Status of PSI air Oxidation Model

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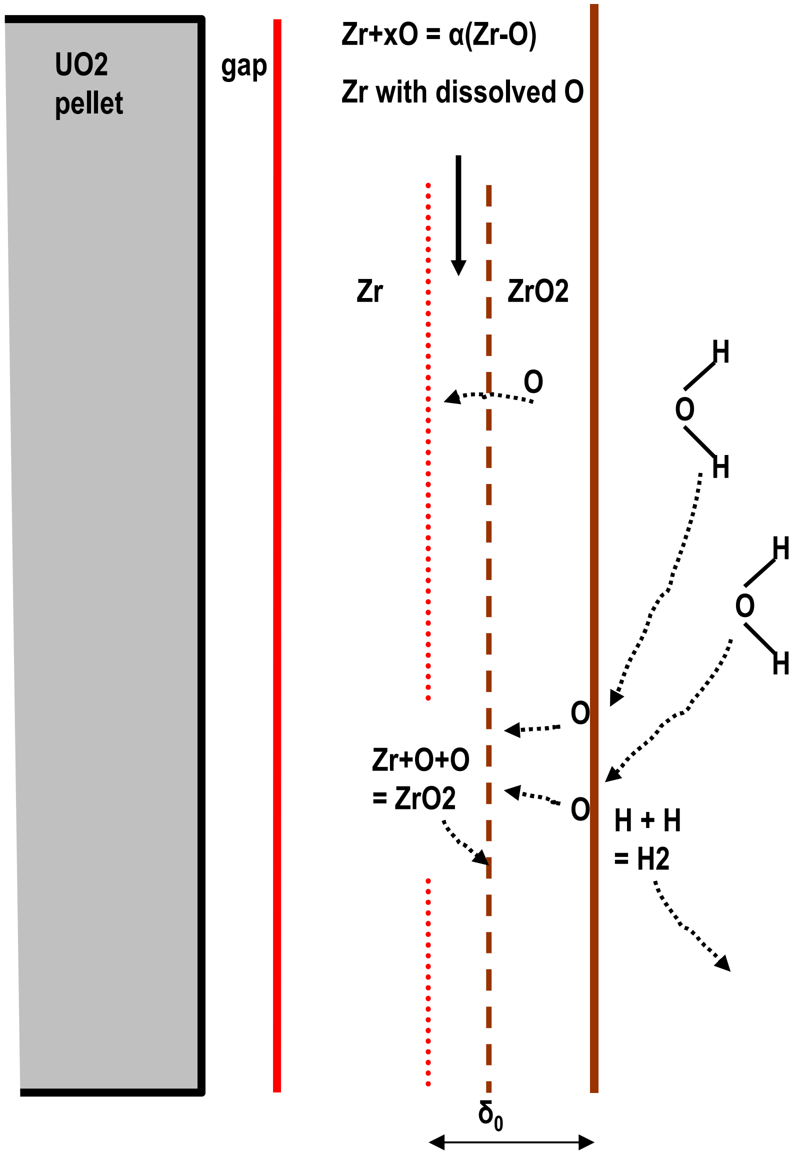
Outline

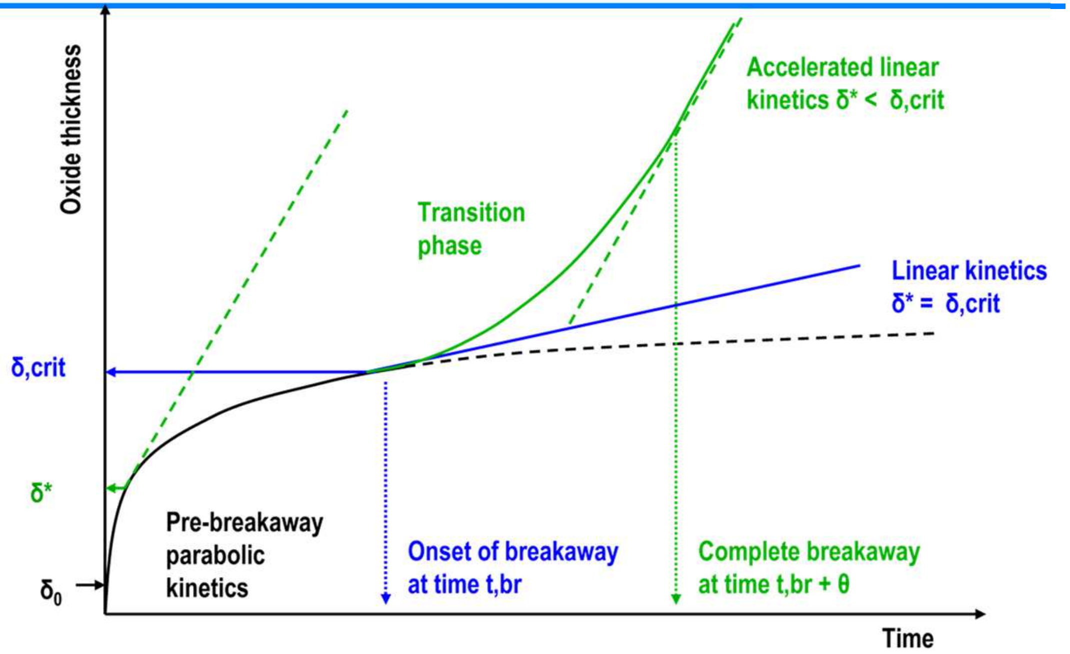
- Background
- Current status of modelling in MELCOR
- Additional “breakaway control” options
- PSI model limitations
- PhD on nitriding model development
- Summary and outlook

