Air Oxidation

Review of MELCOR Model

Marek Stempniewicz

Fabio Alcaro

EU DuC=N

6-7/04/2016

Outline

- Introduction
- Air Oxidation Model in MELCOR
- Breakaway Models
- KIT Isothermal Tests
- New Model for Air Oxidation
- Effect of Nitrogen
- Effect of Steam
- Conclusions

Introduction

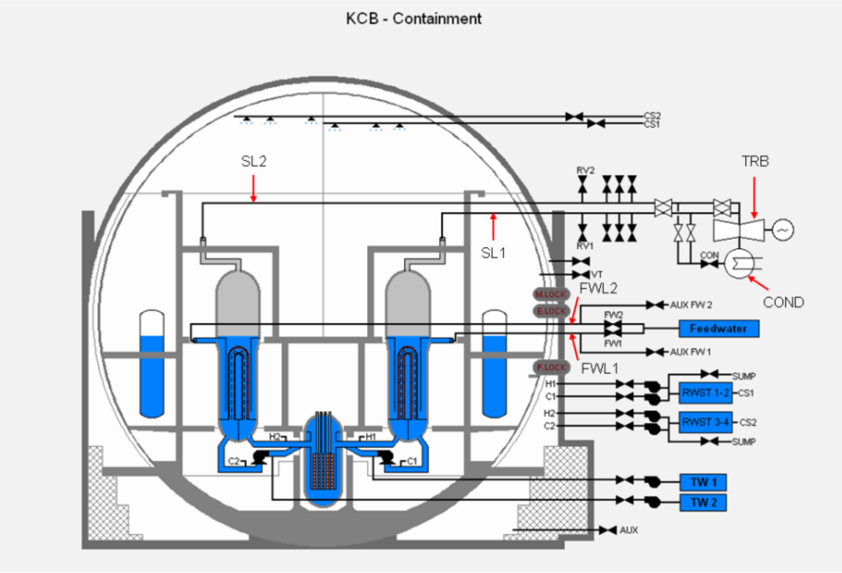
Uses of MELCOR @ NRG:

- ❑ **Post-Fukushima SFP analyses**
  - ➢ Spent Fuel Pool analyses in MELCOR (and other codes) in order to assess the coolability after a SFP LOCA scenario
- ❑ **Severe accident analysis for KERENA**
  - ➢ (Part of) PSA Level 2 analysis
  - ➢ Safety analyses for shutdown and power scenarios
- ❑ **HFR calculations for license renewal**
  - ➢ Severe accident analyses
  - ➢ PSA Level 2 analysis
- ❑ **Severe accident analyses for the KCB power plant**
  - ➢ Safety analysis calculations
- ❑ **KCB power plant desktop simulator**
  - ➢ Development of an interactive simulator of the Borssele NPP
  - ➢ Dutch regulator personnel training
- ❑ **GKN Dodewaard Power Plant**
  - ➢ PSA Level 2 analysis
  - ➢ Direct containment heating analysis (comparison of MELCOR vs CONTAIN)

