Cladding oxidation during air ingress

Part I: Experiments on air ingress

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Part II: Synthesis of modelling results

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OUTLINE

1. **Experiments on air:**
    1. Separate effect tests
    2. Bundle experiments
2. **Synthesis of modelling results:**
    1. Overview of the code matrix
    2. Validation against QUENCH-10 experiment
    3. Validation against QUENCH-16 experiment
    4. Validation against PARAMETER-SF4 experiment
3. **Conclusions and Perspectives**

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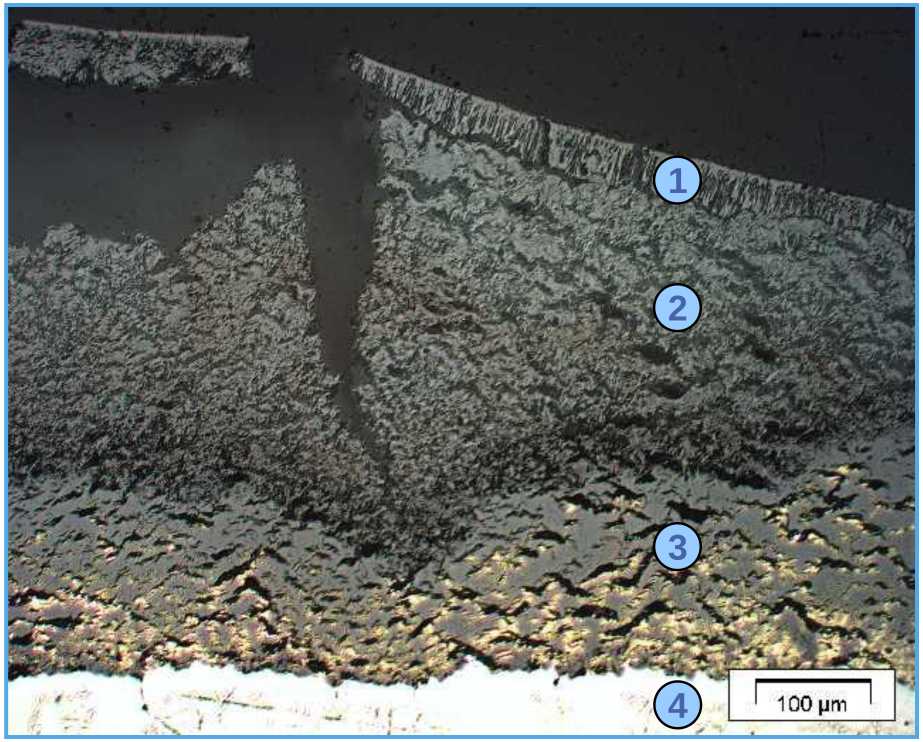
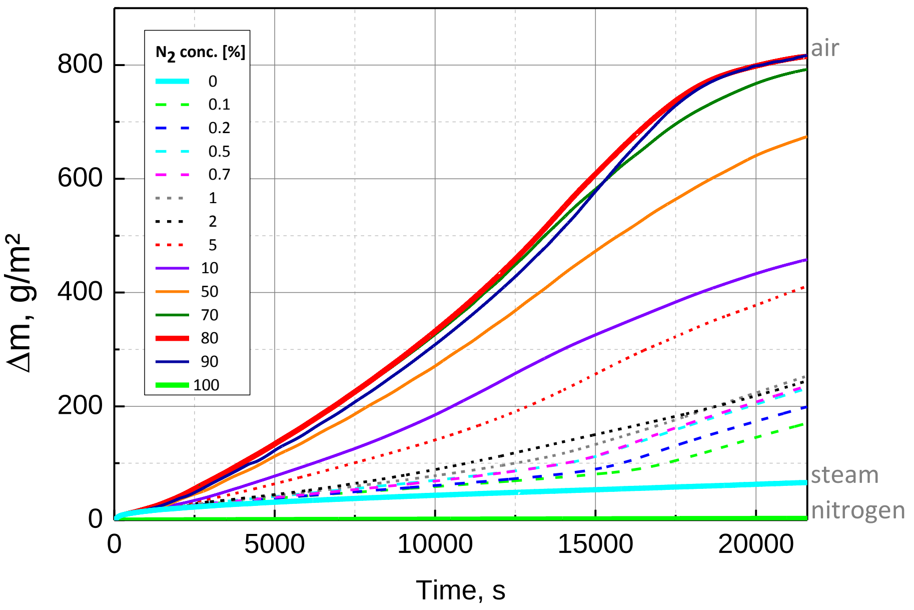
Main results of single effect tests on air ingress



Typical cross-section through an oxide scale after oxidation of Zry-4 in air at 1000°C:
1 – initially formed dense oxide ZrO_2,
2 – porous oxide after oxidation of ZrN,
3 – ZrO_2/ZrN mixture,
4 – α-Zr(O).



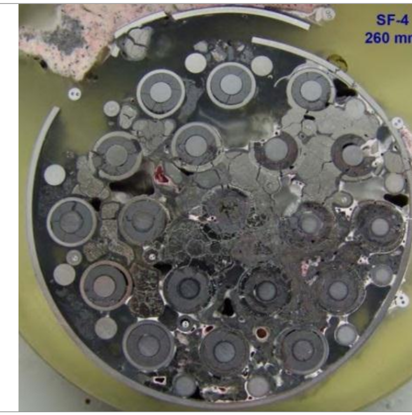
Mass gain versus time of oxidation of Zircaloy-4 at 800°C in steam-nitrogen mixtures.

Overview of bundle air ingress experiments

280 mm

CODEX AIT-1, AIT-2 (Zry-4) performed 1999 at AEKI/Budapest: small bundles with 9 rods

260 mm



PARAMETER-SF4 (E110 claddings) performed 2009 at LUCH/Podolsk: very high temperatures on reflood initiation with following escalation (bundle melting)

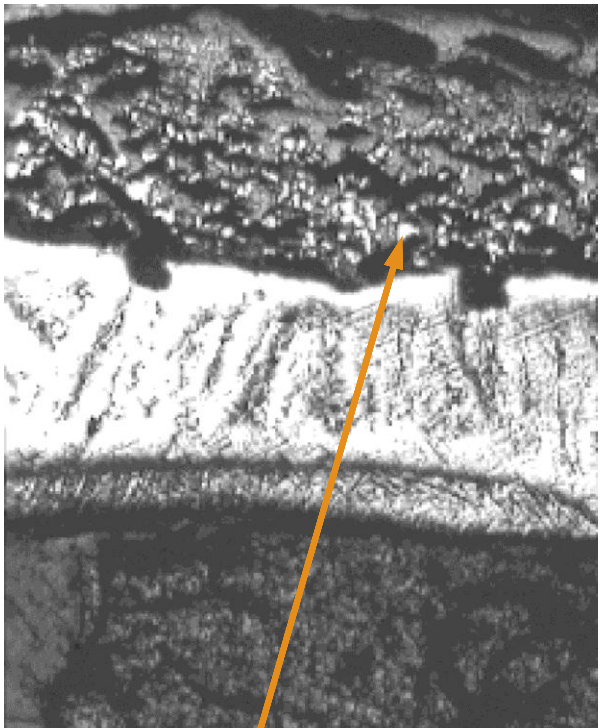
635 mm

QUENCH-10 (Zry-4 claddings) performed 2004 at KIT/Karlsruhe: strong pre-oxidised bundle

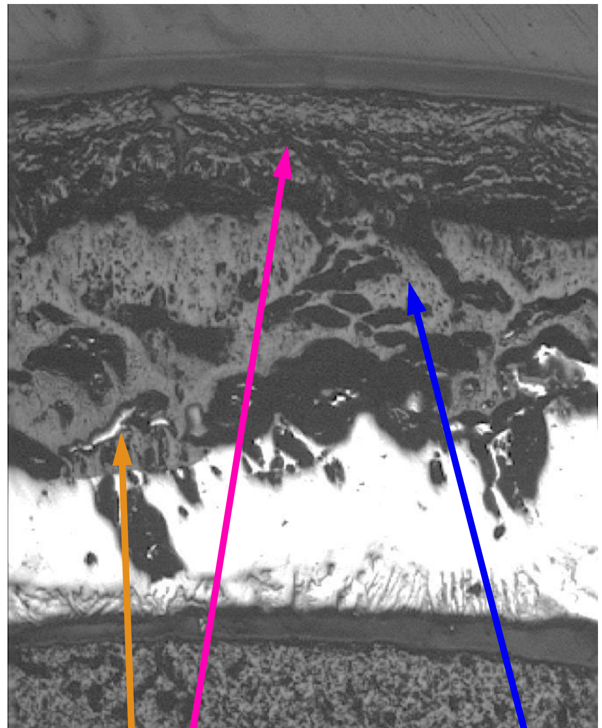
430 mm

QUENCH-16 (Zry-4 claddings) performed 2011 at KIT/Karlsruhe: moderate pre-oxidised bundle

