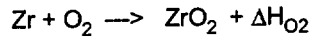# Oxidation of Zircaloy by Steam and Oxygen

The following is an analysis of the chemical energy released from the oxidation of zircaloy in either steam or air. Both oxidation reactions are exothermic, releasing heat as the metal Zr is converted to ZrO_2. The reactions under consideration are as follows:

$$Zr + O_2 \longrightarrow ZrO_2 + \Delta H_{O2}$$

and

$$Zr + 2H_2O \longrightarrow ZrO_2 + 2H_2 + \Delta H_{H2O}$$

where the heats of reaction are:

$$\Delta H_{H2O} := 1385 \cdot \frac{cal}{gm}$$

heat of reaction with steam (per kg Zr)
MELCOR uses 1385 cal/gm

$$\Delta H_{O2} := 2882 \cdot \frac{cal}{gm}$$

heat of reaction with oxygen (per kg Zr)
MELCOR uses 2882 cal/gm

The air oxidation net heat of reaction is larger than that for steam oxidation because it is not necessary to break the water molecule into oxygen and hydrogen, a process that requires energy.

In either case, the oxidation of the Zr metal results in the formation of an oxide layer that physically separates the reacting metal from the oxidant. As the oxide layer thickness increases, isothermal oxidation studies have shown that the rate of additional oxide layer growth varies inversely with the layer thickness for a given temperature. From a mechanistic standpoint, the oxide layer constitutes a barrier for mass transport through which the oxidant molecules must diffuse in order to react with the underlying metal atoms. This observation implies that the growth rate of the oxide layer can be expressed in the following form:

$$\frac{dx}{dt} := \frac{K(T)}{x}$$

where x is the oxide layer thickness. By noting that the weight gain "Δw" of the oxidizing sample is proportional to the growth of the oxide layer, Δx, the growth rate law can be expressed in the more commonly used "parabolic" form as follows:

$$\frac{dw^2}{dt} := K(T)$$

The parabolic law represents what is observed in isothermal furnace tests examining oxide growth as a function of time for a given temperature. The growth rate is observed to be "faster" at higher temperatures for a given oxide layer thinckness. The temperature dependence of K has been the focus of many oxidation studies both in air and steam. The temperature dependence of K is generally represented in an Arrienus form as exemplified in the following sections.

Following are parabolic rate expressions used in the MELCOR code for oxidation of zircaloy in air and in steam, and one expression for oxidation in air recommended by researchers at ISPRA investigating air oxidation of fuel bundles. It is important to realize that one has any number possible dimensional units with which to express the rate constant: mass/unit area of reacted metal, mass per unit area of metal oxide, etc. Different researchers have used different conventions in characterizing their results and it is very important to be clear on this before applying the correlations to any analysis. The ISPRA researchers appear to have made such an error in characterizing MELCOR correlations in their report.

$$K_{H2O}(T) := 29.6e^{\frac{-16820 \cdot K}{T}} \cdot \left(\frac{kg}{m^2}\right)^2 \cdot sec^{-1}$$

rate of Zr metal reacted
in steam (MELCOR Code)

$$K_{O2}(T) := 50.4e^{\frac{-14630K}{T}} \cdot \left(\frac{kg}{m^2}\right)^2 \cdot sec^{-1}$$

rate of Zr metal reacted
in oxygen (MELCOR Code)

$$K_{ISPRA}(T) := 52.67 \cdot 10^4 \cdot e^{\frac{-17597K}{T}} \cdot \left(\frac{mg}{cm^2} \cdot \frac{91 \cdot gm}{32 \cdot gm}\right)^2 \cdot sec^{-1}$$

rate of O_2 mass (converted to
Zr) produced cited as "best fit"
by ISPRA.

The following figure show the temperature dependence of the above three rate constants graphically...

... with units expressed as $(mg/cm^2)^2$ sec^{-1}.