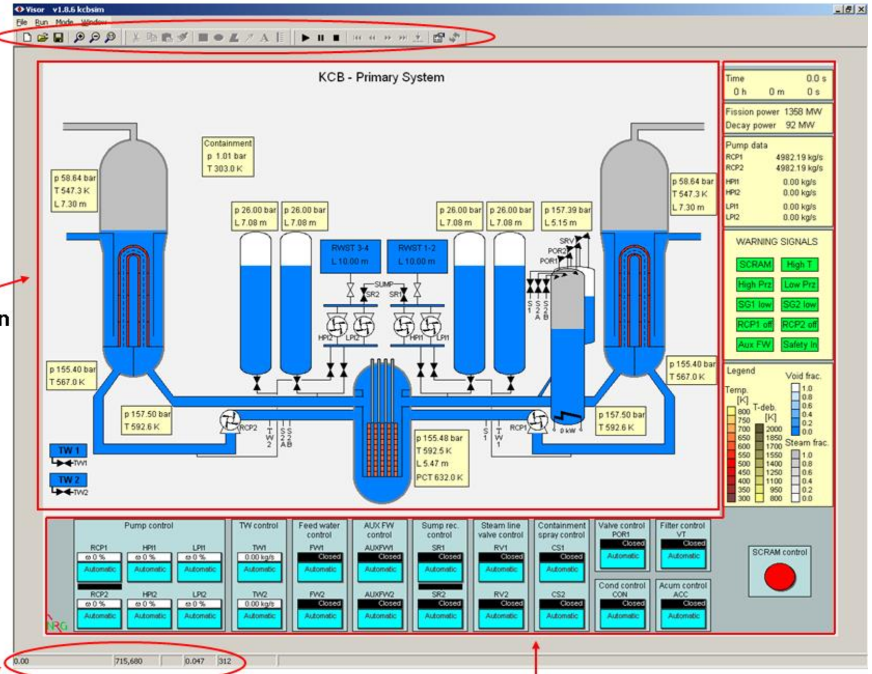
Introduction

Desktop simulator

- ☐ TH codes: MELCOR, RELAP, MAAP and SPECTRA (NRG code)
- ☐ Visor: NRG visualization software compatible with the most widespread TH and SA codes



Window control



Plant mimic screen

Window information

Plant control and display board

Air Oxidation Model in MELCOR (1)

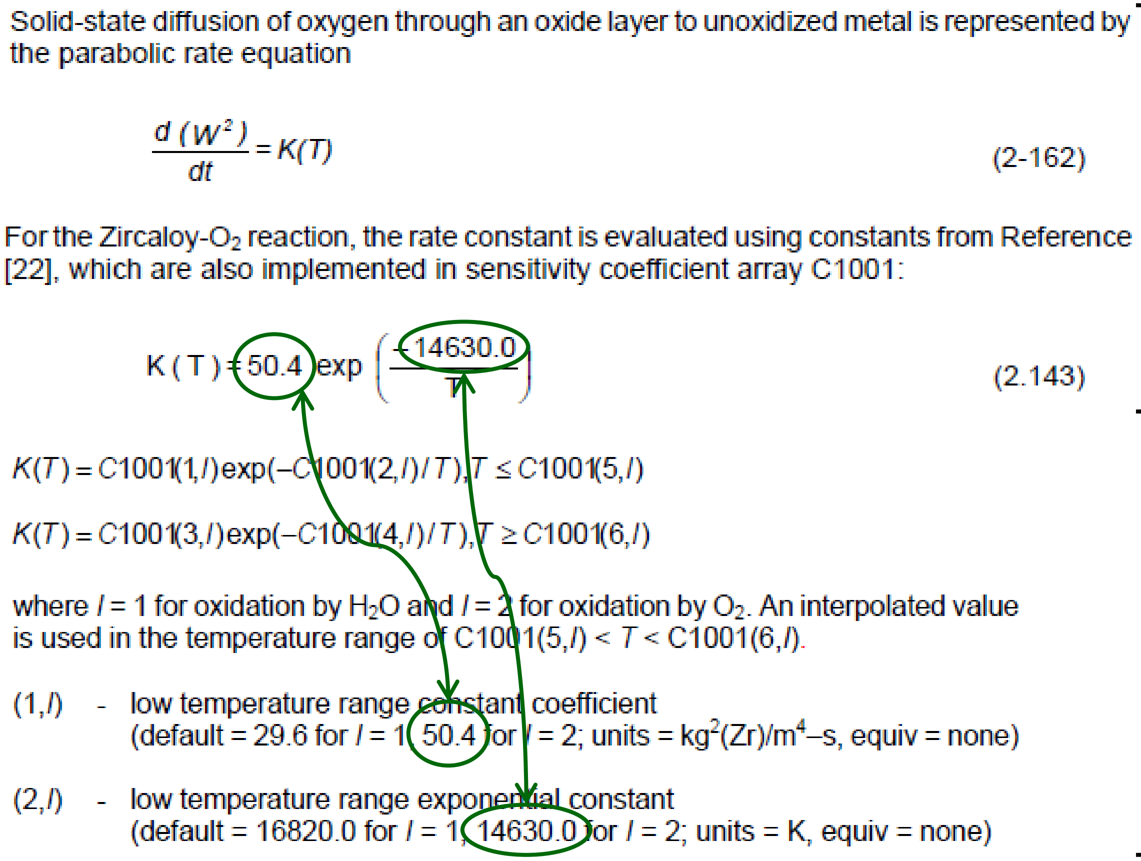
- **MELCOR 1.8.6 (also in 2.1 RM), model of (Benjamin et al., 1979):**