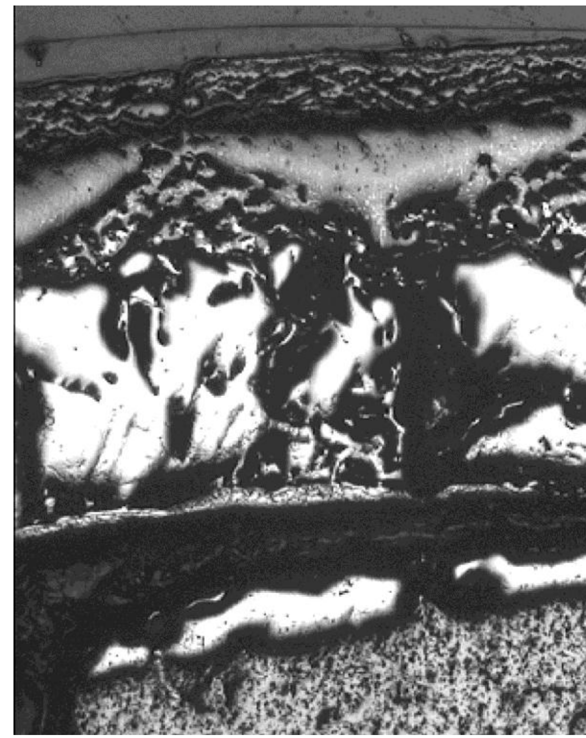
CODEX-AIT1 (9 rods, heated 600 mm, pre-ox. 40 µm): cladding structures at hot elevations with T (535 mm) ≈ 900°C – 1300 °C during air ingress (570 s)



450 mm: **nitrides** inside oxide layer



535 mm: 1) **porous** outer oxide layer (formed during preoxidation in oxygen); 2) **dense** oxide layer (formed during air ingress); 3) single **nitrides** at boundary oxide-metal.



555 mm: similar to 535 mm

Practically total consumption of nitrogen below 500 mm

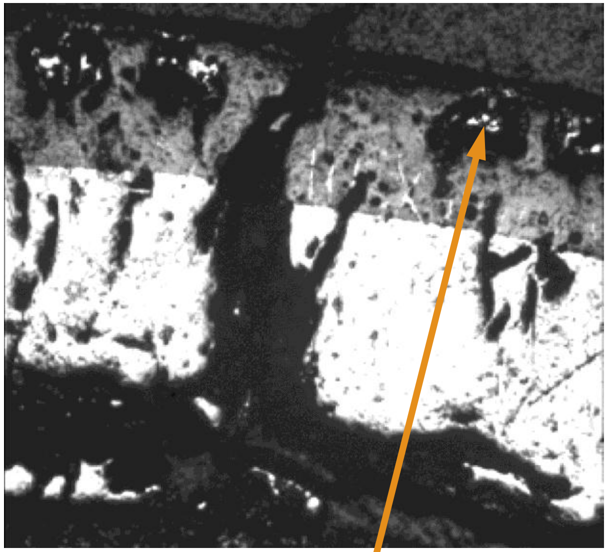
Karlsruhe Institute of Technology

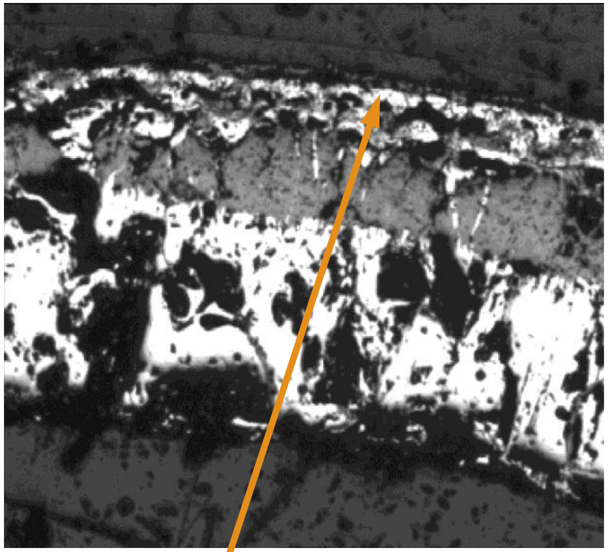
CODEX-AIT2

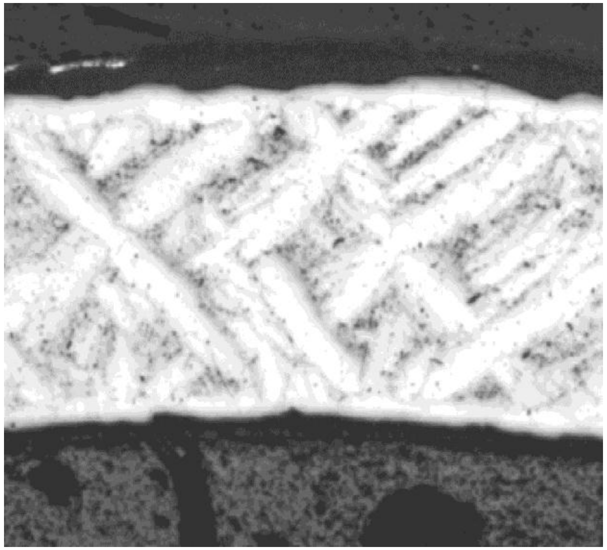
(9 rods, heated 600 mm, pre-ox. 35 µm):

cladding structures at hot elevations

with T (450 mm) ≈ 900°C – 1600 °C during air ingress (570 s)





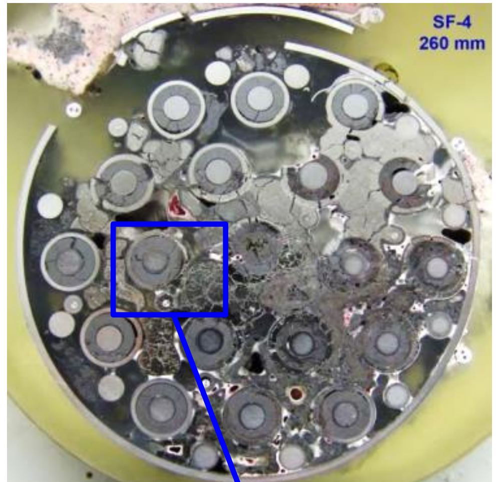


280 mm: single **nitrides** inside “pockets” of upper part of oxide layer	375 mm: **nitrides** inside upper part of oxide layer	555 mm: few oxidised cladding (**steam and air starvation**)

Karlsruhe Institute of Technology

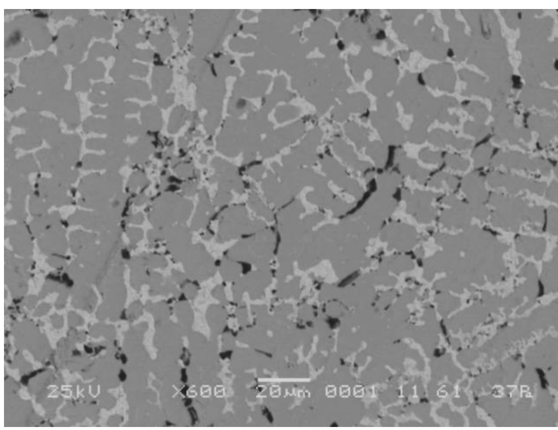
PARAMETER SF-4 test (19 rods, heated 1275 mm, pre-ox 250 µm)
Temperature transient during air ingress (1476 s): T = 1173-2110 K

130 mm: intact bundle

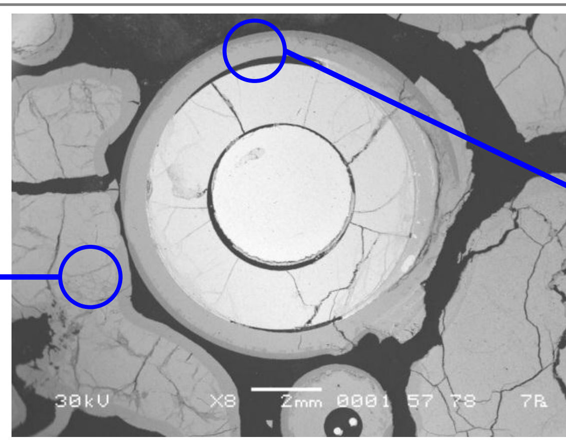


260 mm: melt

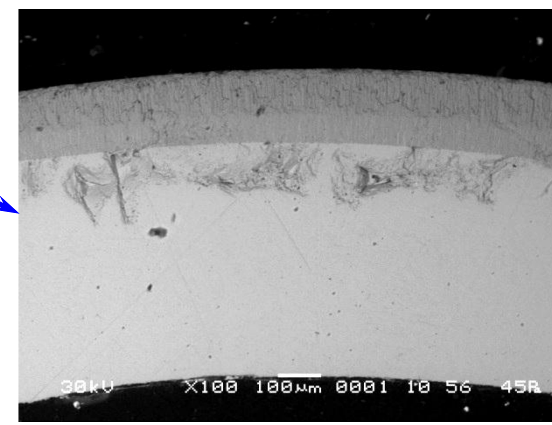
1200 mm: melt; *nitrides dissolved by melt*



