MELCOR COR Oxidation Models

2019 European MELCOR User Group Meeting

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., , for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525

Oxidation Models - General

Objects that can oxidize
- COR components
  - Metals include Zr, SS, and B4C
- Debris in CAV package

Objects that cannot oxidize
- Heat structures

Oxidation behavior for COR components
- Oxidation of Zircaloy and steel by water vapor and/or O_2
- Oxidation of boron carbide (B_4C) in BWRs
- Heat generation by oxidation
- Release of hydrogen (and other gases) to CVH package

Oxidation

Specific models for each oxidizing material

Reaction Kinetics

Zircaloy
- Reactions
- Kinetics

Steel
- Reactions
- Kinetics

Boron Carbide
- Reactions

Zircaloy-H2O reaction,

$$K(T) = 29.6 \exp\left(\frac{-16820.0}{T}\right) \quad \text{for } T < 1853.0$$

$$K(T) = 87.9 \exp\left(\frac{-16610.0}{T}\right) \quad \text{for } T \geq 1873.0$$

Zircaloy-O2

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

B4C Control Rods

Control Blade Geometry
- B4C in small stainless steel tubes (0.25 in OD)
- Exterior stainless steel sheath (cruciform)
- Liquefaction of tubes at 1450 K to 1500 K (eutectic)
- Oxidation of B4c limited to 2%

Rod Geometry
- Pellet geometry with larger diameter
- More resistant to dissolution by SS-B4C
- Complete B_4C liquefaction at 1700 K
  - Oxidation begins at 1500 K (start of B_4C liquefaction)
  - Candling of control material
- Specified by user on COR_B4C record

Before MELCOR 1.8.6, B_4C oxidation modeling reflected only BWR-type control blades

ANL Air Oxidation Experiments

Principal investigators, K. Natesan and W. Soppet

- NUREG/CR-6846, "Air Oxidation Kinetics for Zr-Based Alloys"

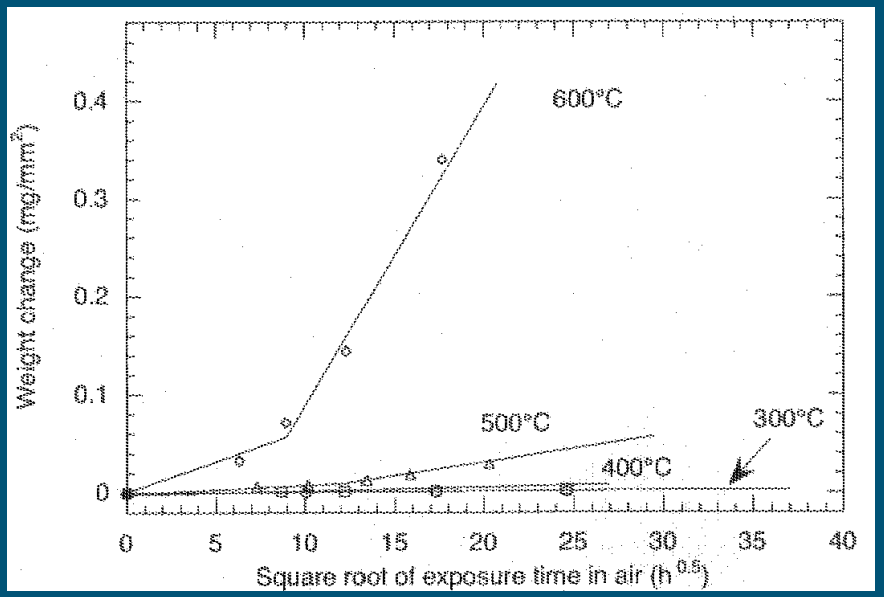
Initial tests (low temperature)

- Thermogravimetic test apparatus (TGA) used to measure specimen weight change
  - Bare samples
  - Steam pre-oxidized (25-30 μm oxide layer thickness)
- Oxidation in dry air or steam
  - Weight gain recorded as a function of sqrt(time)
- All-purpose Correlation from range of data (Zircaloy-4)
  - Bare (i.e., no initial oxide layer) samples in air
  - Bare samples in steam
  - Steam pre-oxidized in air

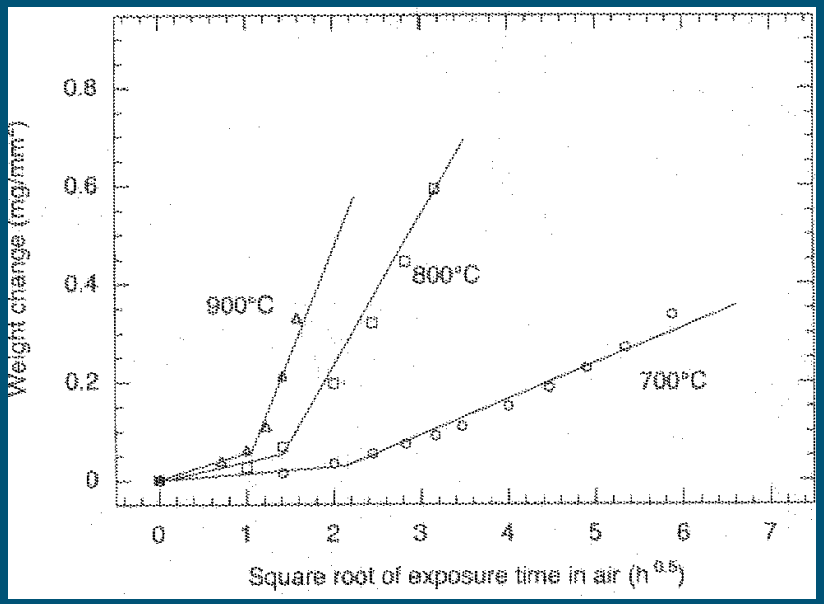
ANL Air Oxidation Experiments

- **Breakaway consistently observed in all ANL oxidation tests**
  - **Whether bare or pre-oxidized**
  - **Not a function of oxide thickness**
  - **Correlate breakaway timing with sample temperatures**

Low temperate data (Zr-4,steam pre-oxidized)



High temperature data (Zr-4,steam pre-oxidized)