Background

- A model was developed at PSI to calculate accelerated oxidation in steam and/or air
- Aimed at air ingress and spent fuel pool scenarios
- It is supposed that the oxidation behaviour is breakaway (or breakaway-like) characterised by transition from **parabolic to linear kinetics**
- Breakaway criteria dependent on temperature and presence (or not) of N2
- Steam or oxygen (not air) is the oxidising species
- N_2 treated as a catalyst, not an active species in modelling thus far;
- Implemented in versions of SCDAPSim and MELCOR
- Options
  - 0: enable breakaway with or without N2 (default)
  - 1: enable breakaway only with N2
  - 2: disable breakaway (reverts to standard parabolic kinetics)

Model concept





- Model consider pre-oxidation in steam does not consider the α(Zr-O)

- The oxide thickness formed during preoxidation provides a protection when the cladding is exposed to air

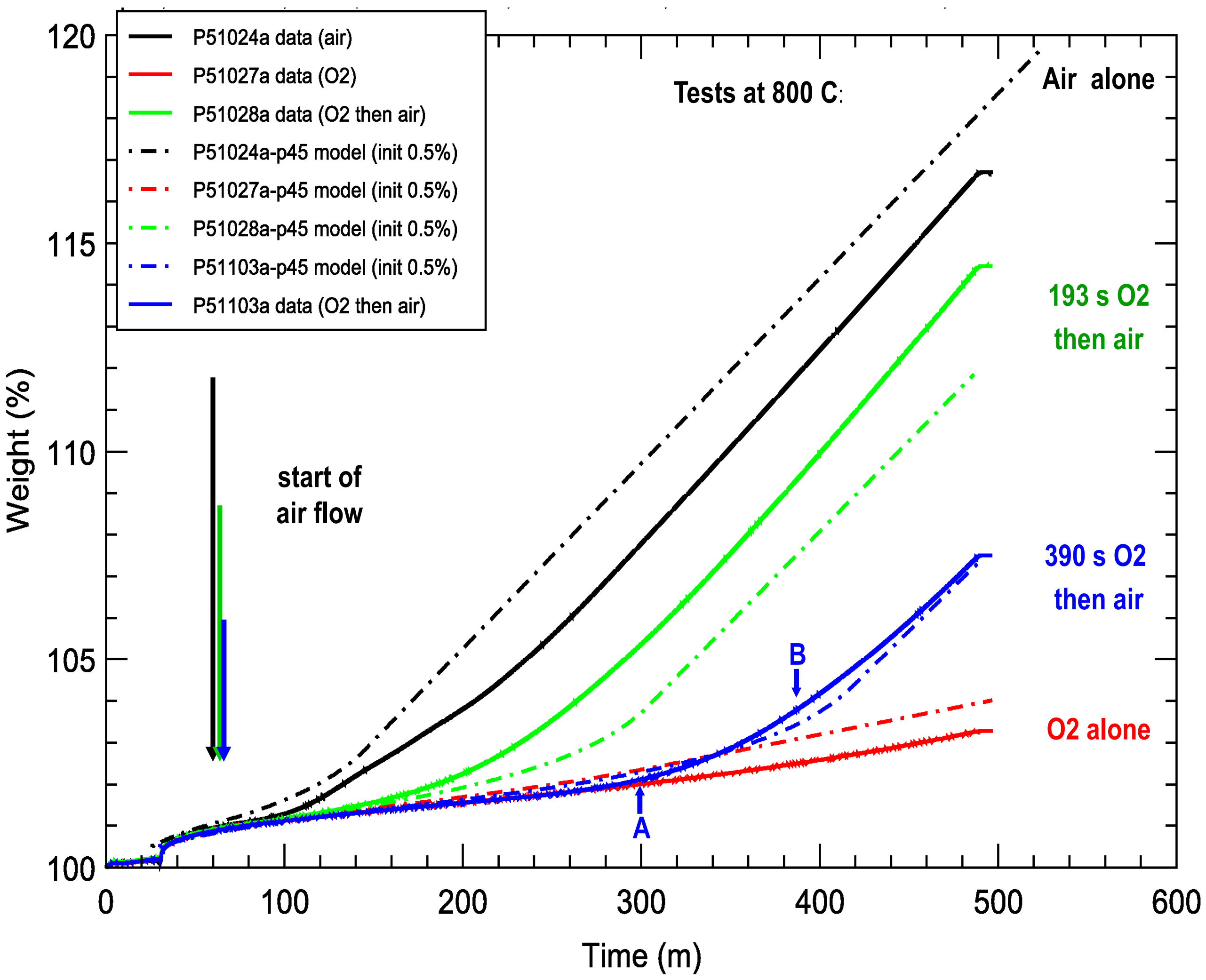
- Breakaway would start at δ* if no protective layer would exist (this marks the onset of breakaway).