The ISPRA report plots the MELCOR-B correlation incorrectly. I think they did not convert mass Zr reacted to mass oxygen reacted. This scales the K(T) by a factor of $(32 \text{ gm } O_2/91 \text{ gm } Zr)^2$, or 0.124. See Figure 138 in ISPRA Report.

steam ox. MELCOR
air ox. MELCOR
air ox. ISPRA
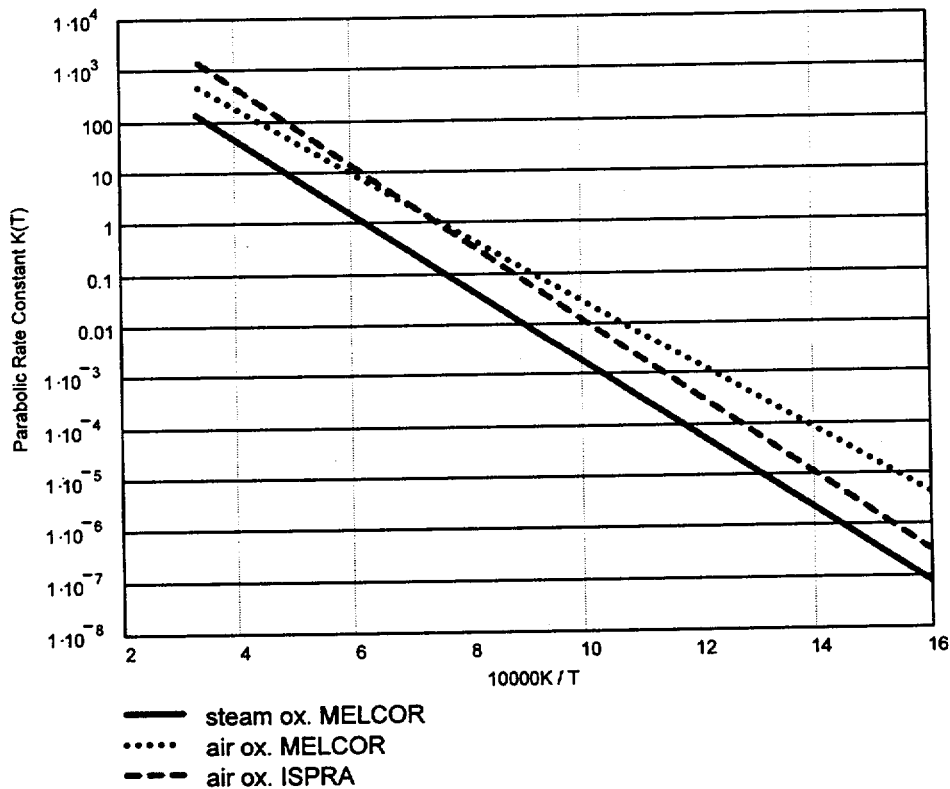
Analysis of Comparative Heating from Steam and Air Oxidation

The following section uses the parabolic law described in the preceeding section to compare the heat generated from oxidizing zircaloy in steam and air. Specifically, we seek to find the temperature at which air oxidation produces the same heat as that of steam oxidation at a different temperature. The motivation for this is to draw on the extensive transient heating studies where steam oxidation of zircaloy clad fuel rods has been observed to lead to a rapid increase in heatup rate (i.e. transient, escalation, runaway, excursion, etc.), and to infer from this an expected analogous behavior in air oxidation. Here it is assumed (*not without basis either*) that the rapid temperature escalation observed in such studies is due in large part to the increasing dominance of oxidation energy over decay heating and total heat losses as suggested by the following general heatup equation:

$$\frac{d}{dt}(mc_p \cdot T) := Q_{oxidation} + Q_{decay} - Q_{loss}$$

To make the desired comparisons we will form expressions for the reaction rate of zircaloy in either steam or air as a function of an existing oxide layer and a given temperature. Some manipulations are necessary to express the mass Zr metal reacted per unit area as a function of the oxide layer thickness. Where the density of Zr and ZrO_2 respectively are given by,

$$\rho_{Zr} := 6.5 \cdot \frac{gm}{cm^3}$$

$$\rho_{ZrO2} := 5.6 \cdot \frac{gm}{cm^3}$$

the mass of Zr per unit area of ZrO_2 layer whose thickness is δ is given by:

$$w_0(\delta) := \left[\delta \cdot \rho_{ZrO2} \cdot \left(\frac{91 \cdot \frac{gm}{mol}}{123 \cdot \frac{gm}{mol}} \right) \right]$$

mass Zr per unit area of ZrO2 whose thickness is δ

The reaction rate in steam as a function of temperature, T, and oxide layer thickness, δ can then be represented by the following equation:

$$RR_{H2O}(T, \delta) := \frac{1}{2} \cdot \frac{K_{H2O}(T)}{w_0(\delta)} \qquad \left(\frac{kg}{m^2 s} \right)$$

The heat generation rate associated with this reaction rate is simply

$$Q_{H2O}(T, \delta) := RR_{H2O}(T, \delta) \cdot \Delta H_{H2O} \qquad \left(\frac{watt}{m^2} \right)$$