SNL Lifetime Breakaway Model

Lifetime rule similar to Larson-Miller creep

- Used to capture the time-at-temperature characteristics of breakaway

Local damage is tracked for all Zircaloy components

$$LF = \int_0^t dt' \frac{t'}{\tau(T)}$$

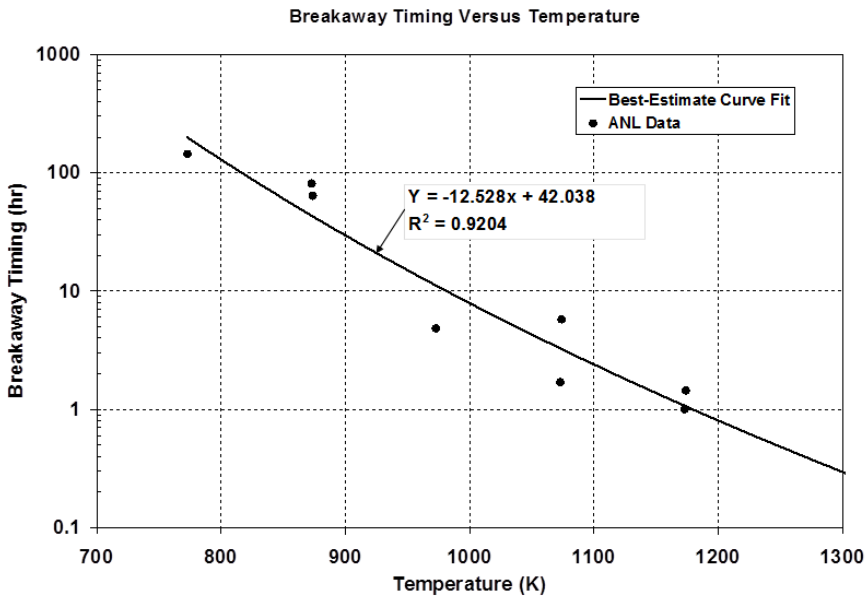
where,

$$\tau(T) = 10^{P_{LOX}}$$

$$P_{LOX} = -12.528 \cdot \log_{10} T + 42.038$$

Parameters come from experimental curve fit

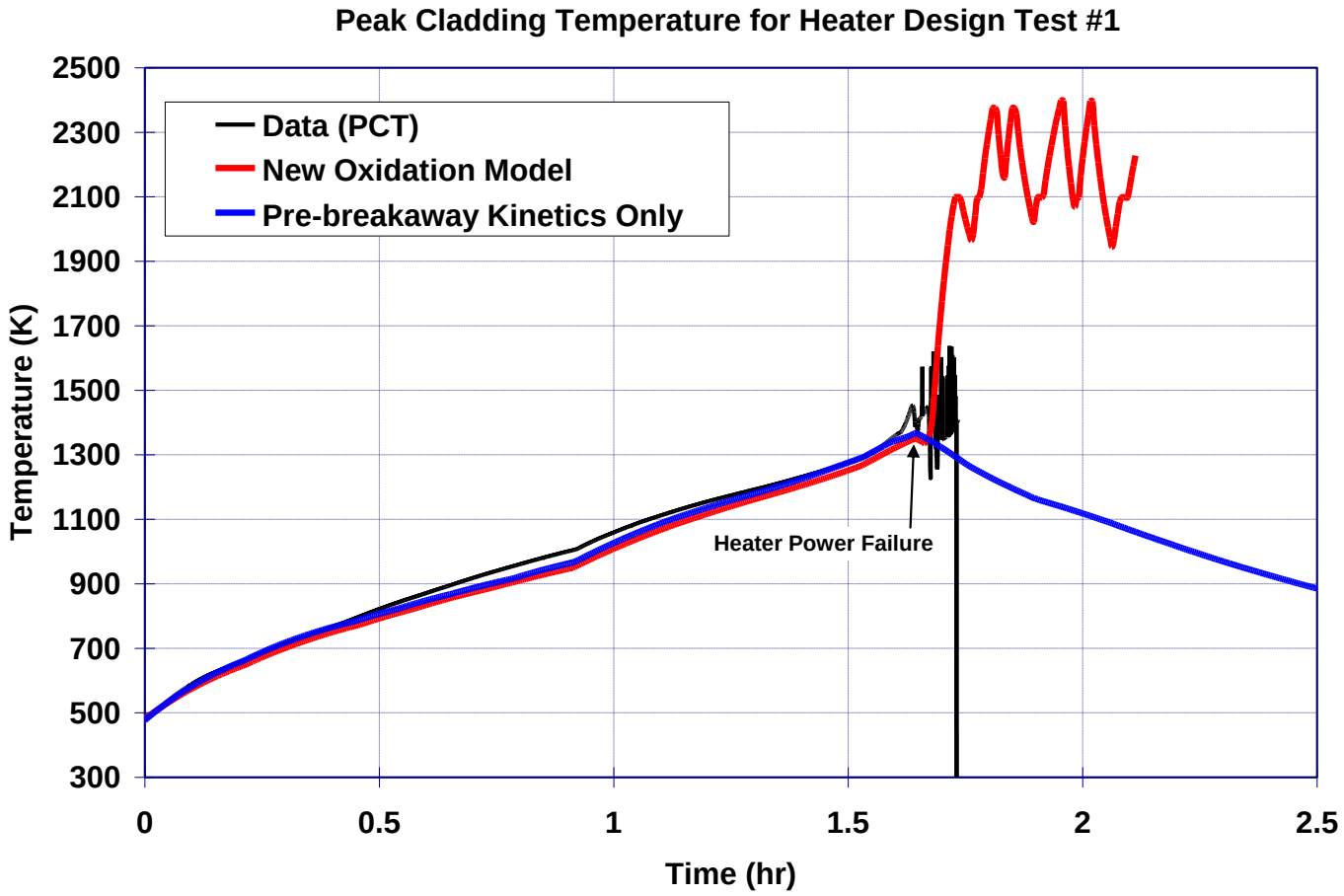
Failure occurs when damage function reaches 1



COR-ZROX-TLEFT(IA,IR)	Time left in lifetime for clad component in cell (IA,IR). (units = sec)
COR-ZROX-LIFE(IA,IR)	**Value of the oxidation breakaway function for clad component in cell (IA,IR). (units = -)**
COR-ZROX-TLEFT.n	Time left in lifetime for clad component in cell n. (units = sec)

Comparison to Heater Design Test #1

Comparison calculations with and without breakaway kinetics



MELCOR SNL Breakaway Model Input Records

COR_OXB

- Enables breakaway air oxidation model
- 3 options
  - 0 – Off
  - 1 = Clad and Canister
  - 2 = All components (not recommended)
- Sensitivity coefficients 1016 and 1017

MELCOR SNL Breakaway Model Input Records

COR_OXB – Zircaloy Air Oxidation Breakaway model

Optional.

The input parameters are

(1) IOXB

Oxidation model option.

(a) 0
Breakaway model is off.

(b) 1
Breakaway model is on for clad and canister.

(c) 2
Breakaway model is on for all Zircaloy components (not recommended).

(type = integer, default = none, units = none)

Example

```
COR_OXB 1
```

MELCOR SNL Breakaway Model Input Records

1016 – Zircaloy Post-Breakaway Oxidation Rate Constant Coefficients

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

$$K(T) = C1016\,(1,I)\exp(-C1016\,(2,I)/T)$$

where I=1 for oxidation by H_2O and I=2 for oxidation by O_2. Currently, although there is provision for using a breakaway model for oxidation by steam, this is thought to be unnecessary and the steam coefficients are zero.

(1,I)	Constant coefficient. (default = 0 for I=1, 2.97e3 for I=2; units = kg^2(Zr)/m^4-s, equiv = none)
(2,I)	Exponential constant. (default = 0 for I=1, 19680.0 for I=2; units = K, equiv = none)

MELCOR SNL Breakaway Model Input Records

1017 – Lifetime Parameters for Breakaway Model

The lifetime parameter for Zircaloy-air oxidation breakaway is given by

$$P_{LOX} = C1017(1) \cdot \log_{10} T + C1017(2)$$

where T is the clad temperature in K. The default values are from a fit by Randy Gauntt. The time to breakaway in seconds is given by

$$\tau = 10^{P_{LOX}}$$

where T is the temperature in K.

(1)	Inherently negative multiplicative constant. (default = -12.528, units = none, equiv = none)
(2)	Inherently positive additive constant. (default = 42.038, units = none, equiv = none)

MELCOR SNL Breakaway Model Input Records

1018 – Maximum Lifetime for Breakaway Model

The maximum lifetime used in the lifetime rule is normally 1.0. However, it was found that a smoother change from pre-breakaway to post-breakaway gave a better fit to experimental data. The results of the Spent Fuel Pool Experiment (SFP) suggest that a maximum lifetime of 1.2 gives a better fit for the default breakaway parameters.