- Accelerated linear kinetics when δ,crit is reached

Background - comparison with SET data

Acceleration to linear kinetics in air greatly delayed by short pre-oxidation in oxygen

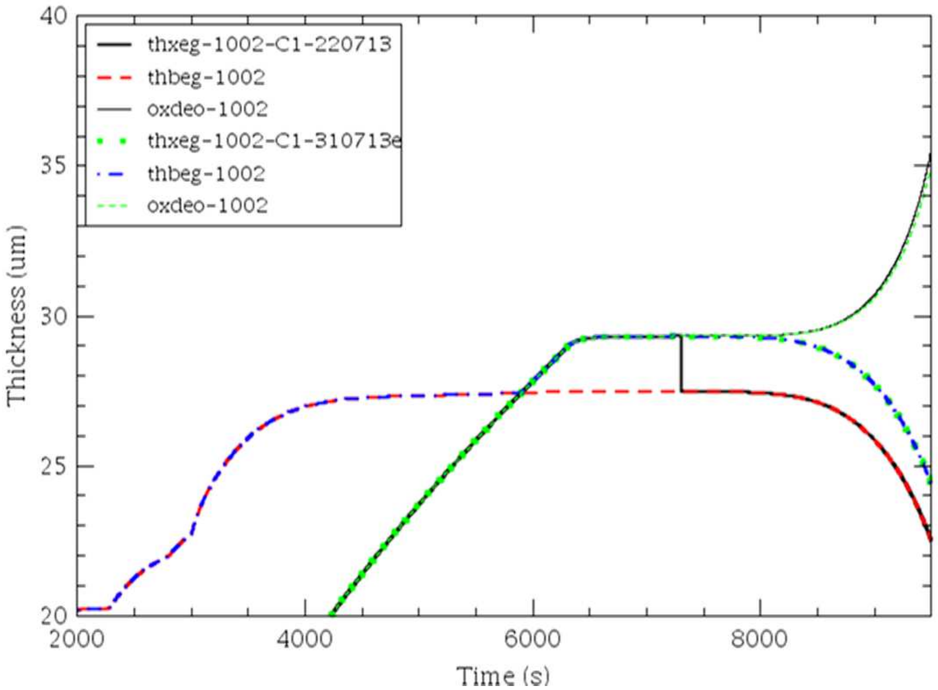
Model uses a criterion for onset of breakaway (A), and a timescale for full transition (B)



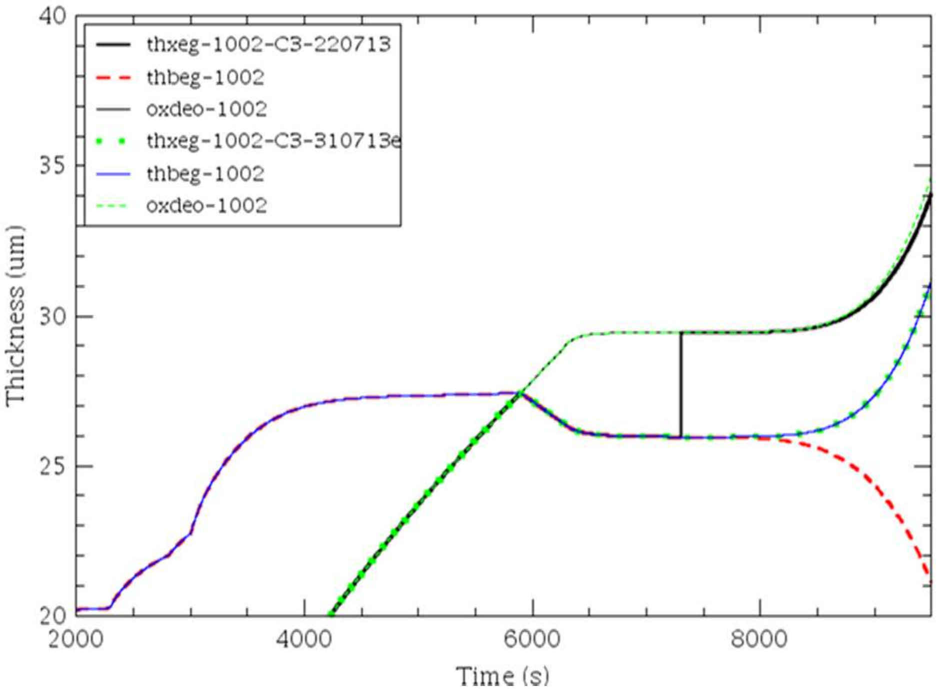
Revised PSI model

- Allow breakaway in steam ,disable for air…
- In developing this option we have identified an anomalous behavior when breakaway was disabled
  - Transition to breakaway was happening too fast
  - The code logic was revised to avoid this anomaly