For example, the heat production rate for a sample of zircaloy oxidizing in steam with a current oxide layer thickness of 20μm at temperature T=1500K is

$$Q_{H2O}(1500K, 20\mu m) = 1.397 \frac{watt}{cm^2}$$

The effect of a thicker oxide layer can be seen from evaluating the same function with a thicker oxide layer at the same temperture of 1500K.

$$Q_{H2O}(1500K, 30\mu m) = 0.932 \frac{watt}{cm^2}$$

Here an increase in the oxide layer thickness from 20μm to 30 μm led to a decrease in heat generation from ~1.4 watt/cm^2 to ~0.9 watt/cm^2, or a decrease of 1/3. Analagous functions are defined below for the MELCOR air oxidation rate and the ISPRA-recommended rate constant.

$$RR_{O2}(T, \delta) := \frac{1}{2} \cdot \frac{K_{O2}(T)}{w_o(\delta)}$$

MELCOR reaction rate for oxygen as a function of temperature for the same oxide thickness δ

$$Q_{O2}(T, \delta) := RR_{O2}(T, \delta) \cdot \Delta H_{O2}$$

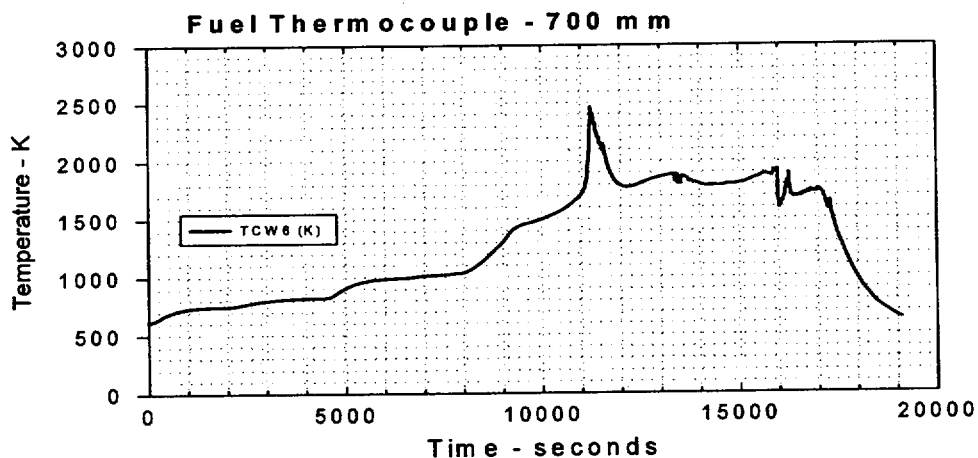Heat generation as a function of temperature for MELCOR air oxidation

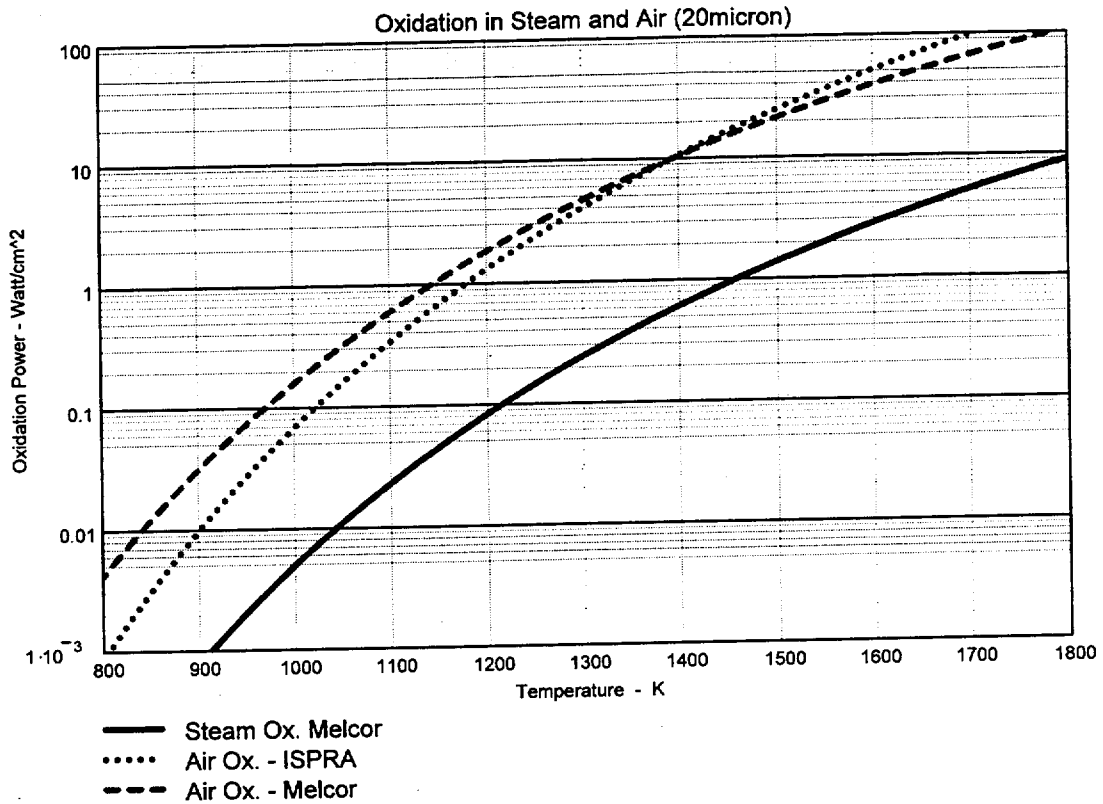$$RR_{ISPRA}(T, \delta) := \frac{1}{2} \cdot \frac{K_{ISPRA}(T)}{w_o(\delta)}$$