(1) - Maximum lifetime.
(default = 1.2, units = none, equiv = none)

PSI Air Oxidation Model

Initially, oxidation kinetics follows a parabolic law

- Uses Arrhenius law similar to default MELCOR

$$C = A \exp(-B/T)$$

- Oxide Thickness
  - Does not account for oxygen dissolved in metallic zirconium, α(Zr-O)

$$d(\delta)/dt \sim C'/\delta_{eff}$$

$$\delta = \Delta m \frac{M(ZrO_2)}{\rho(ZrO_2)M(O_2)}$$

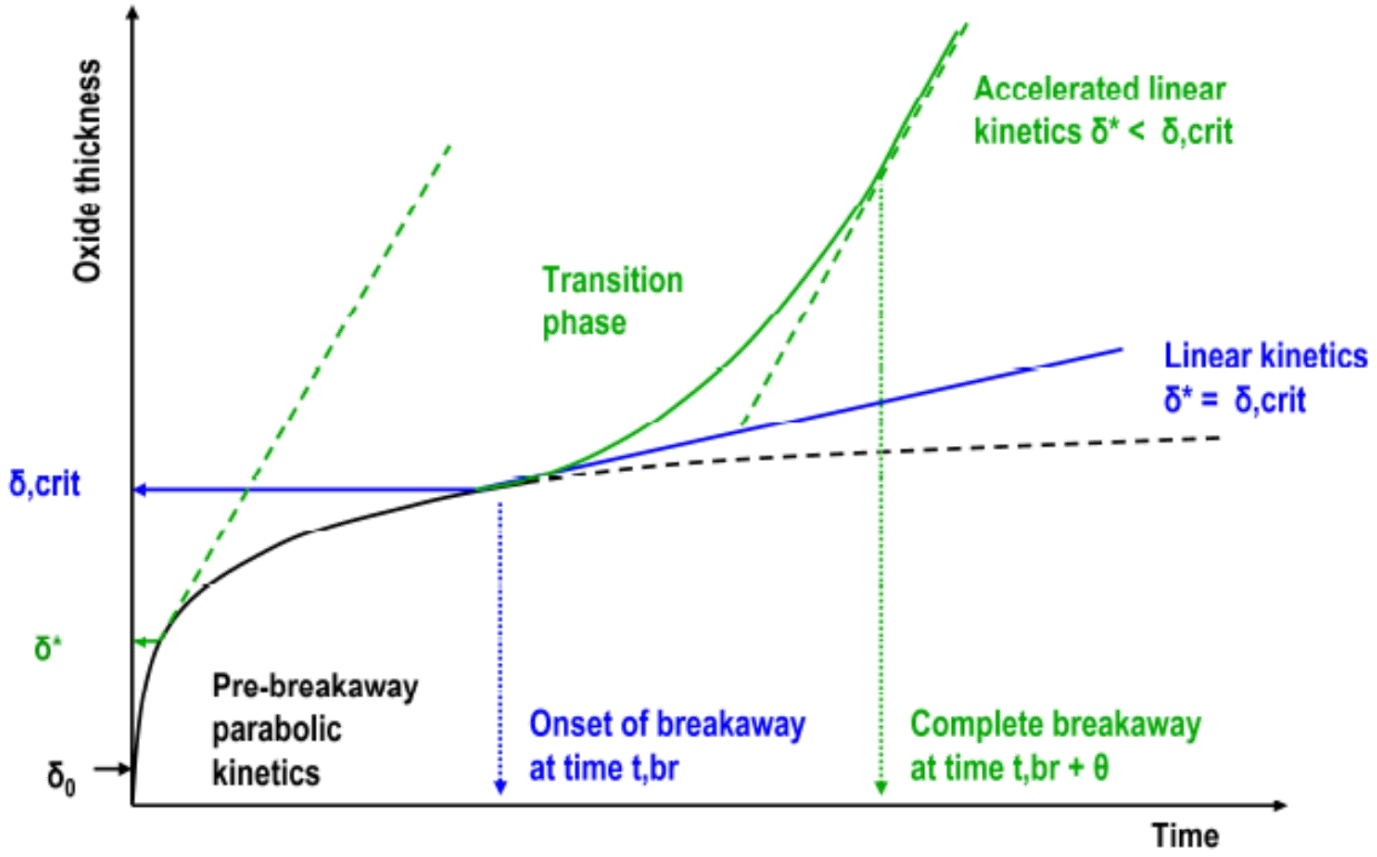
Δm is the mass gain / area
M(X) is the molecular weight of species X

- Alternate oxidation models are available to user
  - i.e., (Urbanic-Heidrick, etc)

Transition to linear initiates at critical thickness

- When δ reaches δ,crit transition to linear (breakaway) is initiated
- The 'effective' oxide thickness (more porous microstructure) decreases from δ,crit to δ* during transition
- When oxide thickness reaches δ*, transition is complete

PSI Air Oxidation Model



Jonathan Birchley, Leticia Fernandez-Moguel, Simulation of air oxidation during a reactor accident sequence: Part 1 – Phenomenology and model development, Annals of Nuclear Energy, Volume 40, Issue 1, February 2012, Pages 163-170, ISSN 0306-4549

Considerations for Application of PSI Model

- Critical thicknesses, δ,crit and δ^* are dependent on Temperature
  - Since effective thickness, δ_{eff}, decreases, oxidation rate increases during transition
- Transition is physical and numerically stable
- Empirical fits to important data
  - Empirical fits to δ,crit and δ^*
  - Empirical fit for rate of change in δ_{eff} during transition

$$\delta^*_{eff} = \left(\delta, crit - \delta^*\right) \cdot f(t)$$

Where the degradation fraction, f(t), changes with time during transition at an empirically fitted rate

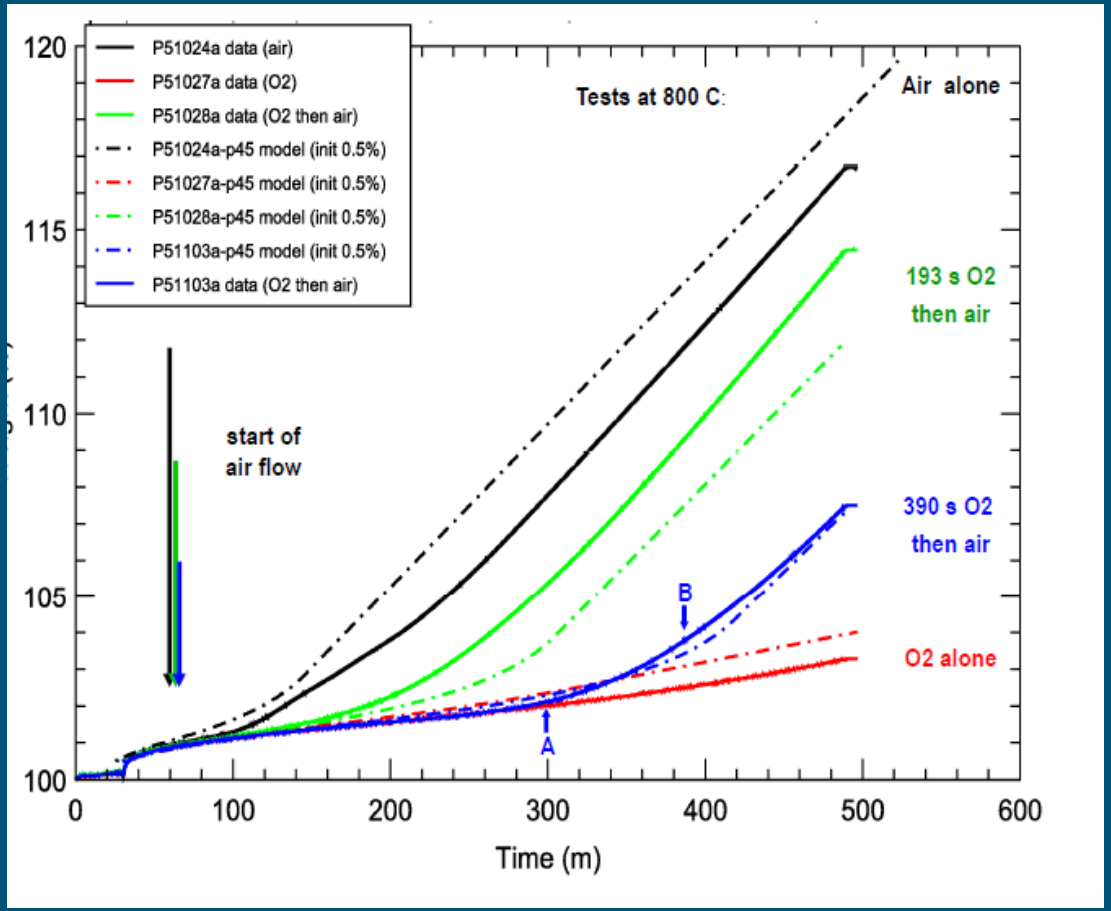
- When local breakaway is calculated, it is not deactivated.
- Model does not reproduce large hydrogen generation during reflood (i.e., Q-16)
  - Does not account for previously damaged oxide layer
  - Does not account for nitriding