Breakaway only in air



Breakaway only in steam



- Six additional options for assesment purposes were added
- Implemented in SCDAPSim and MELCOR
- Consistecy between 2 code was checked

Additional options

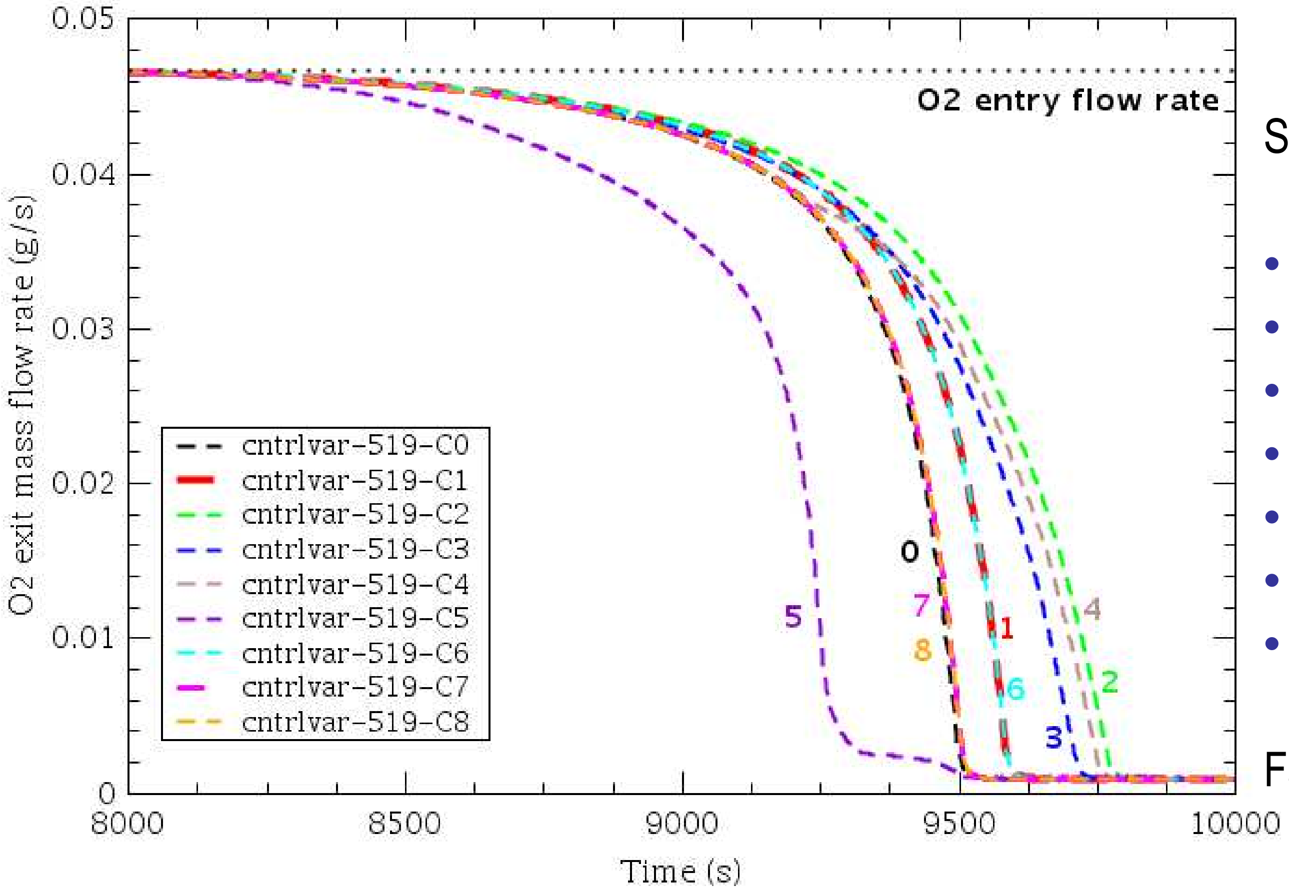
- **We do not believe the model is sound enough to be able to recommend, unconditionally, one option over the others**
  - the breakaway mechanism is still unclear, or at least depends on processes not modelled
  - hence the need to optionally and selectively turn it off
- **Additional options following discussion at the last European MEL COR User Group**
  - 3: disable breakaway with N2
  - 4: enable breakaway with or without N2, with N2 the same as without (i.e. air is like steam)
  - 5: enable breakaway with or without N2, without N2 the same as with (i.e. steam is like air)
  - 6: disable breakaway without N2 unless already in breakaway
  - 7: disable breakaway with N2 unless already in breakaway
  - 8: disable breakaway with N2 if preoxidised without N2 and not already in breakaway
- **We would recommend**
  - 0 as baseline
  - 5 for cases where N2 is present but difficult to model
  - 2, 4 (instead of 3), 6 (instead of 1), 7 for sensitivity studies
  - 8 to address inhibiting effect of in O2 or steam pre-oxidation on breakaway in air