$$\frac{d{m_{Zr}}^2}{dt} = 50.4 \exp\left[-14630/T\right]$$

- **MELCOR 2.1 (description only in UG), model of (Natesan and Soppet, 2004) for the pre- and post-breakaway (both parabolic):**
  - pre-breakaway $$\frac{dm^2}{dt} = 26.7 \exp\left[-17490/T\right]$$
  - post-breakaway $$\frac{dm^2}{dt} = 2970 \exp\left[-19680/T\right]$$

Air Oxidation Model in MELCOR (2)

- The zircaloy oxidation section (2.5.1) of the COR package reference manual has not been modified since version 1.8.6 (September 2005)



Solid-state diffusion of oxygen through an oxide layer to unoxidized metal is represented by the parabolic rate equation

$$\frac{d\,(W^2)}{dt} = K(T) \qquad (2\text{-}162)$$

For the Zircaloy-O_2 reaction, the rate constant is evaluated using constants from Reference [22], which are also implemented in sensitivity coefficient array C1001:

$$K(T) = 50.4 \exp\left(\frac{-14630.0}{T}\right) \qquad (2.143)$$

$$K(T) = C1001(1,I)\exp(-C1001(2,I)/T), T \le C1001(5,I)$$

$$K(T) = C1001(3,I)\exp(-C1001(4,I)/T), T \ge C1001(6,I)$$

where *I* = 1 for oxidation by H_2O and *I* = 2 for oxidation by O_2. An interpolated value is used in the temperature range of C1001(5,*I*) < *T* < C1001(6,*I*).

(1,*I*) - low temperature range constant coefficient
(default = 29.6 for *I* = 1, 50.4 for *I* = 2; units = $kg^2(Zr)/m^4$–s, equiv = none)

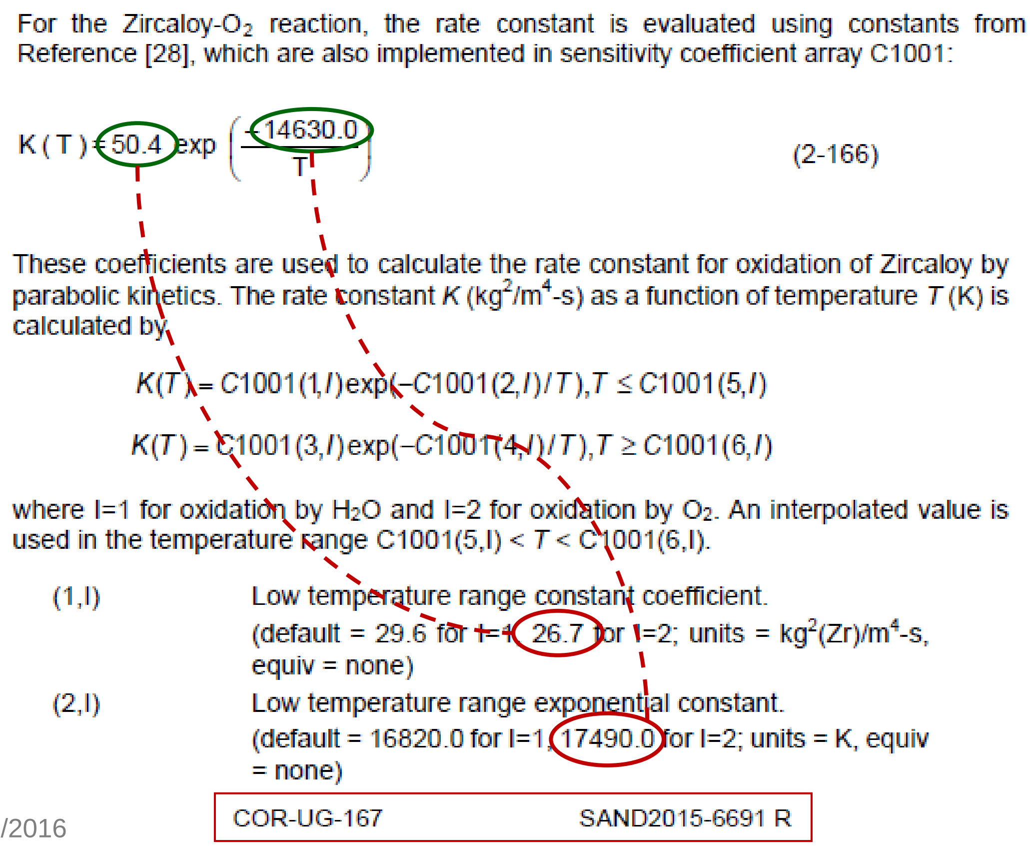
(2,*I*) - low temperature range exponential constant
(default = 16820.0 for *I* = 1, 14630.0 for *I* = 2; units = K, equiv = none)