oxidised relocated melt

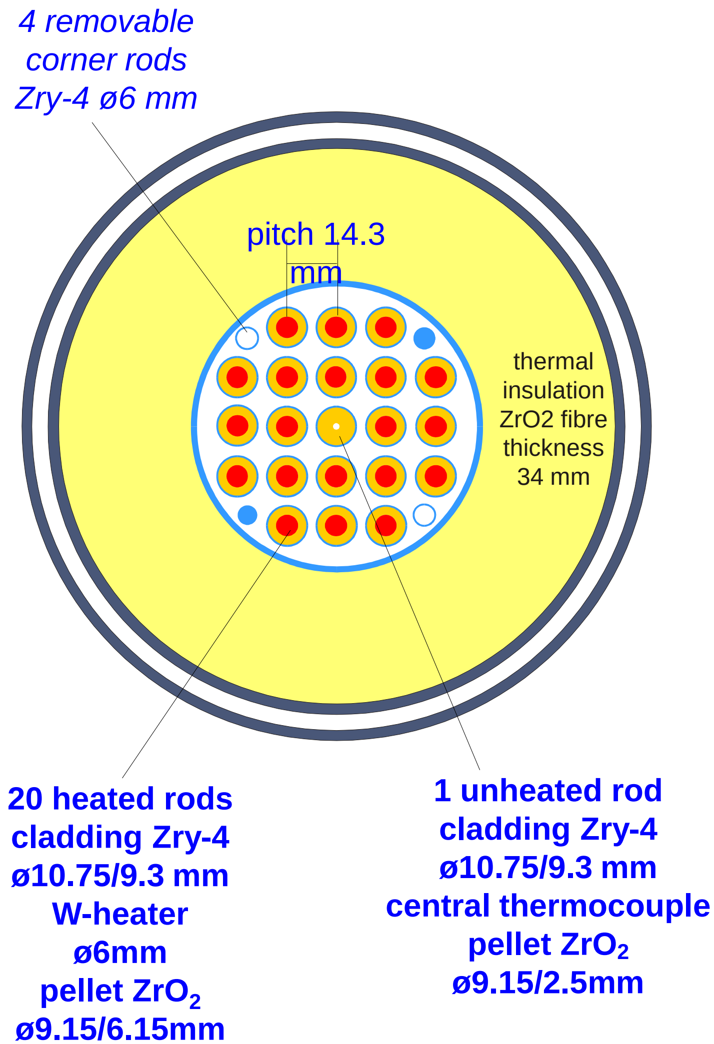


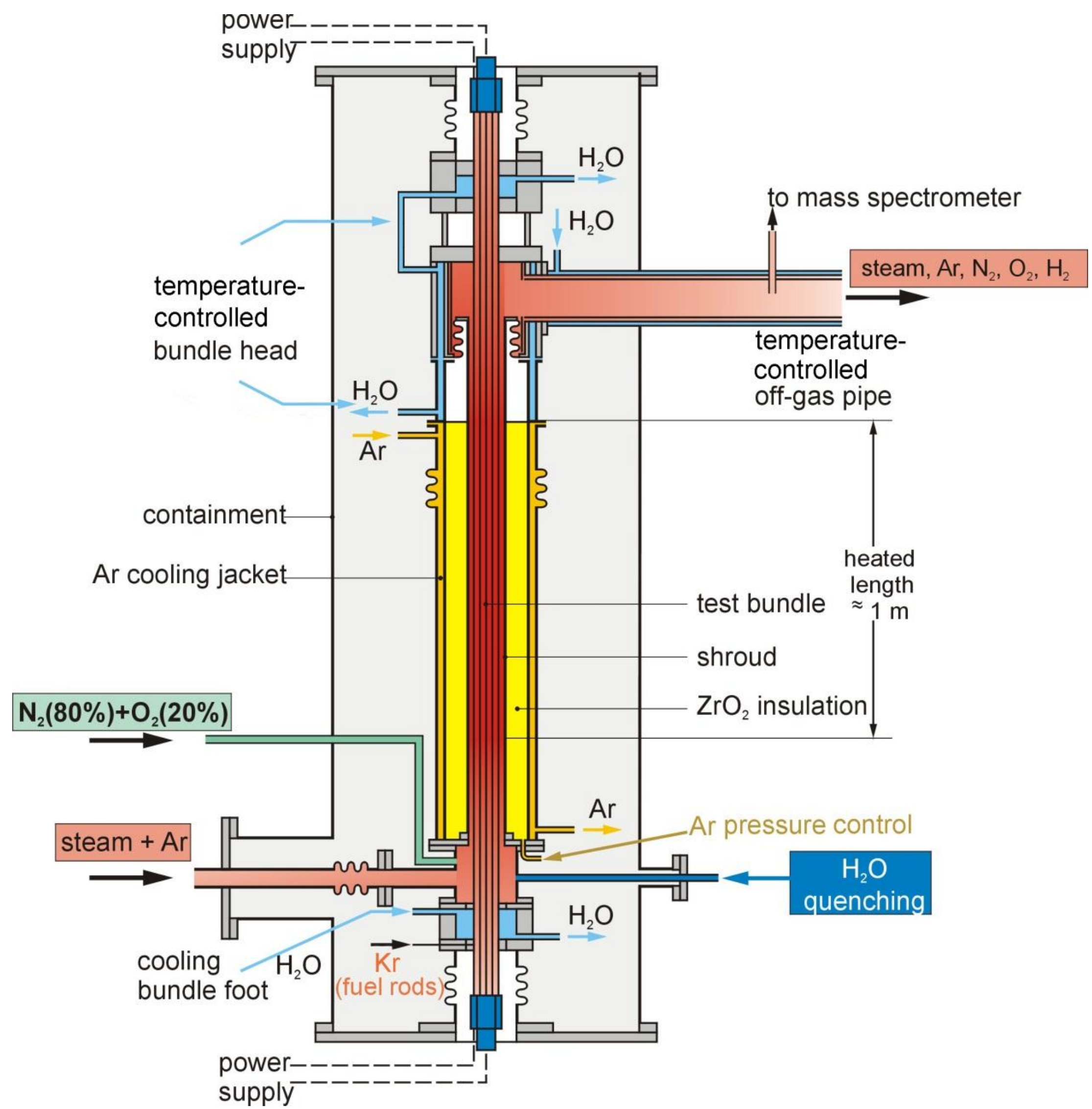
260 mm: melt



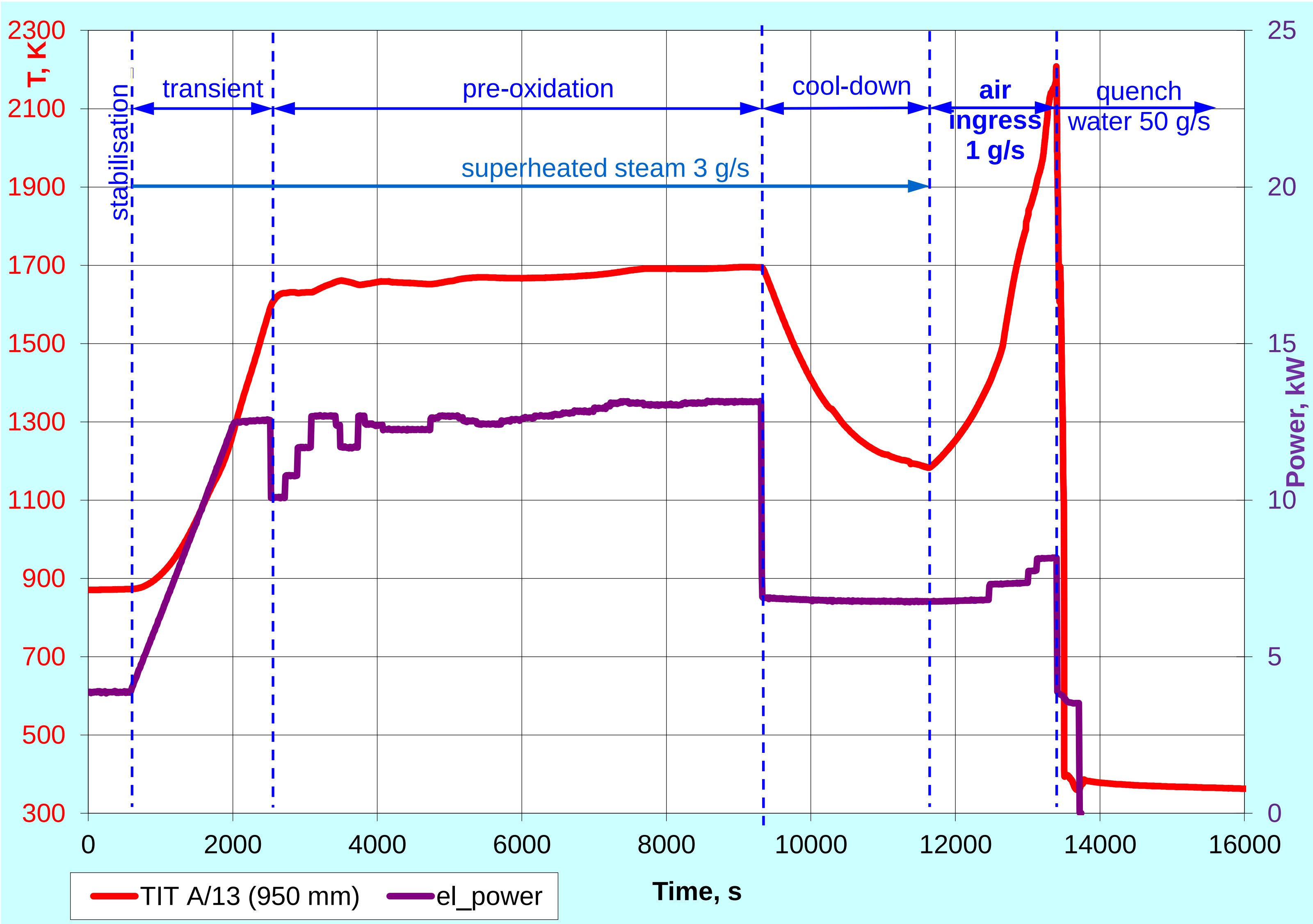
homogeneous ZrO2 : 200 µm;
no nitrides

QUENCH facility

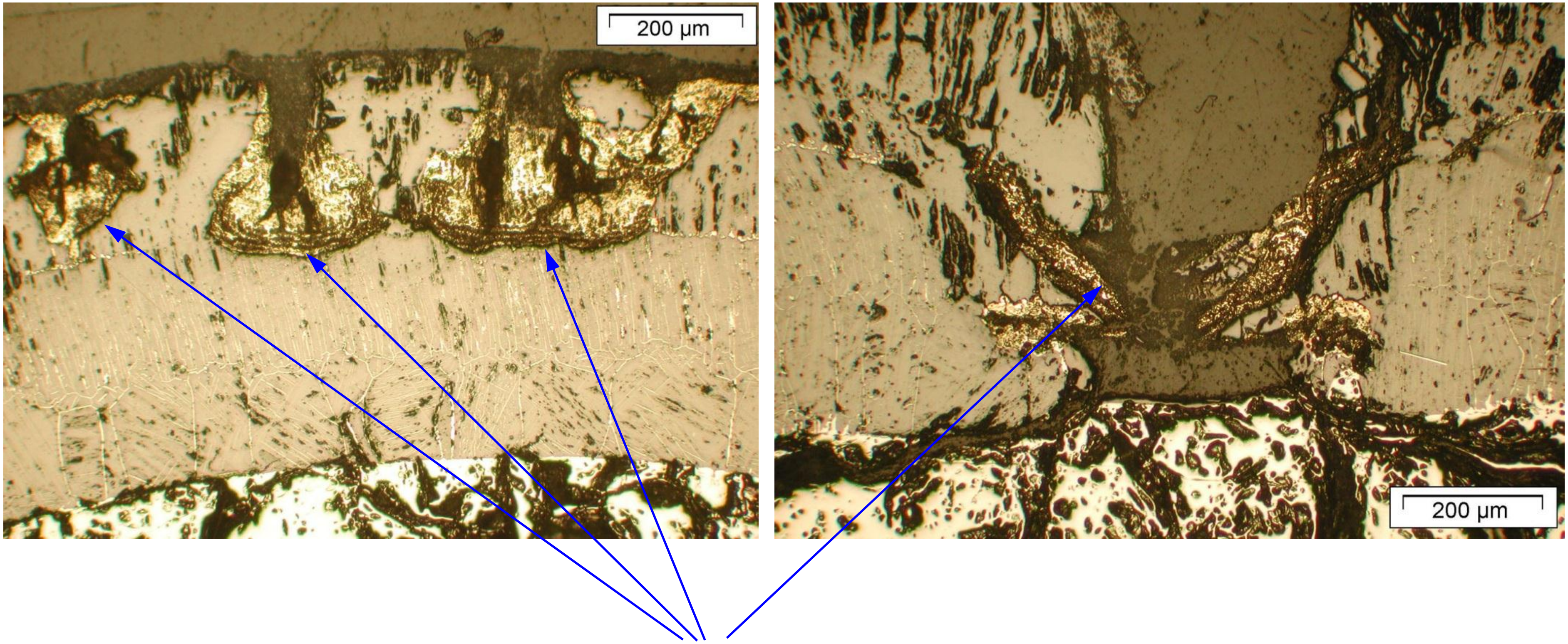




QUENCH-10 test performance

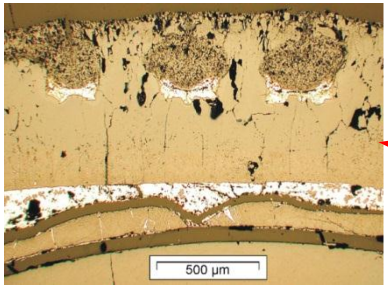


QUENCH-10: Nitride formation on the end of the air ingress phase (withdrawn Zry-4 corner rod)