- Changes implemented in local version of M1.8.6

Simulation of QUENCH-16 – benchmark case

Rate of oxygen consumption depends on choice of breakaway option

In baseline case limited breakaway in steam promoted breakaway in air

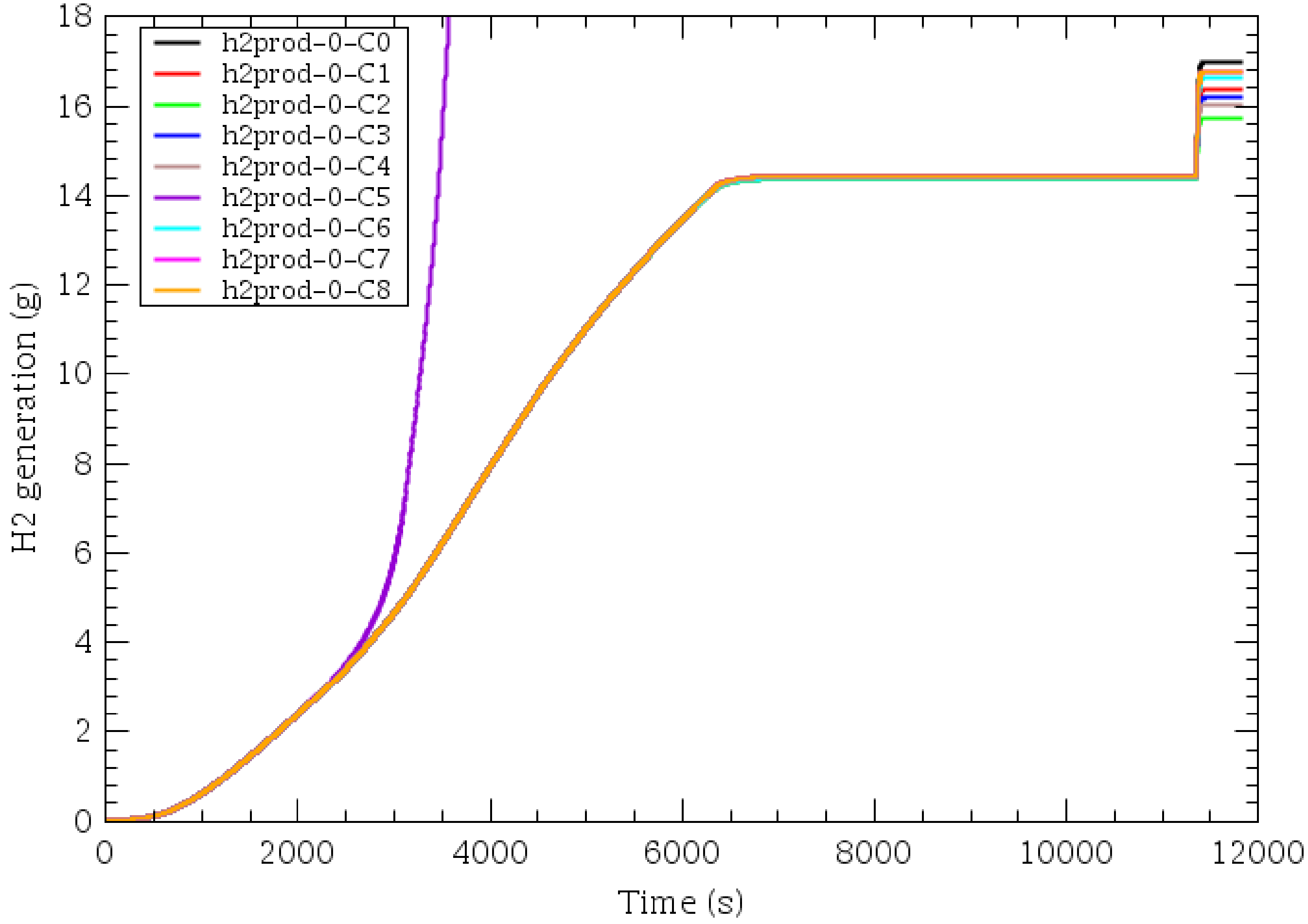


Slowest

2	(no breakaway)
4	(no breakaway air)
3	(air is like steam)
1, 6	(no breakaway steam)
0	(baseline)
7, 8	(similar to baseline)
5	(steam is like air)

Fastest

Simulation of QUENCH-16 – benchmark case



Hydrogen production insensitive to breakaway option except option 5 (steam is like air)

