramer, N. A., TREAT Fuel Assembly Cladding Oxidation Measurements Report, Argonne National Laboratory, ANL Report, October 1983.
- [21] Mouring, R. W., TREAT Zr-3 Fuel Cladding Oxidation Measurements using Electro-magnetic Techniques, Argonne National Laboratory, ANL Report, July 1977.
- [22] Lyman, T., Ed., *Metals Handbook*, American Society for Materials, 1973.
- [23] Hanson, M., Anderko, K., *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
- [24] Wachs, K. M., TREAT Eddy Current Oxide Evaluation, Technical Evaluation Report, Idaho National Laboratory, 2016, January 25.
- [25] Solbrig, C. W., Intra-Laboratory Memo to L. J. Harrison, Tech Spec Requirements to Measure Cladding Thickness and Elongation, March 6, 1989.
- [26] Neuman, L., Log of Maximum Metal Loss and Lateral Elongation as of 20 October 1995, 1995.