Reaction rate favored by ISPRA

$$Q_{ISPRA}(T, \delta) := RR_{ISPRA}(T, \delta) \cdot \Delta H_{O2}$$

Heat from reaction using ISPRA correlation

The following figure presents the cladding temperture from the Phebus FPT-1 test at the 700mm level in the fuel bundle. This figure presents a typical example of the temperature escalation observed when the oxidation energy produced dominates the collective fission heating and heat losses. In this case, the transient would appear to begin in the neighborhood of 1600K (~1300C). At this temperature, the oxidation heating begins to exceed other sources of heat generation or loss. While without more detailed analysis we cannot know from this what is the oxide layer thickness, and therefore cannot discern the magnitude of the specific chemical energy. We can nevertheless gain some insight from the following figures comparing air oxidation energy versus steam oxidation energy.

Fuel Thermocouple - 700 mm

Oxidation in Steam and Air (20micron)

Legend:
- —— Steam Ox. Melcor
- ••••• Air Ox. - ISPRA
- – – – Air Ox. - Melcor

(Y-axis: Oxidation Power - Watt/cm^2; X-axis: Temperature - K)

The analysis presented here recognizes that other factors can be at play that may affect the onset of a temperature escalation. These include factors that can change the resistance to oxygen transport throught the oxide layer such as the phase change in the neighborhood of 1760K of the ZrO_2, or ballooning and fracture of the oxide shell. Neverthess, we expect the general trends observed in the steam oxidation transient tests to be similarly characteristic of air oxidation conditions. Indeed, very similar behavior was seen in the early Niels tests (pre-CORA) performed at KfK and in the CODEX and DRESSMAN testing done more recently at FzK.

The following figure shows the oxidation specific power from both air and steam oxidation as a function of temperature for an assumed 200μm thick oxide layer.