Reference Manual
(ver. 1.8.6)

User's Guide
(ver. 1.8.6)

Air Oxidation Model in MELCOR (3)

- ☐ **From MELCOR version 2.1 (build 3166) the default values of the sensitivity coefficients for zircaloy-air oxidation have been changed**
- ☐ **No information is given in the Reference Manual regarding the new correlation!**



For the Zircaloy-O_2 reaction, the rate constant is evaluated using constants from Reference [28], which are also implemented in sensitivity coefficient array C1001:

$$K(T) = 50.4 \exp\left(\frac{-14630.0}{T}\right) \qquad (2\text{-}166)$$

Reference Manual (ver. 2.1)

These coefficients are used to calculate the rate constant for oxidation of Zircaloy by parabolic kinetics. The rate constant K (kg^2/m^4-s) as a function of temperature T (K) is calculated by

$$K(T) = C1001(1,I)\exp(-C1001(2,I)/T), T \le C1001(5,I)$$

$$K(T) = C1001(3,I)\exp(-C1001(4,I)/T), T \ge C1001(6,I)$$

where I=1 for oxidation by H_2O and I=2 for oxidation by O_2. An interpolated value is used in the temperature range C1001(5,I) < T < C1001(6,I).

(1,I)	Low temperature range constant coefficient. (default = 29.6 for I=1, 26.7 for I=2; units = $kg^2(Zr)/m^4$-s, equiv = none)
(2,I)	Low temperature range exponential constant. (default = 16820.0 for I=1, 17490.0 for I=2; units = K, equiv = none)

COR-UG-167 SAND2015-6691 R

User's Guide (ver. 2.1)