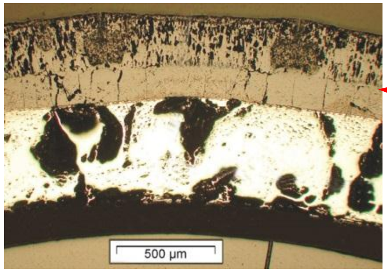


Nitride formation under oxygen starvation conditions
at the elevation 850 mm

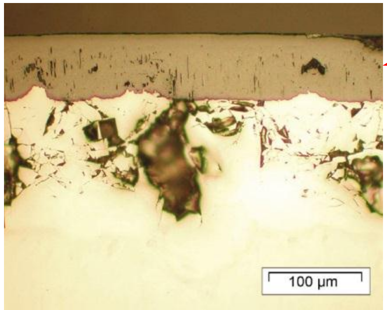
QUENCH-10: Axial change of oxide layer structure and residual nitrides after reflood



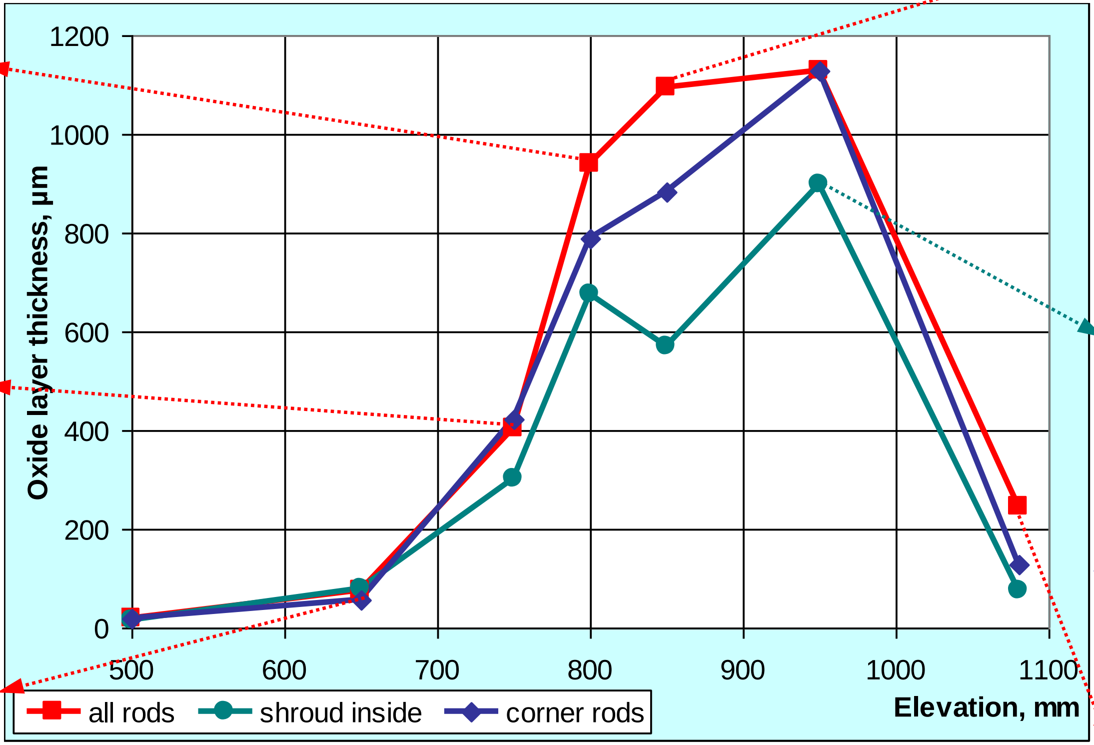
clad. 800 mm: residual nitrides at bottom of fragile regions