Oxidation in Steam and Air (200micron)
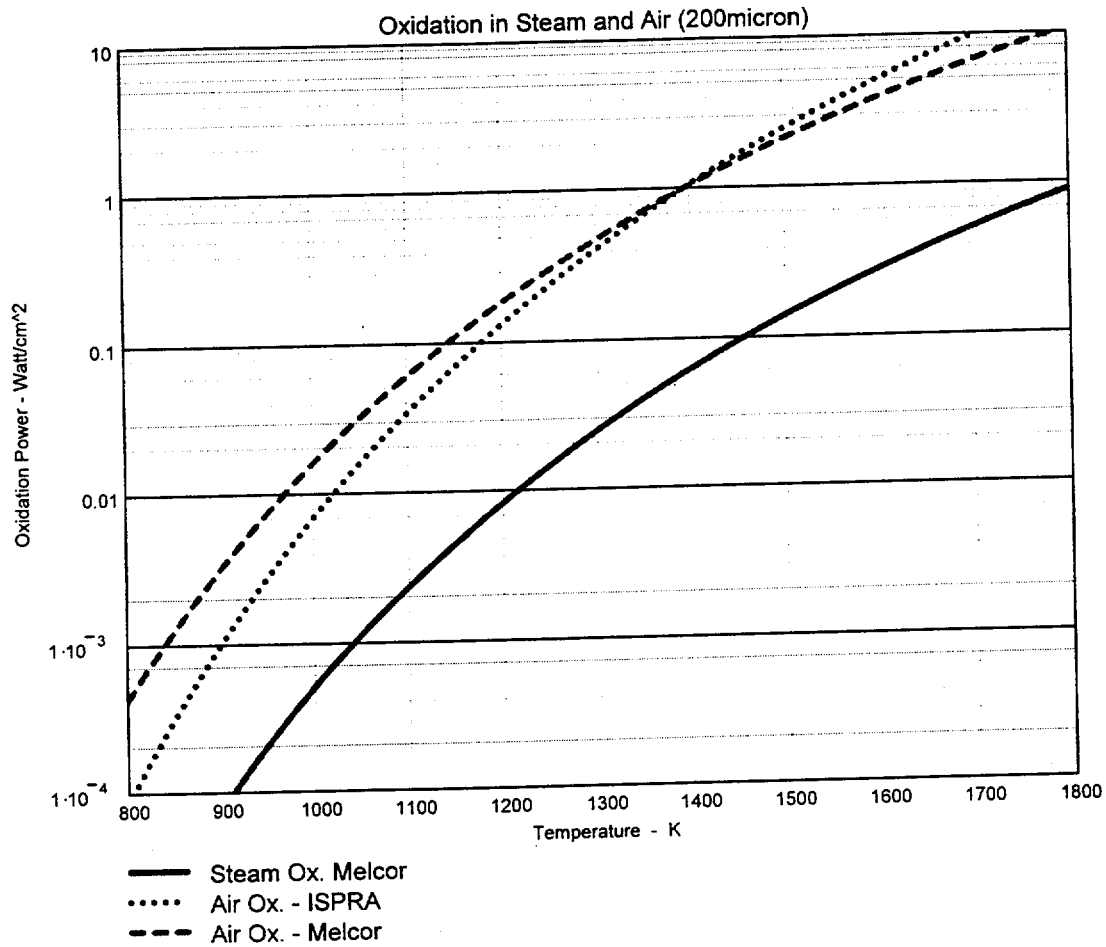
Referring to the Phebus temperature escalation at ~1600K, if the oxide thickness were 200μm, we could see from the above figure that the specific oxidation power apparently responsible for the temperature escalation under these conditions would be about 0.3 watt/square centimeter. We can also see from the above figure that the same oxidation power would result from oxidation in air at a lower temperature of about 1250K or about 1000C. Interesting, but as I said, we cannot know from the temperature history itself what the oxide layer thickness actually was. Indeed, 0.3 watt/square cm doesn't seem enough to be responsible for the observed escalation. A smaller oxide layer might be likely. But there is hope.

The following figure demonstrates that it is not that important that we do not know the precise oxide layer thickness. This time if we assume that the oxide layer is much smaller, 20 μm, then the steam oxidation power at ~1600K is seen to be about 3 watt/square cm. This might seem enough to bring about such an escalation. Interestingly, the air oxidation temperature for a 20μm oxide layer that produces this same higher specific chemical power is again about 1250K, the same as was obtained by assuming a much thicker oxide layer.

Air oxidation rates for MELCOR correlations and for the ISPRA "Best Fit"

... with units expressed as $(mg/cm^2)^2 sec^{-1}$.

The ISPRA report plots the MELCOR-B correlation incorrectly. I think they
did not convert mass Zr reacted to mass oxygen reacted. This scales the K(T) by a factor
of $(32 \ gm \ O_2 /91 \ gm \ Zr)^2$, or 0.124. See Figure 138 in ISPRA Report.

$$\frac{K_{H2O}(T_{Zr}) \cdot \left(\frac{32}{91}\right)^2}{\left(\frac{mg}{cm^2}\right)^2 \cdot sec^{-1}}$$

——

$$\frac{K_{O2}(T_{Zr}) \cdot \left(\frac{32}{91}\right)^2}{\left(\frac{mg}{cm^2}\right)^2 \cdot sec^{-1}}$$

• • • • •

$$\frac{K_{ISPRA}(T_{Zr}) \cdot \left(\frac{32}{91}\right)^2}{\left(\frac{mg}{cm^2}\right)^2 \cdot sec^{-1}}$$

— — —

$$\frac{10000K}{T_{Zr}}$$

——— steam ox. (MELCOR)
• • • • • air ox. MELCOR
— — — air ox. ISPRA