PSI Assessment with SET data

Model uses a criterion for onset of breakaway (A) and a timescale for full transition (B)

The oxide thickness formed during preoxidation provides a protective layer when cladding is later exposed to air

- Breakaway would start at δ^* without protective layer



Fernandez-Moguel, "Status of PSI air Oxidation Model," From EMUG 2014 Meetings

PSI Air Oxidation

MELCOR original oxidation modeling is still available

PSI model improves flexibility for steam oxidation

- New steam oxidation models are available to users:
  - Cathcart-Pawel/Urbanic Heidrick
  - Leistikov-Schanz/Prater-Courtright
  - Leistikov
  - Urbanic-Heidrick
  - Sokolov
- Previously, these models were only available through sensitivity coefficients

Several Air oxidation models to choose from

Several options for enabling breakaway

COR_OX – PSI Oxidation model of Zircaloy-4 for cladding

Optional.
The user may activate and set parameters for PSI cladding oxidation model.

(1) MODEL – Key for PSI oxidation model activation:
0 – MELCOR oxidation model is used;
1 – PSI oxidation model is used.
(type = integer, default = 0, units = none)

The following data must be input if MODEL = 1 only:

(2) STEAM – Steam oxidation model:
<0 – Use parameters from sensitivity cards
0 – Cathcart-Pawel/Urbanic-Heidrick;
1 – Leistikov-Schanz/Prater-Courtright;
2 – Leistikov;
3 – Urbanic-Heidrick;
4 – Sokolov;
5 – Grosse.
(type = integer, default = 0, units = none)

(3) AIR – Air oxidation model:
<0 – Use parameters from sensitivity cards
0 – Hofmann-Birchley;
1 – Hayes-Roberson/Leistikov-Berg (NUREG1);
2 – Powers (NUREG2) (Birchley);
3 – Melcor (Birchley);
4 – Mozart (Birchley).
(type = integer, default = 0, units = none)

(4) OXYGEN – Oxygen oxidation model:
<0 – Use parameters from sensitivity cards
0 – Hofmann

(5) NOBRK – Breakaway switch:
0 – switch on for steam and air;
1 – switch off for steam, on for air;
2 – switch off for steam and air.
(type = integer, default = 0, units = none)

Implementation

- Partitioning of CVH oxidant inventory among COR cells
  - Account for flow blockages
    - Steam in CVs connected to more than one ring is partitioned by unblocked area
  - Account for steam starvation
    - Calculation is performed in direction of flow
- Partitioning among surfaces in a cell
  - Partioned among active surfaces
    - Loop over surfaces - selects active surface areas
  - Loop over materials – Zr, SS, B4C, Gr
  - Loop over intact components/conglomerate
  - Loop over oxidizers
- ORNL modification for two or more reacting materials in OS/SS/NS components
  - 60% to Zr,
  - 40 % to other material(s), either
    - 40% SS or
    - 20% SS, 20% B4C

Additional Considerations

Two-sided components residing in channel with a surface in contact with bypass can oxidize
- Volume expansion accommodated through borrowing virtual volume from bypass

Zirconium emissivity is calculated as a function of oxide thickness

Oxidation can be disabled on a cell-by-cell basis by CF
- Flow blockage modeling
- COR_NOX record

Oxidation calculated for submerged surfaces
- Gas film between unquenched surfaces and pool

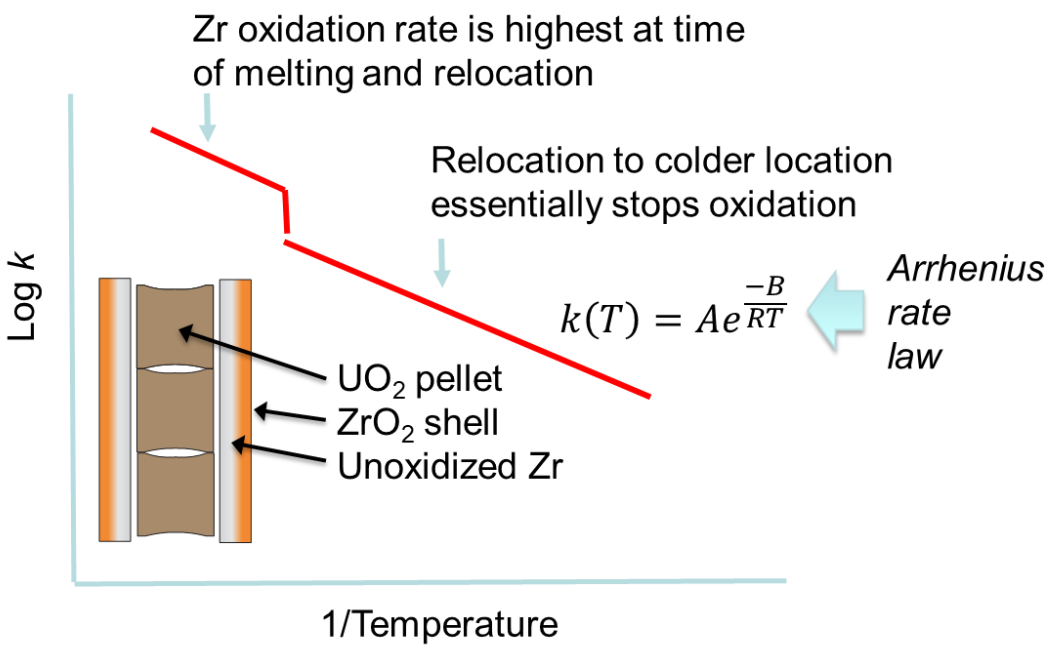
Debris surface area is partitioned between Zr, SS, and other materials
- Surface area for Zr oxidation from volume fraction of Zr + ZrO2
  - Modeled as layers with ZrO2 outer layer
- Surface area for SS oxidation from volume fraction of SS + SSOX
  - Modeled as layers with SSOX outer layer