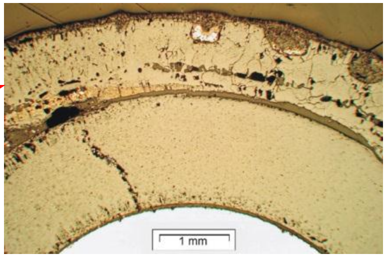


clad. 750 mm: fragile regions

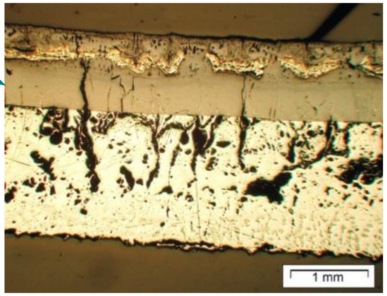


clad. 650 mm: regular oxide layer

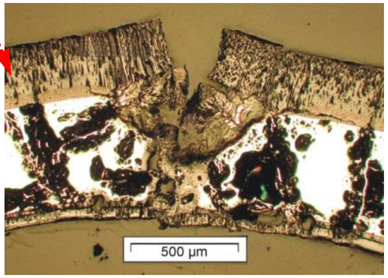




clad. 850 mm: residual nitrides at bottom of fragile regions

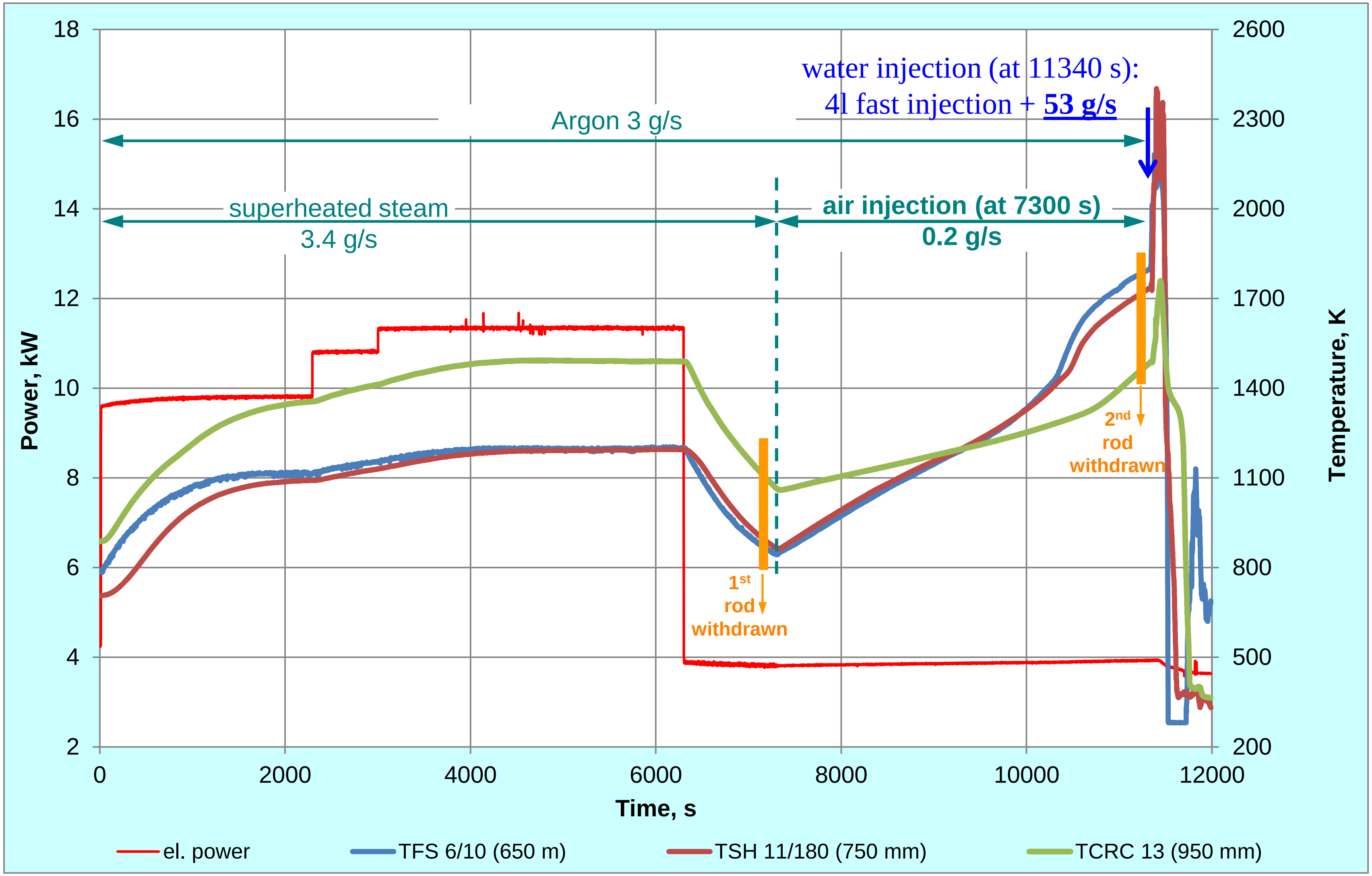


shroud 950 mm: residual nitrides at bottom of fragile surface layer

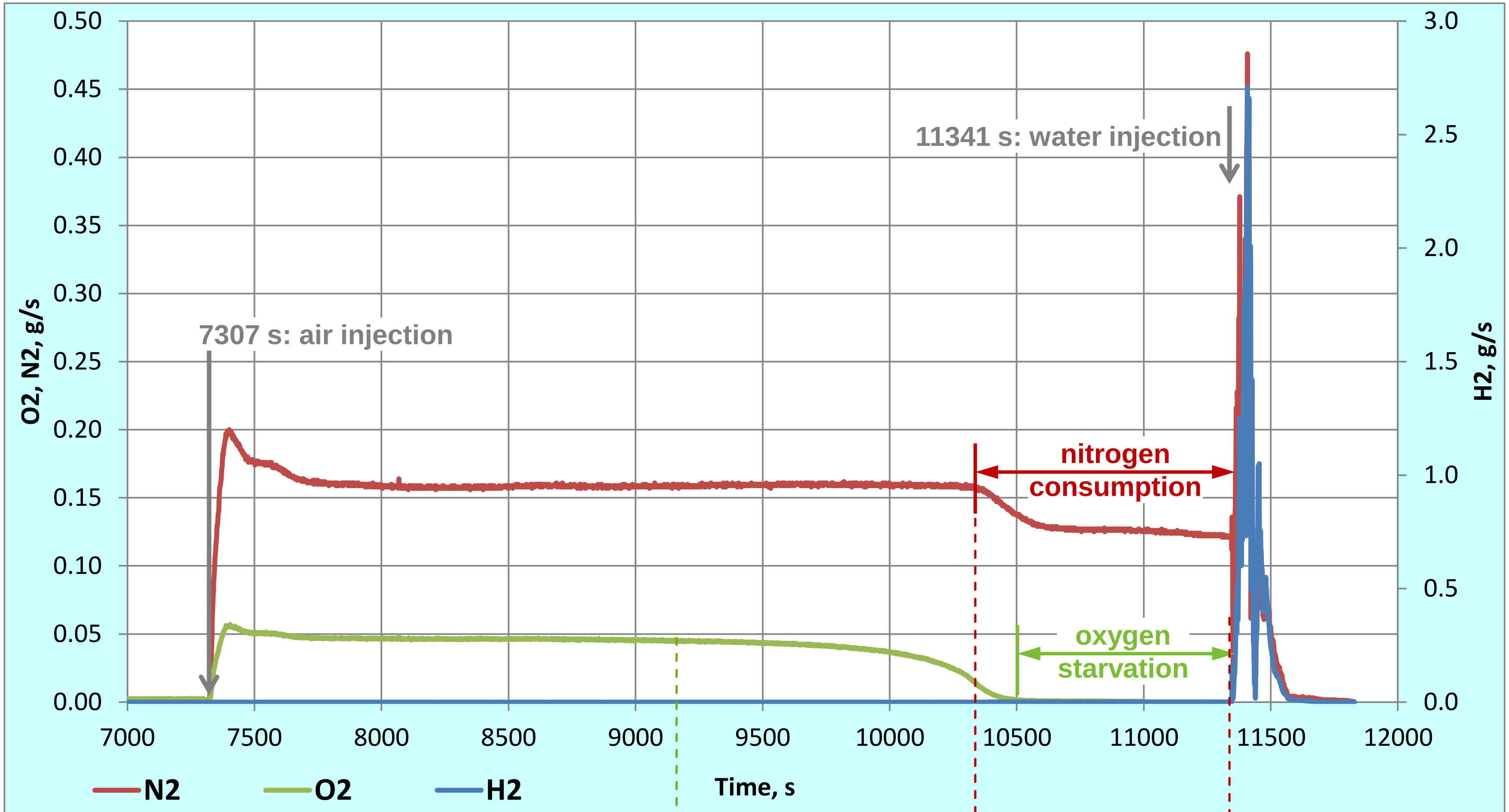


clad. 1080 mm: nitrides at scale wedge crack

QUENCH-16 test progression



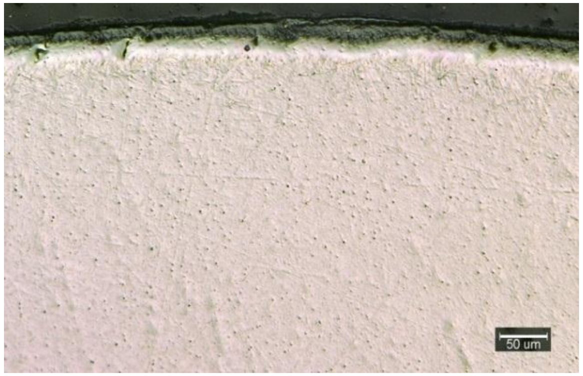
QUENCH-16: Consumption of nitrogen and oxygen during air ingress phase (data of mass spectrometer)



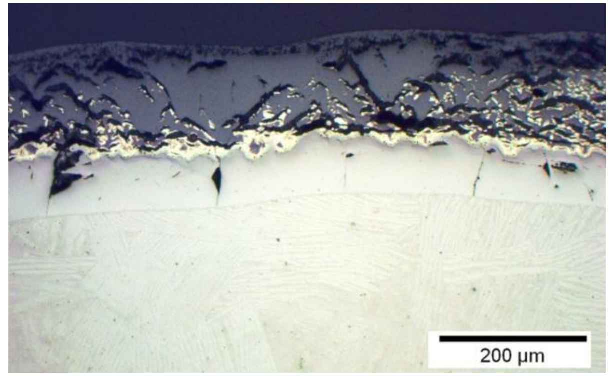
nitrogen uptake: 29 g (Q10: 8 g)

oxygen uptake: 58 g (Q10: 84 g)