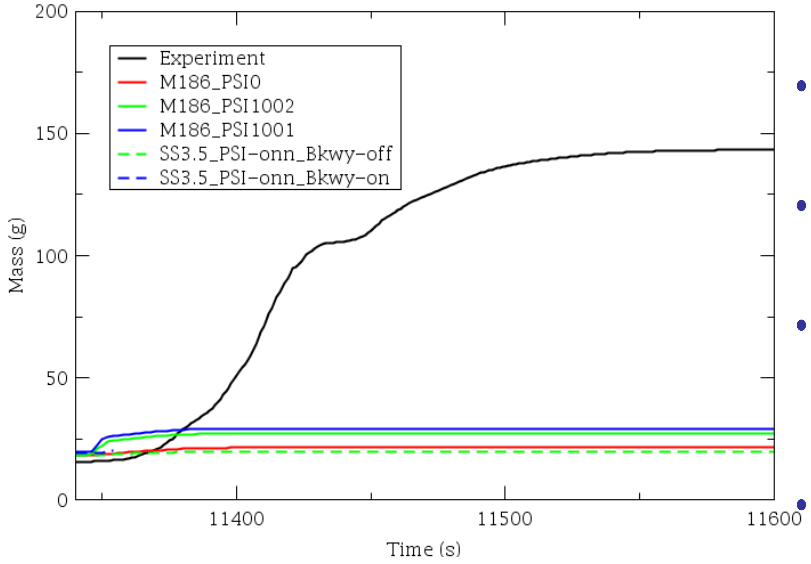
Massive excursion, 300 g hydrogen calculated

Implications for spent fuel uncovery

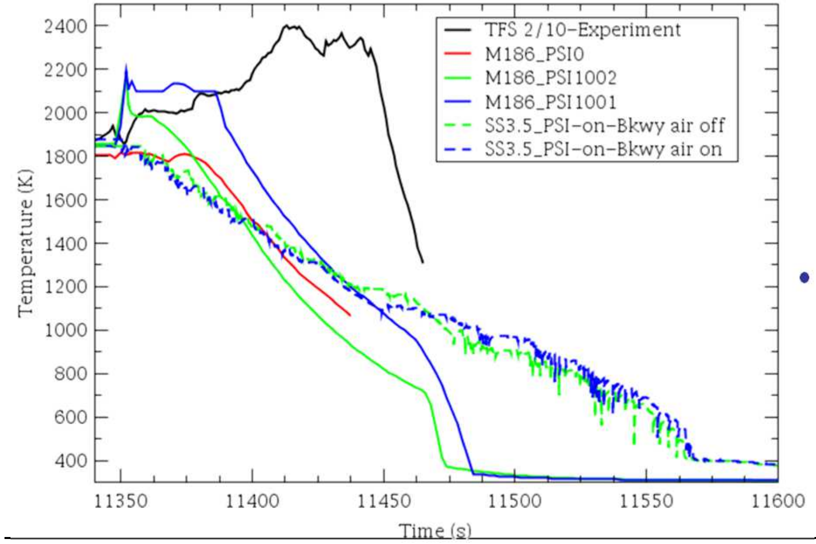
PSI model limitations

Q16: Reflood

Hydrogen generation



Temperature @ 650 mm elevation



- No excursion was expected for the Q16 experiment
- **High T's were observed during reflood**
- Neither of the codes reproduced it. The did not calculated anywhere near the total $\mathbf{H_2}$ observed during reflood.
- Possible mechanism for triggering the strong oxidation were identified:
  - **ZrN formation**
  - **reoxidation of the ZrN and N_2 release during reflood**
  - **dissolution of the oxide into an α-Zr(O) region**
- **PhD (S. Park) in progress in order to address this issues**

PhD Research status – Air oxidation existing tests

Separate Effect Tests	FZK (KIT)	IRSN
Zr-alloy	Zry-4, Zirlo, M5	Zry-4, M5
Pre-oxidation	steam or oxygen or air at various temperatures	steam or oxygen at 500°C and autoclave at 360°C
Temperature range	800-1600°C	600-1200°C
Breakaway	below 1100°C	below 1100°C
ZrN formation	observed under oxygen starvation	observed under oxygen starvation

More SETs are required at specific nitriding conditions

Integral Tests	QUENCH-10	QUENCH-16	SFP
Zr-alloy	Zry-4	Zry-4	Zry-4
Pre-oxidation	steam at 1620-1690K for 6780 sec.	steam at 1300-1430K for 4000 sec.	none
Air ingress temperature range	1190-2200K for 1800 sec.	1000-1873K for 4040 sec.	Ignition test Phase 1: 5.0 kW Phase 2: 15.0 kW
Breakaway	observed	observed	observed
ZrN formation	observed	observed	observed