Oxidation Time Scales and Relocation of Materials

parabolic rate law → $\frac{d\delta^2}{dt} = k(T)$

$\delta = oxide\ shell\ thickness$

$k(T) = reaction\ rate$

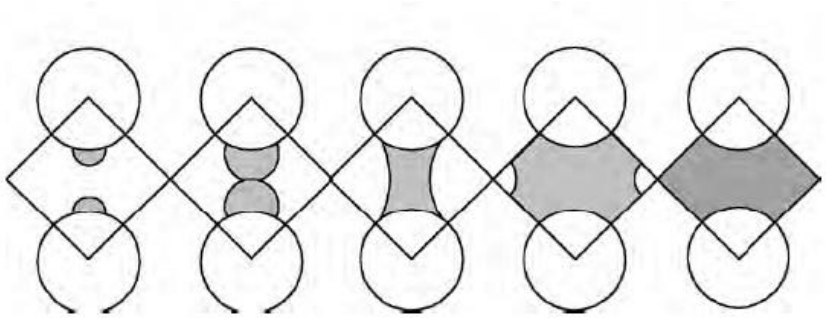


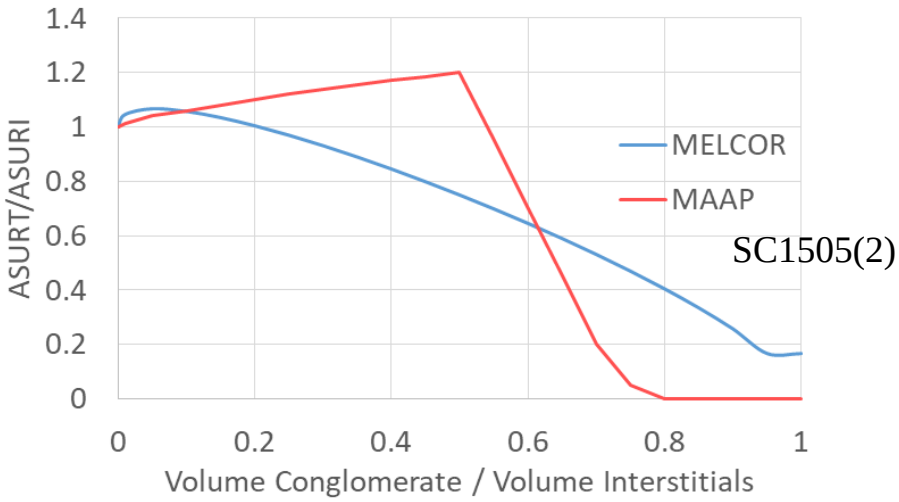
- $Zr + 2H_2O \rightarrow ZrO_2 + 2H_2 + energy$
- Reaction rate is autocatalytic (accelerates with T)
- Decay power heatup rate ~1K/s
- Oxidation power heatup rate ~15K/s
- *Short time between start of oxidation and relocation of liquefied Zr*

Modified Surface Areas Due to Conglomerate Freezing

The MELCOR candling model calculates modified surface areas used for both oxidation and heat transfer

- Similar to rodded geometry but modified for spheres
- Oxidation and convective heat transfer use reduced surface areas:
  - ASURC - Conglomerate
  - ASURY - exposed intact surface area
- Sensitivity coefficient used to set minimum surface area
  - SC1505(2) = 0.05 SOARCA Best Practice
  - Was 0.001 in M186
  - Currently 0.001 for M2.2 default





SC1505(2)

How Are they Used

- ASURT - Convective Heat Transfer
- ASURI - Radiation
- ASURI - Intact component area
- ASURC, ASURY – Oxidation

ASURT=ASURC+ASURY

What's Missing – Oxidation during candling

Oxidation disabled during candling

- Molten material is held up within a component
  - if the oxide thickness is greater than a critical value Δr_{hold}
  - if the component temperature is less than a critical value T_{breach}
  - if no candling from the component in that cell has yet taken place.
- Hot Zr in contact with steam during candling
  - Metallic Zr gets a free pass to relocate to a colder location
    - Error in timing or quantity of hydrogen generation
    - Energy of oxidation may allow candling to progress further than calculated

1. Molten mass $M_{m,0}$ originates with temperature $T_{m,0}$ and hence a certain amount of superheat

$$Q_{sh,0} = M_{m,0} c_{p,m} \left(T_{m,0} - T_{mp}\right) \textit{Superheat}$$

2. Heat transfer to surface at each axial level

$$\Delta q_i = h_{m,o} \Delta z_i \left(T_{m,i} - T_{s,i}\right)$$

3. Fraction of molten mass frozen at each elevation
   Molten film cooled only to melting point

$$\Delta M_{m,i} = \frac{\Delta q_i - Q_{sh,i}}{H_i} \qquad \textit{Mass frozen}$$

4. Masses and energies updated

$$M_{m,i} = M_{m,i-1} - \Delta M_{m,i}$$

$$Q_{sh,i} = Q_{sh,i-1} - \Delta M_{m,i} \cdot E_{LHF} + Q_{Ox,i-1}$$

Energy of oxidation, change in mass due to oxidation, and change in melt temperature and properties not accounted for

Comparison to Experiment

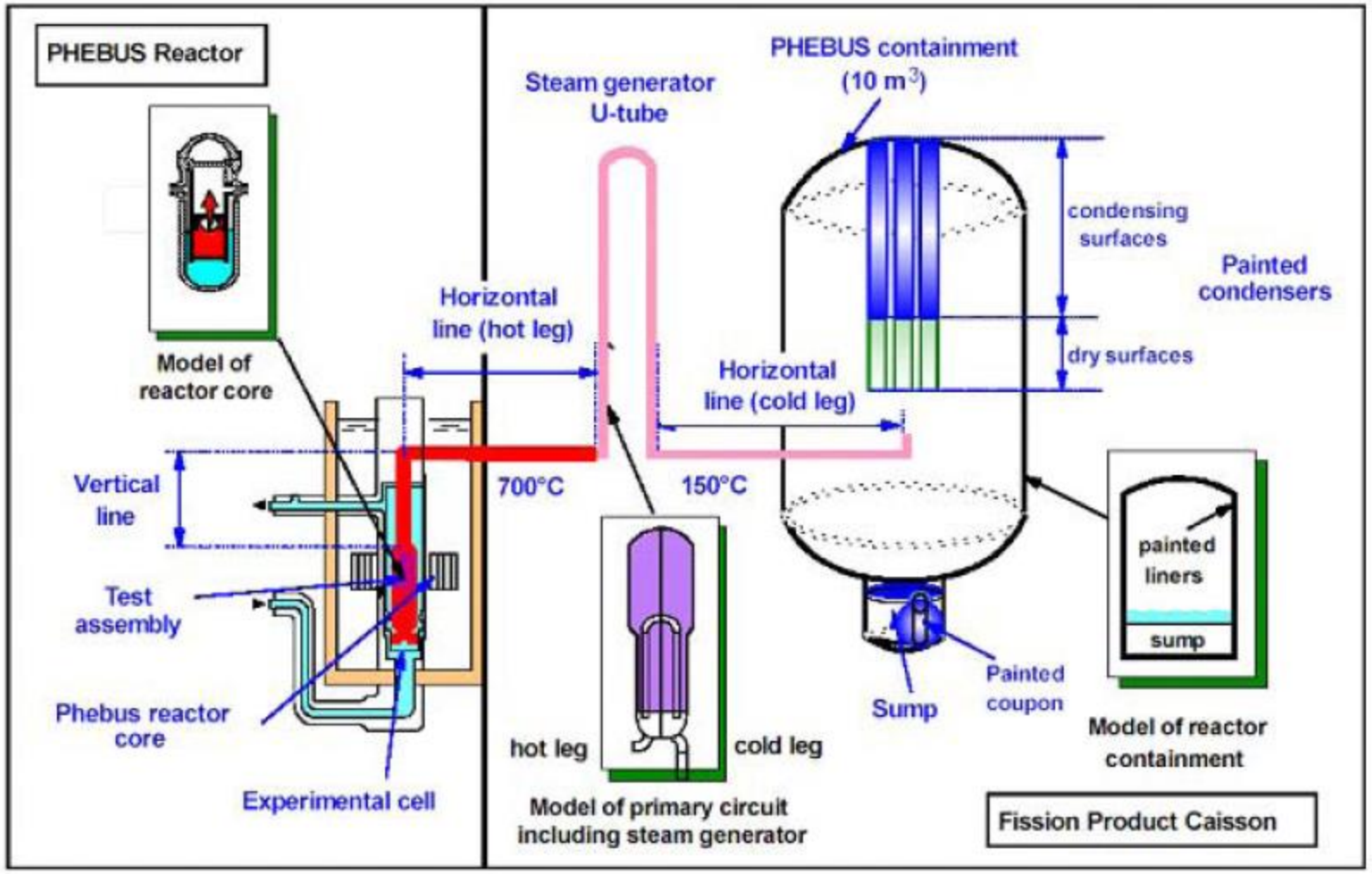
Comparisons are indirect, based on H2 generation and temperature rise