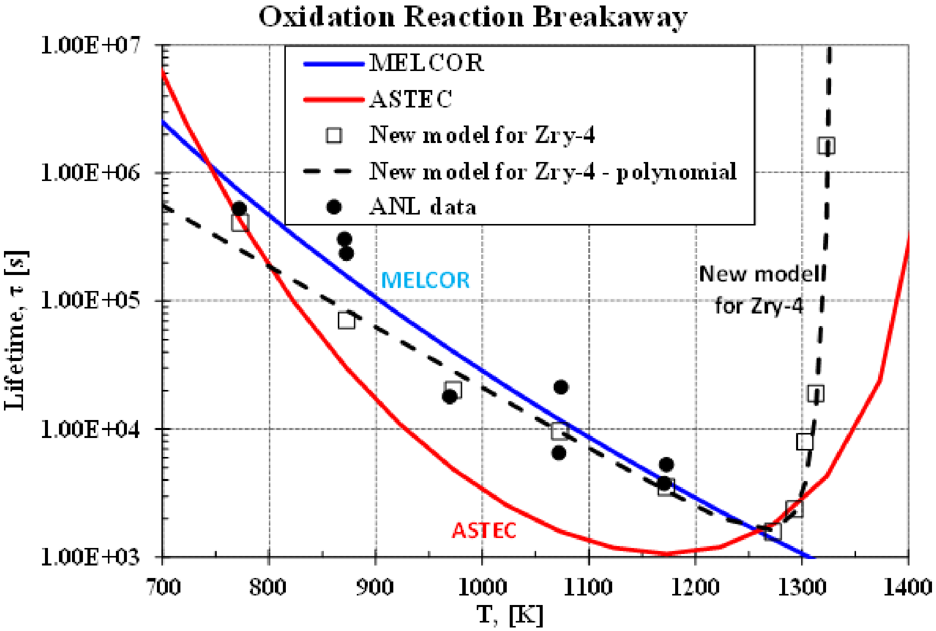
Breakaway Model

- ☐ **Breakaway correlation in MELCOR 2.1 (UG):**

$$\log_{10}(\tau) = 42.038 - 12.528 \times \log_{10}(T)$$

- ☐ **Breakaway may occur at all temperatures.**

- ☐ **Experimental observations show:**
  - ➢ breakaway occurs only at temperatures lower than about 1050°C or 1320 K.
  - ➢ Pre-breakaway reaction is parabolic, $dm^2/dt = A \times \exp(-B/T)$
  - ➢ Post-breakaway reaction is linear: $dm/dt = A \times \exp(-B/T)$.



Comparison of breakaway models (Stempniewicz, 2016)

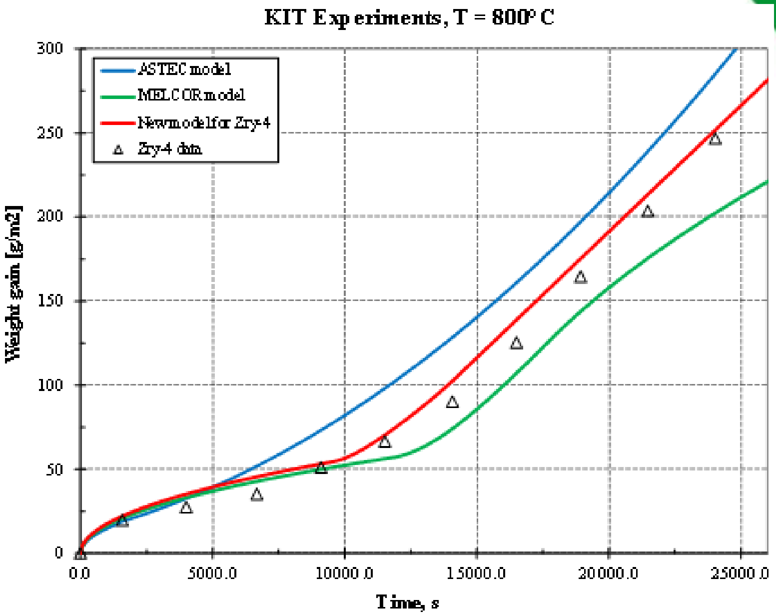
KIT Isothermal Tests

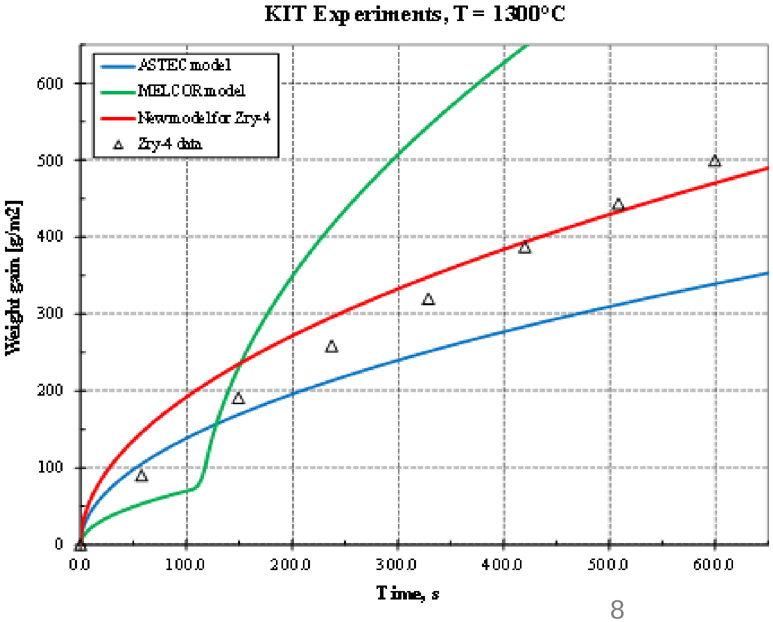
- ❑ **Isothermal oxidation tests were performed at KIT (Steinbrück and Böttcher, 2011).**
  - ➢ Lower temperatures (800°C) – clear breakaway to linear reaction.
  - ➢ Higher temperatures (1300°C) - no breakaway.