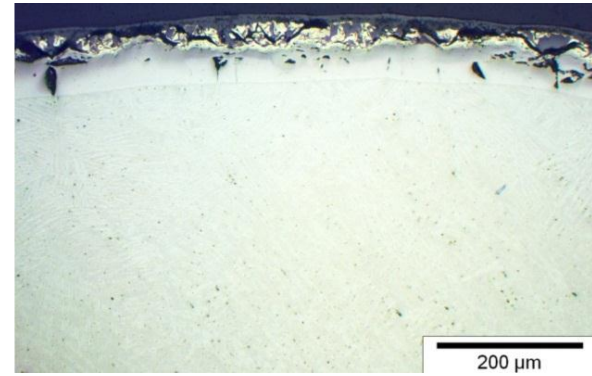
QUENCH-16: Layer structures <u>on the end of the air ingress phase</u> (withdrawn corner rod); nitride formation between 300 and 900 mm



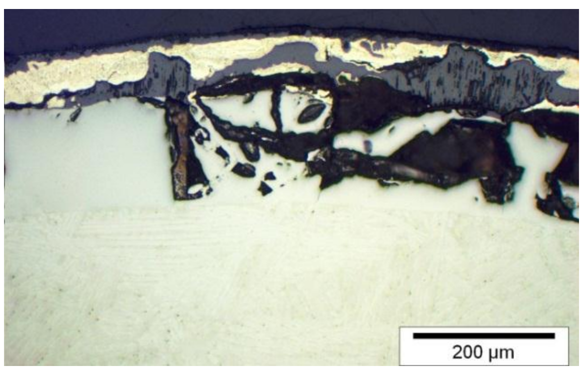
250 mm (1070°C): no nitrides



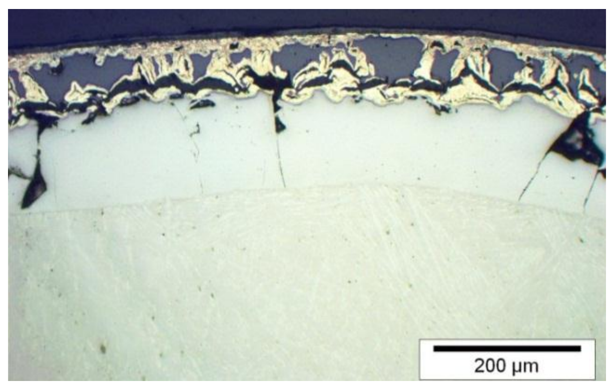
450 mm (1530°C): strong corrosion; nitrides



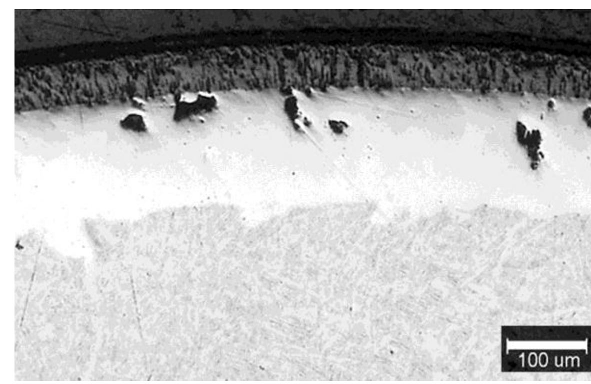
650 mm (1400°C): moderate corrosion; nitrides



750 mm (1460°C): strong corrosion; nitrides

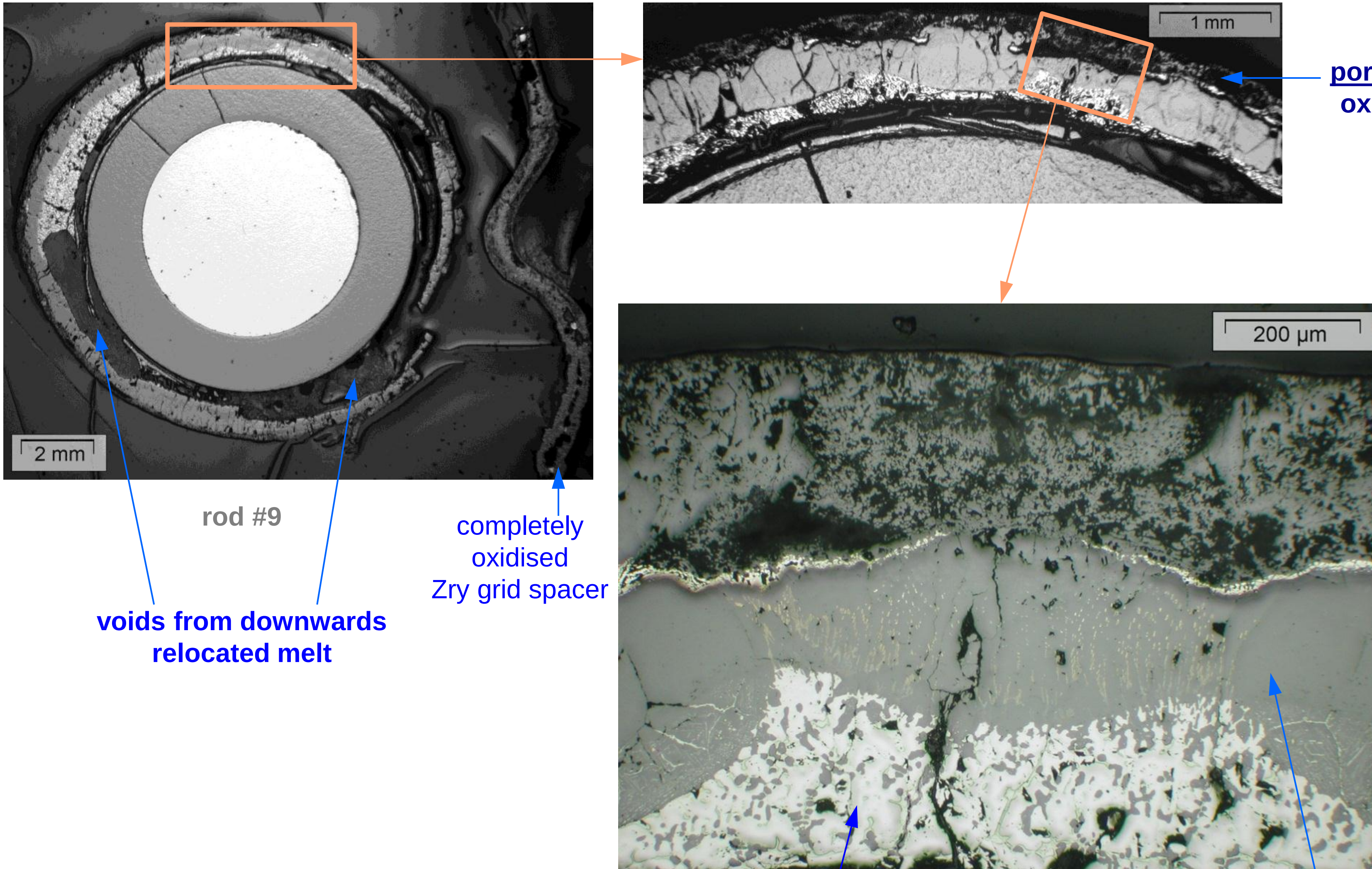


850 mm (1570°C): strong corrosion; nitrides



950 mm: no nitrides

QUENCH-16: Secondary oxidation and melting at elevation 550 mm



Summary of bundle tests

Test	Max ZrO_2 before air ingress, µm	Air flow rate, g/s/rod	Initial T_{pct} at air injection, K	Durations of (air ingress) \(oxygen starvation), s	T_{pct} at re-flood/cool-down, K	Nitrides	Hydrogen production during reflood, g
CODEX AIT-1	**40** (disso-lution from 50)	3.5/(9+5) = **0.25**	1173	570 \ NA	2273	**distributed** inside ZrO_2 or along α	cool-down in Ar
CODEX AIT-2	20 (steam +air) + 15 (air leak)	2.5/(9+5) = **0.18**	1073	800 \ NA	2173	localised **"pockets"** inside ZrO_2	cool-down in Ar
PARAMETER SF-4	**250**	0.5/(19+12.6) = 0.016	1173	1476 \ NA	2110	dissolved in melt	86
QUENCH-10	**500**	1/(21+9.6) = **0.033**	1190	1800 \ 80	2200	localised **"pockets"** at outer side of ZrO_2	5 (1 g re-oxidation of nitrides)
QUENCH-16	**135**	0.2/(21+9.6) = **0.007**	1000	4035 \ 800	1873	**distributed** inside ZrO_2	128 (7 g re-oxidation of nitrides + 96 g metal oxidation + 25 g melt oxidation)

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OVERVIEW OF THE CODE MATRIX

- **For this study, the involved codes are:**
  - ASTEC V2.1 (IRSN)
  - ATHLET-CD (GRS)
  - MAAP (EDF)
  - MELCOR (PSI)
  - SCDAPSim (PSI)
  - SOCRAT (IBRAE)