Phebus FPT1, FPT3
- H2 and Temperature data

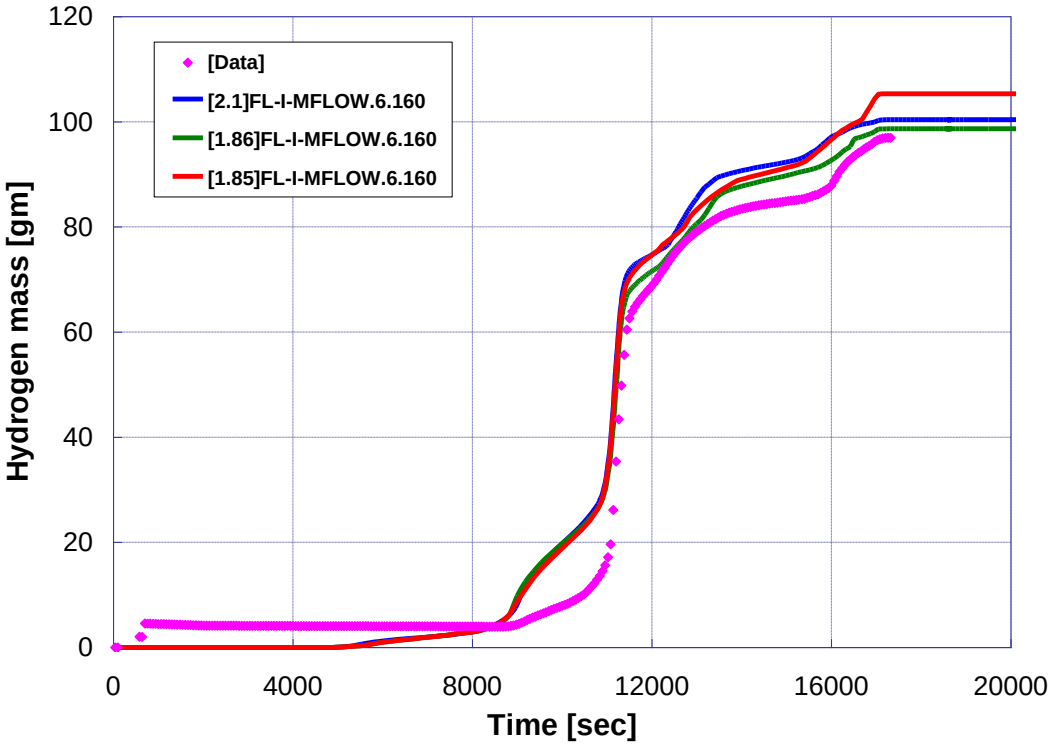
CORA13
- H2 and Temperature data

LOFT-FP2
- Temperature only

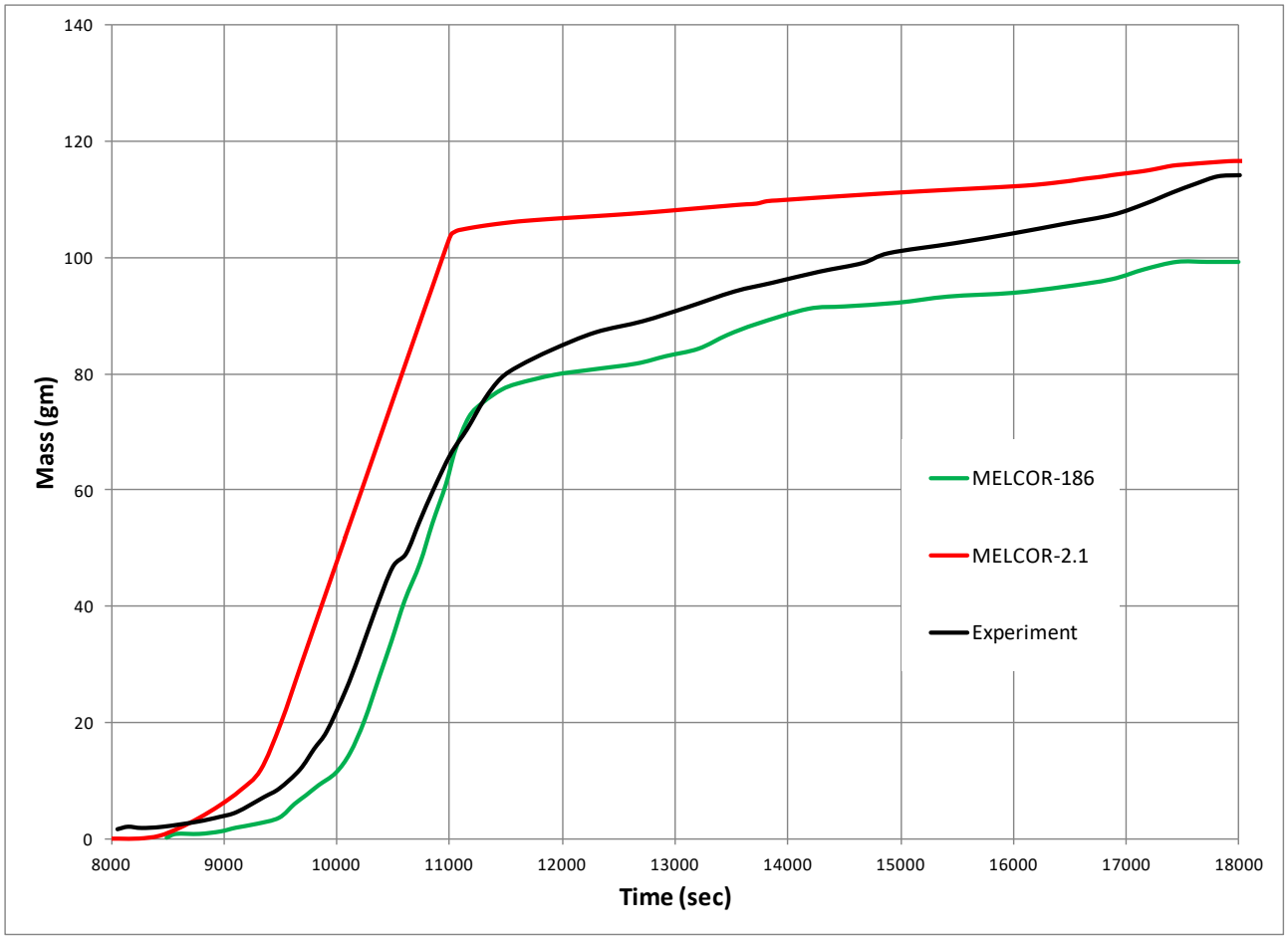
PHEBUS Facility