PhD Research status – Air oxidation Models

	MELCOR and SCDAP	MAAP	ASTEC	ATHLET-CD	SOCRAT
Model developer	J. Birchley and L. Fernandez-Moguel (PSI)	Emilie Beuzet et al. (EdF)	O. Coindreau et al. (IRSN)	T. Hollands et al. (GRS)	Vasiliev A.D. (IBRAE)
Oxidation parameter	oxide thickness	oxide thickness	weight gain	weight gain	oxygen diffusion
Oxidant in air	oxygen	oxygen	oxygen	oxygen	oxygen
Pre-transiton	parabolic	parabolic	parabolic	parabolic	-
Transition initiator	presence of nitrogen	-	zirconia phase transformation	-	-
Post-transition	linear/accelerated	linear/accelerated	linear/accelerated	linear	-
Nitriding model	nitrogen acts as a catalyst	not yet	nitrogen acts as a catalyst	ZrN formation reaction rate under very low oxygen partial pressure	enhanced diffusion coefficient of oxygen at ZrN/Zirconia

Nitrogen role on degradation

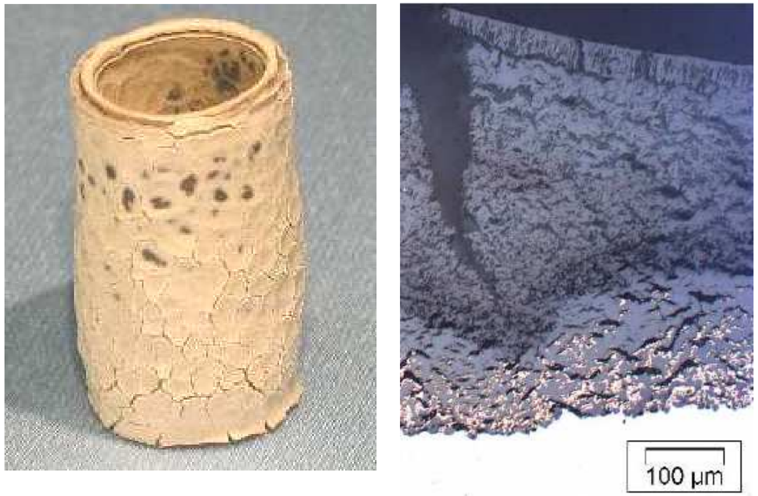
- ZrN is formed significantly after oxygen consumption
- Heat releases
- The heat released from ZrN formation and reoxidation is comparable as the heat from oxidation by oxigen
- Phase transformation

Thermodynamics ↔ Kinetics

Mechanical changes

- Increased reaction rate

- Volume change
- ZrN formation leads to micro porous oxide, ca. 32% less than $\overline{V}_{ZrO_2}$
- ZrN reoxidation leads to macro cracked oxide, ca. 46.6% of volume increase in the region of ZrN reoxidation



Zry-4 cladding oxidation for 1 hour at 1000° C in air

M. Steinbrück et al., Prototypical Experiments on Air Oxidation of Zircaloy-4 at High Temperatures, Forschungszentrum Karlsruhe, FZKA 7257, January 2007

Self sustaining nitrogen reaction

- Self sustaining nitrogen-assisted degradation: $\mathrm{ZrN} \rightarrow \mathrm{ZrO}_2 \rightarrow \mathrm{ZrN} \rightarrow \cdots \rightarrow \mathrm{ZrO}_2$

  – only a few initial nitrogen amount can continue the degradation reaction to the fully oxidized oxide

  i. Initially ZrN is formed near the interface between oxide and metal
  ii. as the further oxidation occurs inwardly, the newly formed inside-oxide puts the formed ZrN outwardly and then the ZrN is embedded in the oxide
  iii. some amount of the generated nitrogen during the ZrN reoxidation would be trapped in oxide and it is available for further ZrN formation
  iv. finally ZrN is fully oxidized to ZrO_2

  – nitrogen acts as a catalyst by degrading cladding and hence increasing the reaction rate

  – but nitrogen is not just a catalyst since its reactions change the chemical compositions by forming ZrN

Aspects on further code model development

- Cladding degradation by nitriding: enhanced diffusion of oxidant and hence accelerated kinetics

\- currently several codes implemented the cladding degradation by nitriding as a catalyst effect

- Exothermic heat release from ZrN formation and reoxidation

\- most reactor system codes do not implement ZrN formation, and none of them represents reoxidation

- Hydrogen generation from ZrN reoxidation by steam during reflooding

\- $\mathrm{ZrN} + 2\mathrm{H_2O} \rightarrow \mathrm{ZrO_2} + 2\mathrm{H_2} + \frac{1}{2}\mathrm{N_2}$

Summary and Outlook (PhD work)

1st role of nitrogen: cladding degradation

- Air oxidation: micro porous and macro cracked oxide forms due to ZrN formation and reoxidation

2nd role of nitrogen: exothermic heat release

- Air oxidation: ZrN formation and reoxidation release high heat in addition to heat by oxygen oxidation