- ❑ **MELCOR model**
  - ➢ parabolic post-breakaway reaction ...
  - ➢ ... and non-existent breakaway

- ❑ **ASTEC model (Coindreau et. al. 2010) - better qualitative and quantitative agreement with the tests.**

- ❑ **New set of correlations recently proposed (Stempniewicz, 2016), provides improved agreement for a broad temperature range.**





New Model for Air Oxidation

- ☐ **Description in (Stempniewicz, 2016)**
  - ➢ Consists of a set of correlations applicable for a wide range of temperatures.
  - ➢ Increased accuracy compared to the earlier models.
  - ➢ Applicable for Zry-4 only.

- ☐ **Breakaway occurs only at lower temperatures (breakaway correlation →∞ at about 1050°C or 1320 K)**

- ☐ **Pre-breakaway, parabolic:**

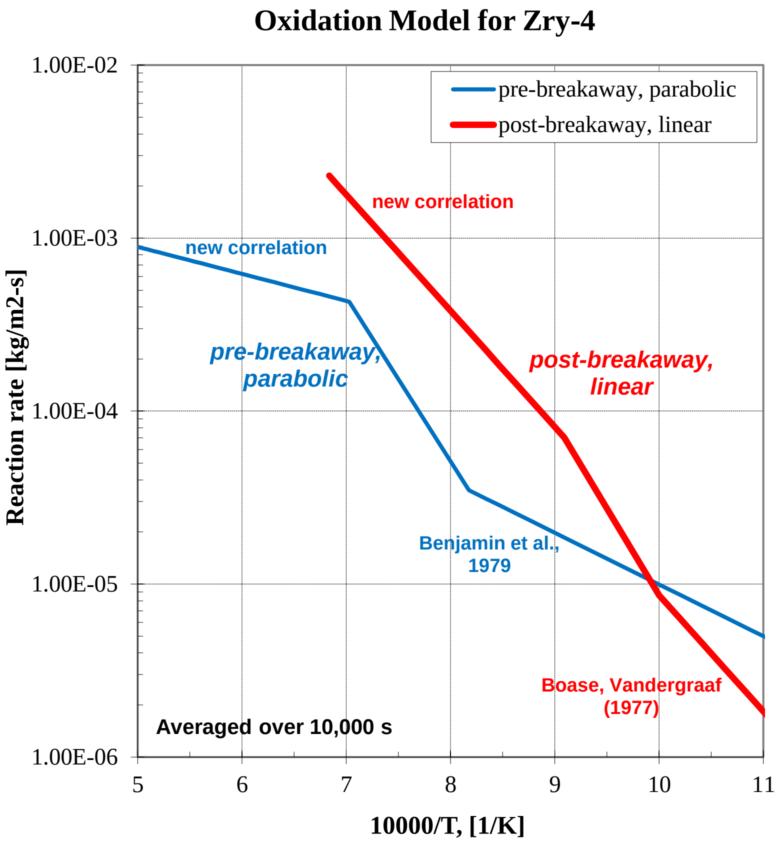
$$\mathrm{d}m^2/\mathrm{d}t = A\times\exp(-B/T)$$

- ▪ *A*, *B*: (Benjamin et al., 1979) for *T*<1223 K
- ▪ *A*, *B*: new coefficients for *T*>1423 K.