Phebus FPT1 Hydrogen Generation



FPT3 Hydrogen Generation

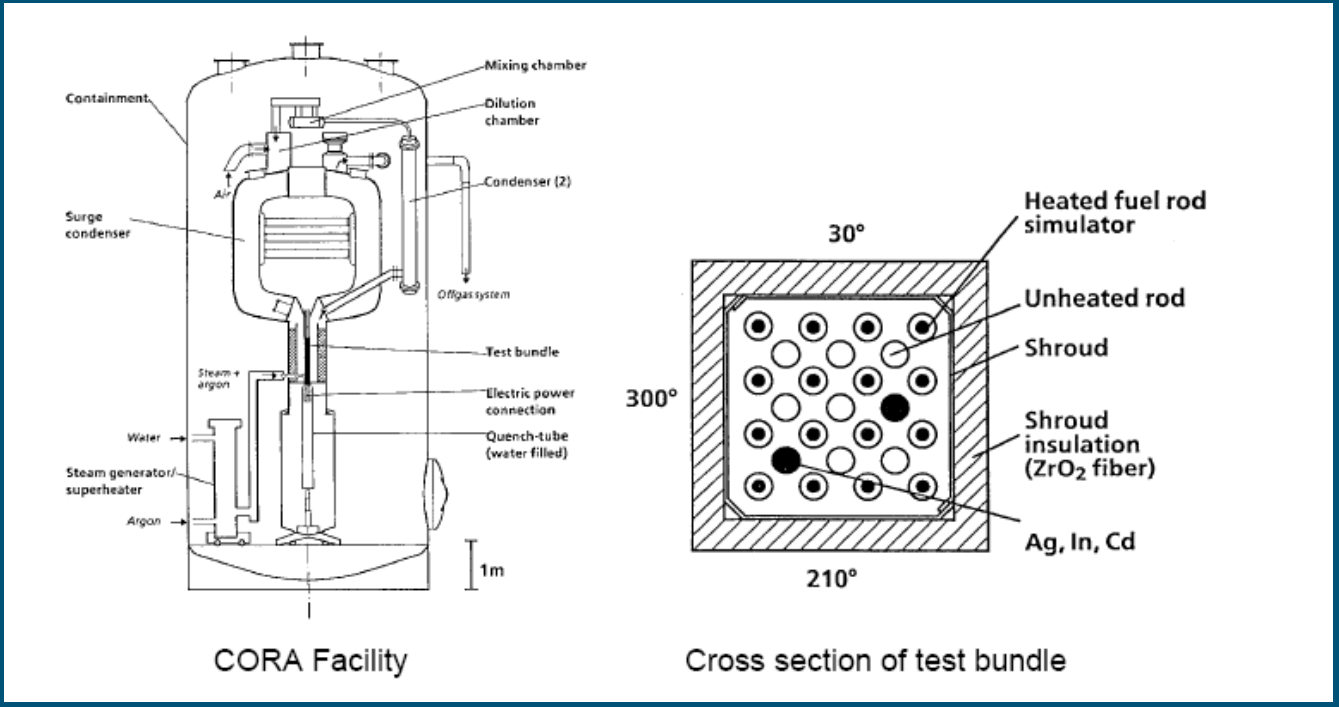


CORA 13 (ISP 31)

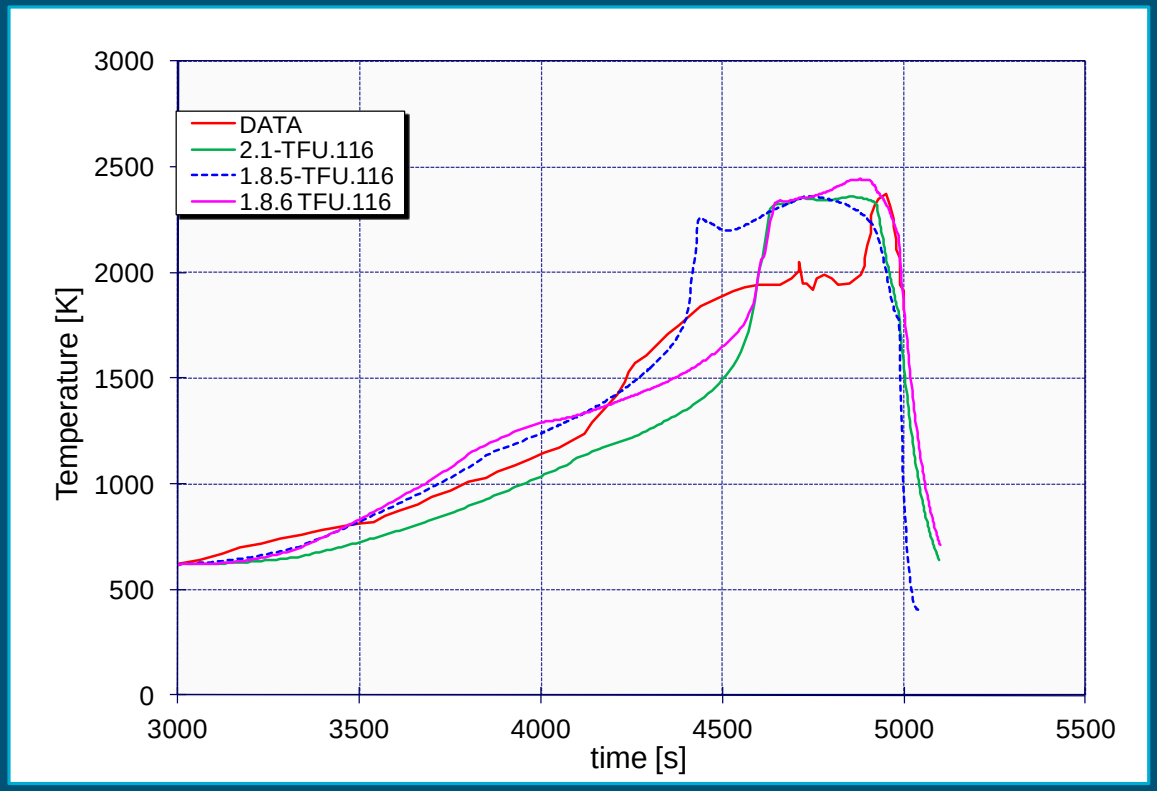
Intermediate scale fuel bundle heatup facility