PhD project (S. Park) on developing a nitriding model

I. Identify nitriding conditions based on available data

II. Further SETs for specific nitriding conditions

III. Analyzing SETs data with Zr-O-N thermodynamic study (thermocalc)

IV. Developing and validating a nitriding model

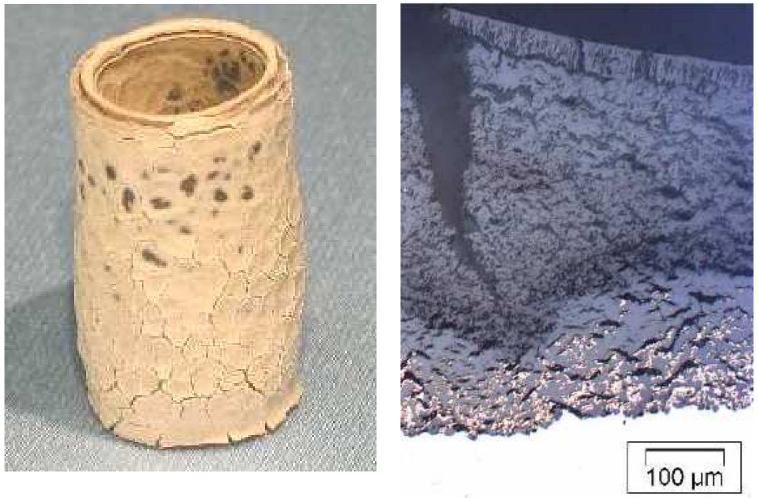
Status summary and outlook

- Summary of current implementation described in PSI memo, available on request (without recent updates)
- New options address inherent flaws in original model
- New options implemented in a local version of SCDAPSim/Mod3.5
- Implementation in a local version of MELCOR 1.8.6
- Will be used at PSI for analyses of spent fuel uncovery sequences where a steam/air mixture is the normal environment
- PSI model does not address yet issues of reactions with N_2 and ZrN
  - Currently PhD is on going in order to address this issue

Thank you for your attention

Nitrogen role – cladding degradation

- Thermodynamically, the formation of $\mathrm{ZrO_2}$ is much favorable than that of ZrN. Thus, ZrN is formed significantly after oxygen consumption
  – after kinetic transition, oxygen and nitrogen access to the interface between metal and oxide through the cracks, and oxygen is consumed first
  – the consumed oxygen would stabilize the α-Zr which can dissolve the oxygen up to about 30 at.%
  – at the interface, nitrogen reacts with the oxygen stabilized α-Zr(O) or the sub-stoichiometric zirconium oxide, $\mathrm{ZrO_{2-x}}$



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- Molar volumes of ZrN (14.8 $\mathrm{cm^3}$) and $\mathrm{ZrO_2}$ (21.7 $\mathrm{cm^3}$)
- ZrN formation leads to micro porous oxide
  – $\overline{\mathrm{V}}_{\mathrm{ZrN}}/\overline{\mathrm{V}}_{\mathrm{ZrO_2}} = 0.68$: $\overline{\mathrm{V}}_{\mathrm{ZrN}}$ is about 32% less than $\overline{\mathrm{V}}_{\mathrm{ZrO_2}}$
  – ZrN inclusion in oxide leads to micro porous and less coherent oxide and it likely causes ZrN reoxidation
- ZrN reoxidation leads to macro cracked oxide
  – 46.6% ($\Delta\overline{\mathrm{V}}_{\mathrm{ZrN\to ZrO_2}}/\overline{\mathrm{V}}_{\mathrm{ZrN}}$ = 6.91/14.8) of volume increase in the region of ZrN reoxidation occurred
  – due to this significant volume expansion, the oxide scale experiences the local stresses and it leads to macro cracked oxide

Nitrogen role – exothermic heat release

- Oxidation by steam: $2H_2O + Zr \rightarrow ZrO_2 + 2H_2 \;\; \Delta H_{rxn} = -616 \text{ kJ/mol Zr}$
- Oxidation by oxygen: $O_2 + Zr \rightarrow ZrO_2 \;\; \Delta H_{rxn} = -1094.8 \text{ kJ/mol Zr}$
- ZrN formation: $\frac{1}{2} N_2 + Zr \rightarrow ZrN \;\; \Delta H_{rxn} = -365.4 \text{ kJ/mol Zr}$
- Exothermic heat from ZrN formation is about 33% of the heat compared to oxidation by oxygen
- ZrN reoxidation: $ZrN + O_2 \rightarrow ZrO_2 + \frac{1}{2} N_2 \;\; \Delta H_{rxn} = -729.4 \text{ kJ/mol Zr}$
- Exothermic heat from ZrN reoxidation is about 67% of the heat compared oxidation by oxygen
- The heat released from ZrN formation and reoxidation is same as the heat from oxidation by air.
- During reflood quench in steam the superficial ZrN layer is converted to oxide and also exthermic heat is released: $ZrN + 2H_2O \rightarrow ZrO_2 + 2H_2 + \frac{1}{2} N_2$