- ☐ **Post-breakaway, linear (*T*<1320 K):**

$$\mathrm{d}m/\mathrm{d}t = A\times\exp(-B/T)$$

- ▪ *A*, *B*: (Boase et al., 1977) for *T*<1000 K
- ▪ *A*, *B*: new coefficients for *T*>1100 K.



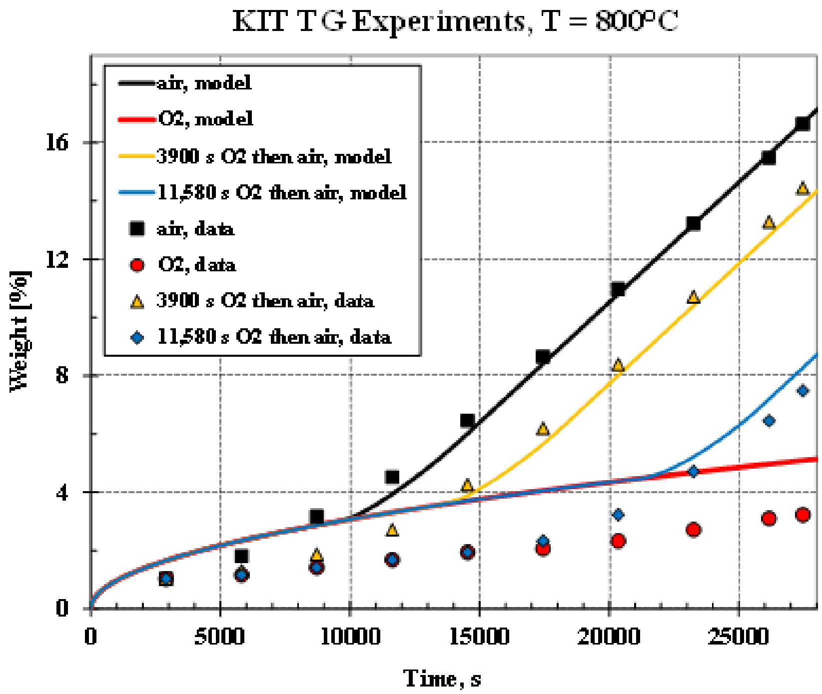
New Zry-4 oxidation model (Stempniewicz, 2016)

Effect of Nitrogen

- **Zirconium nitride (ZrN) increases porosity and breaks up coherent microstructure of the oxide scale and possibly causes breakaway (Birchley and Fernandez-Moguel, 2012).**

- **Models of (Birchley and Fernandez-Moguel, 2012) and (Stempniewicz, 2016) were developed based on air oxidation data. Nitrogen is treated as a catalyst, not an active species.**

- **TG tests at KIT (Steinbrück, 2009):**
  - performed with air, oxygen alone, and different periods of pre-oxidation in oxygen followed by air.
  - results of the (Stempniewicz, 2016) model are compared to measured data. The trends and magnitudes are reasonably well captured by the model.



KIT TG test data and model (Stempniewicz, 2016)