OVERVIEW OF THE CODE MATRIX

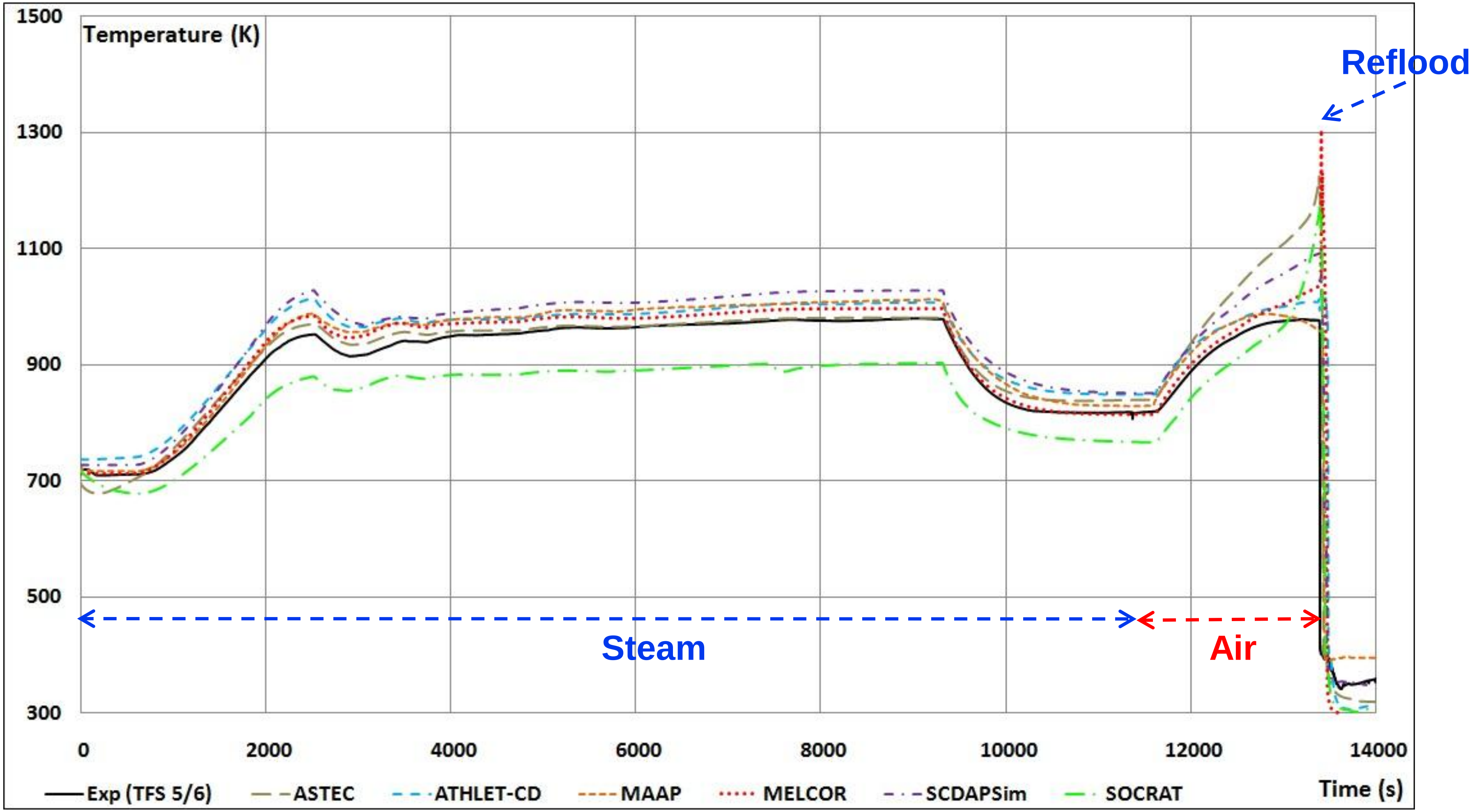
Code	Steam Oxidation	Air Oxidation	Nitriding	Nitrides Reoxidation	Cladding failure criterion	Oxide layer description
ASTECV2.1	“Best-Fit”: Cathcart-Pawel / Transition / Prater-Courtright	MOZART at low temperature, KIT at high temperature	KIT-Hollands	ZrON oxidized as ZrO2- not used in this study	For T ≥ 2300 K and ZrO2 thickness < 300 µm	Dense ZrO2 and α-Zr(O) layers
ATHLET-CD	**CathCart-Prater / Courtright**	**Steinbrück**	**Hollands**	**None**	**T = 2300K (dox ≤ 0.25 mm) T = 2500K (dox ≥ 0.35 mm)**	**Porosity factor 1≤ FPor≤ 2 if ∂ZRN > 0**
MAAP	Cathcart-Urbanic	NUREG	KIT-EDF	ZrN oxidized as Zr	For T ≥ 2500K or F_{Zrox} ≥ 0.5	Only a dense ZrO_2

OVERVIEW OF THE CODE MATRIX

Code	Steam Oxidation	Air Oxidation	Nitriding	Nitrides Reoxidation	Cladding failure criterion	Oxide layer description
MELCOR	Cathcart-Urbanic	Cathcart/Urbanic and Uetsuka and Hoffman with PSI breakaway model	None	None	For T ≥ 2400K	Only a dense ZrO_2
SCDAPSim	**Cathcart-Urbanic**	**Cathcart/Urbanic and Uetsuka and Hoffman with PSI breakaway model**	**None**	**None**	**For T ≥ 2500K and $Fr_{Zrox} \geq 0.6$**	**Only a dense ZrO_2**
SOCRAT	Oxygen diffusion in cladding 3-layer system	Oxygen diffusion in cladding 3-layer system, enhanced	None	None	For T ≥ 2300K and dox< 0.0003 m	ZrO2 with enhanced oxygen diffusion coefficient