Measured H_2 generation, relocation, temperatures

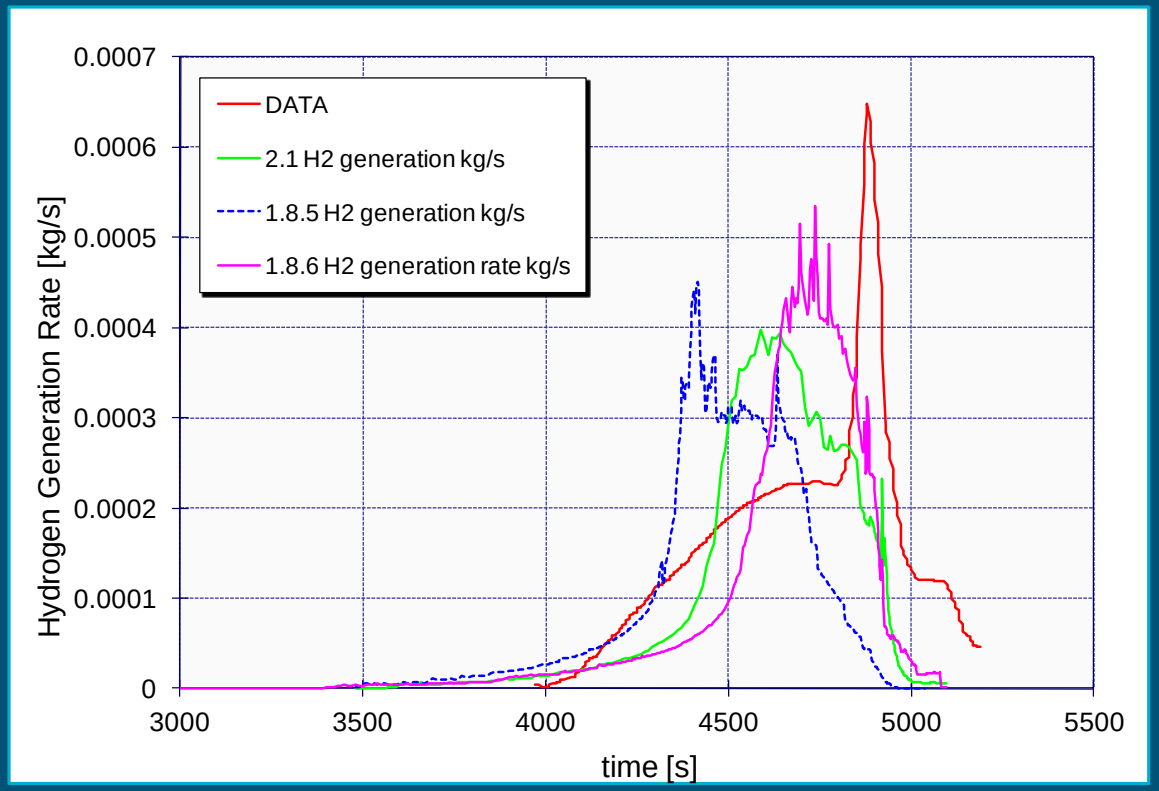
Test time was 5051 s



CORA-13 Fuel Temperature at 1150mm

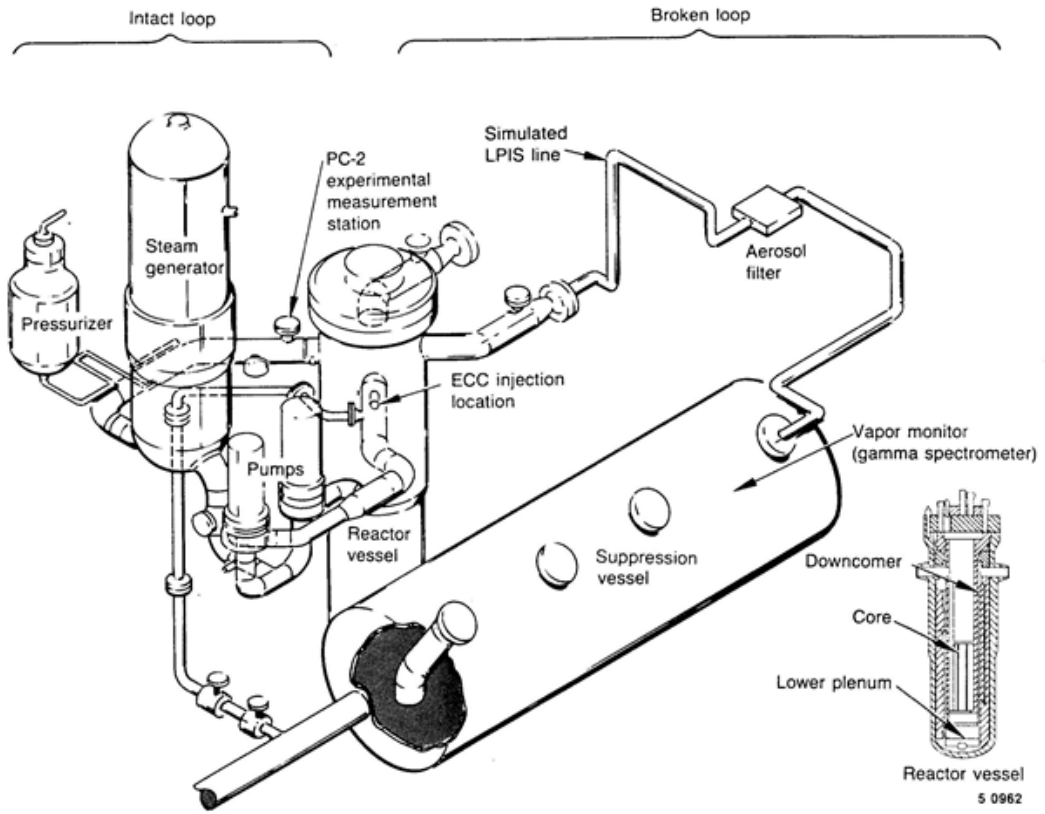


CORA-13 Hydrogen Generation



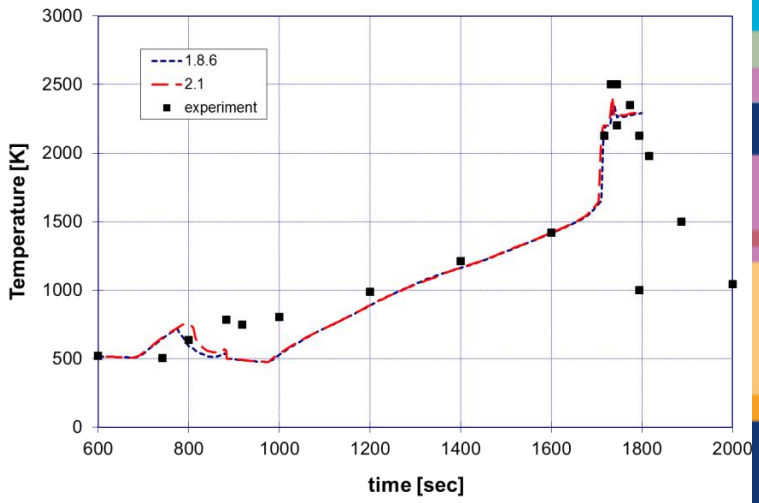
LOFT-FP2

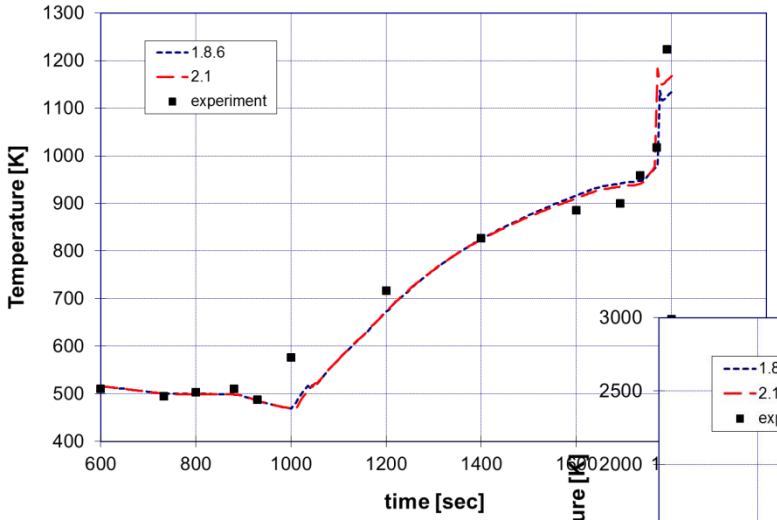
- Experiment is to a 50 MW(t) volumetrically scaled PWR system



LOFT-FP2 Cladding Temperature

At 0.25 m





At 1.07 m