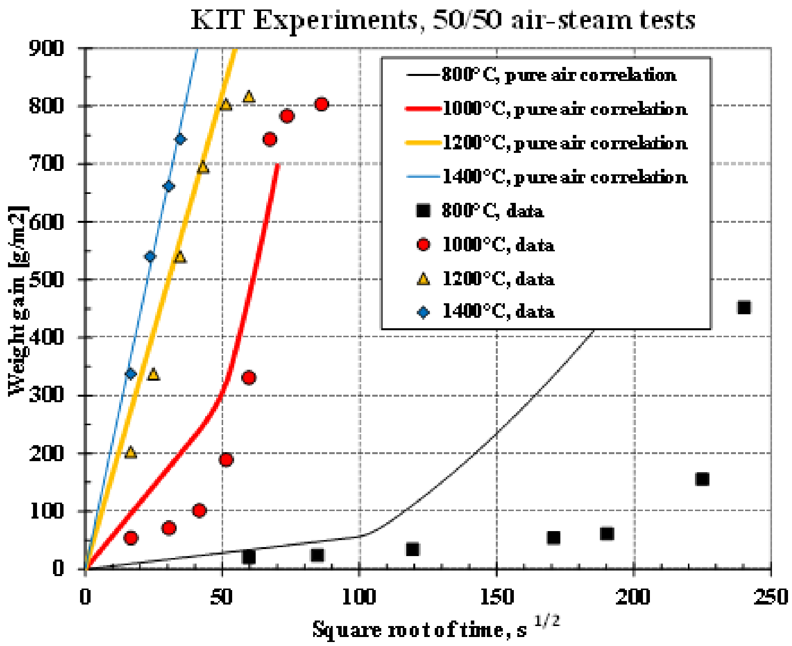
Effect of Steam

- **Oxidation in air-steam environment – KIT tests (Steinbrück, 2009), *T* = 800, 1000, 1200 and 1400ºC.**

- ***T*=800 and 1000ºC, transition to faster kinetics after ~10 h, 50 min, respectively. For comparison, air oxidation: transition after ~3 h and 30 min, respectively.**

- **Conclusion: presence of steam delays breakaway due to reduced nitrogen attack.**

- **Model of (Stempniewicz, 2016) appropriate for pure air oxidation:**
  - 800ºC: breakaway at ~3 hours (square root of time ~100 $s^{1/2}$), experiment: ~10 h (square root of time ~200 $s^{1/2}$).
  - presence of steam delays breakaway, which is not taken into account in the current model.
  - A suitable model correction is yet to be developed.



KIT test data and model (Stempniewicz, 2016)

Conclusions

- ☐ **Air oxidation model in MELCOR**
  - ➢ Pre- and post-breakaway models available in MELCOR 2.x, however not described in the Reference Manual.
  - ➢ Critical remarks:
    - ▪ breakaway is possible at all temperatures,
    - ▪ post-breakaway reaction rate is parabolic.
- ☐ **New Models**
  - ➢ Model of (Birchley and Fernandez-Moguel, 2012) implemented in MELCOR but not described.
  - ➢ Model of (Stempniewicz, 2016) has improved accuracy for Zry-4 – may be recommended for implementation in the future versions.

References

(Benjamin et al., 1979)

A.S. Benjamin, D.J. McCloskey, D.A. Powers, S.A. Dupree, "Spent Fuel Heatup Following Loss of Water During Storage", SAND77-1371, NUREG/CR-0649, Sandia National Laboratories, Albuquerque, NM, March 1979.

(Birchley and Fernandez-Moguel, 2012)

J. Birchley, L. Fernandez-Moguel, “Simulation of air oxidation during a reactor accident sequence: Part 1 - Phenomenology and model development”, Annals of Nuclear Energy, 40, pp. 163-170, 2012.

(Boase and Vandergraaf, 1977)

D.G. Boase, T.T. Vandergraaf, “The Canadian Spent Fuel Storage Canister: Some Material Aspects”, Nuclear Technology, Vol. 32, pp. 60-71, January 1977.

(Natesan and Soppet, 2004)

K. Natesan, W.K. Soppet, “Air Oxidation Kinetics for Zr-Based Alloys”, NUREG/CR-6846, ANL-03/32, June 2004.

(Coindreau et al., 2010)

Coindreau, O., Duriez, C., Ederli, S., "Air oxidation of Zircaloy-4 in the 600– 1000°C temperature range: modeling for ASTEC code application", Journal of Nuclear Materials 405, 207–215, 2010.

References

(Steinbrück, 2009).

M. Steinbrück, “Prototypical experiments relating to air oxidation of Zircaloy-4”, Journal of Nuclear Materials, 392, pp. 531-544, 2009.

(Steinbrück and Böttcher, 2011).

Steinbrück, M., & Böttcher, M. (2011). "Air oxidation of Zircaloy-4, M5® and ZIRLO™ cladding alloys at high temperatures", Journal of Nuclear Materials, 414, 276-285, 2011.

(Stempniewicz, 2016)

M.M. Stempniewicz, “Air Oxidation of Zircaloy Part 2 - New Model for Zry-4 Oxidation”, Nuclear Engineering and Design, IN PRESS, 2016

Thank you for your attention!
Questions?