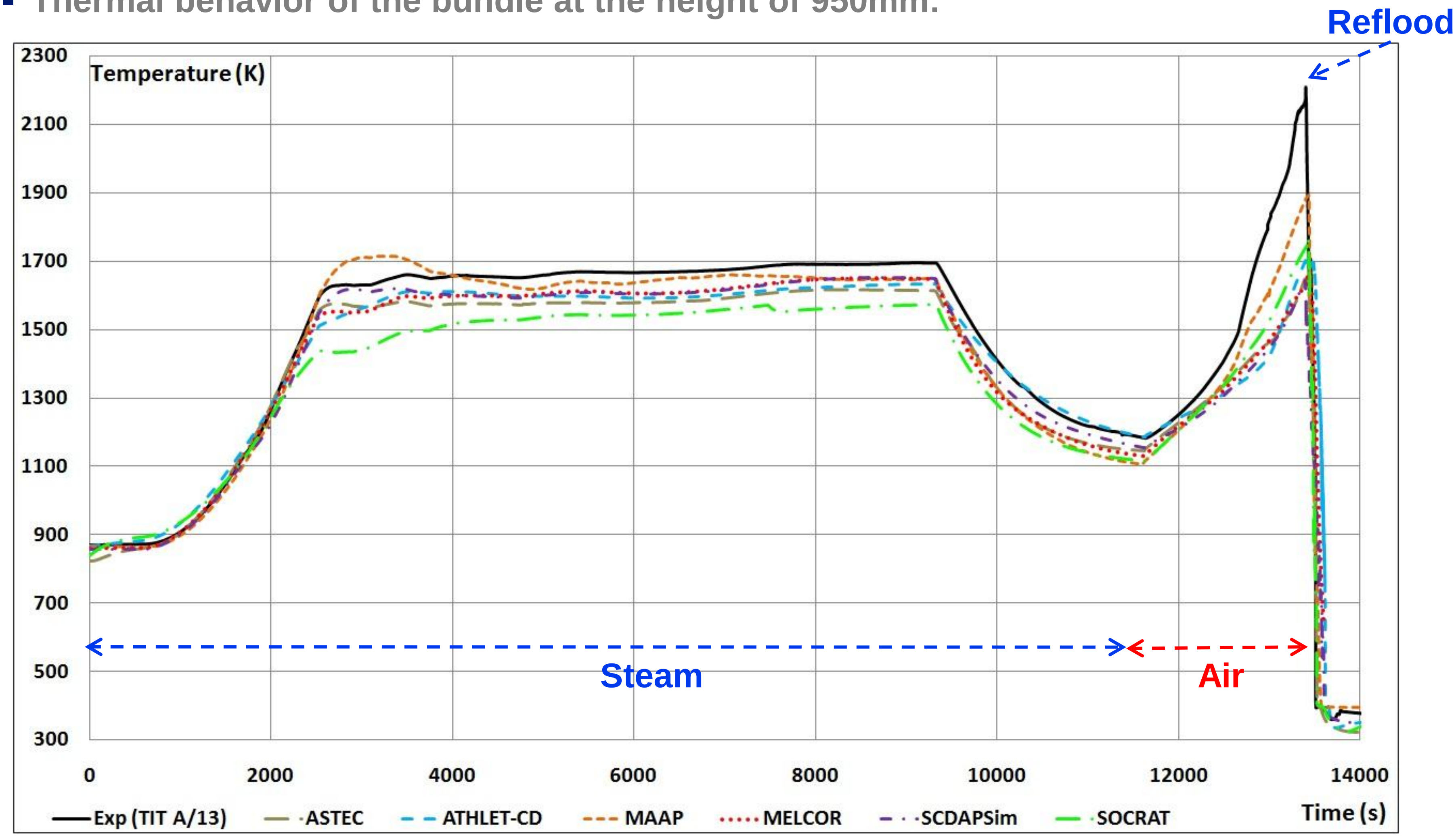
VALIDATION AGAINST QUENCH-10 EXPERIMENT

- **Thermal behavior of the bundle at the height of 250mm:**



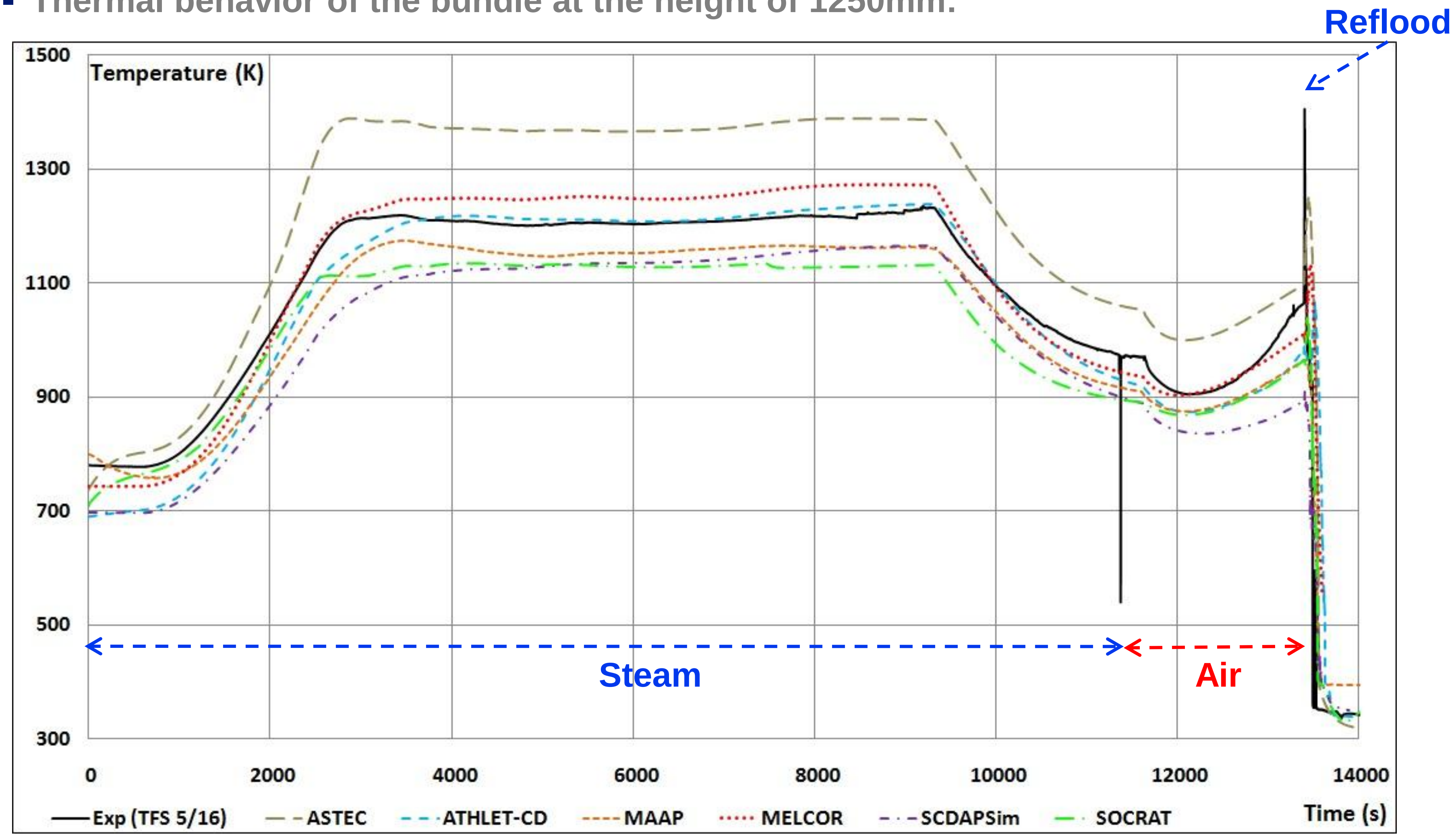
VALIDATION AGAINST QUENCH-10 EXPERIMENT

- **Thermal behavior of the bundle at the height of 950mm:**



VALIDATION AGAINST QUENCH-10 EXPERIMENT

- **Thermal behavior of the bundle at the height of 1250mm:**



VALIDATION AGAINST QUENCH-10 EXPERIMENT

- **Gases behavior → Hydrogen Production:**

	at the end of P-ox phase (g)	at the end of air phase (g)	Total (g)
Experiment	47	47	53
ASTEC V2.1	**58**	**58**	**70**
ATHLET-CD	46.9	46.9	53.8
MAAP	**42**	**42**	**44.5**
MELCOR	47	47	56
SCDAPSim	**47.8**	**47.8**	**49**
SOCRAT	33.8	33.8	46.2

➔ Hydrogen production is in good agreement for most of the codes with the experiment, for both the pre-oxidation phase and the reflood phase, particularly for ATHLET-CD and MELCOR.

VALIDATION AGAINST QUENCH-10 EXPERIMENT

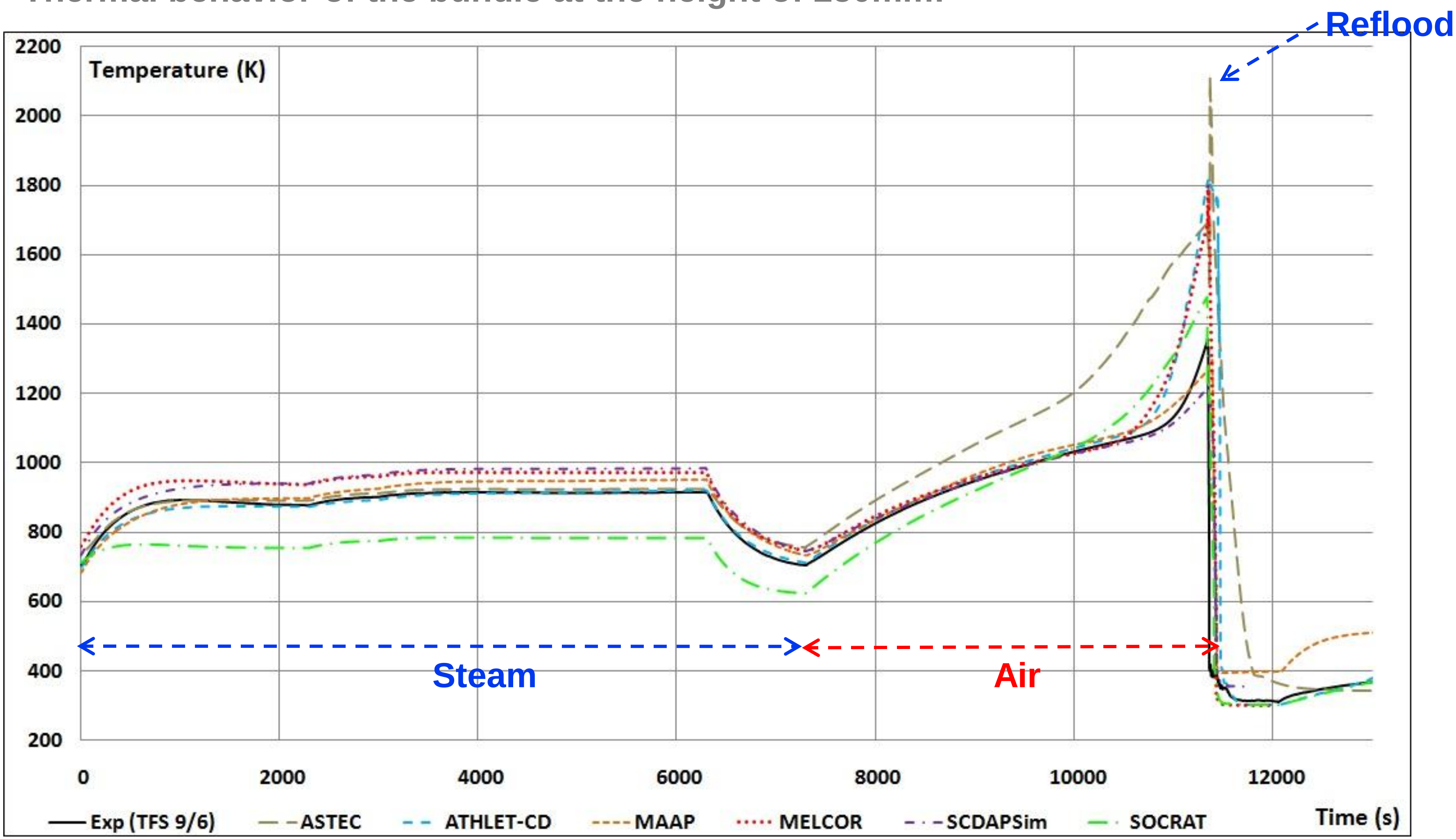
- **Gases behavior → Air:**

	Starvation time (s)	**Starvation elevation (mm)**	**Oxygen consumption (g)**	**Nitrogen consumption (g)**
Experiment	13300	>800	84	8
ASTEC V2.1	**13200**	**500**	**73**	**4**
ATHLET-CD	> 13400	>750	57	0.4
MAAP	**13100**	**>350**	**164**	**10.3**
MELCOR	13240	750	63.43	-
SCDAPSim	**13140**	**750**	**43.53**	**-**
SOCRAT	13116	750	52	0

➔ Starvation time and location are well predicted by most of the codes while oxygen consumption is scattered.

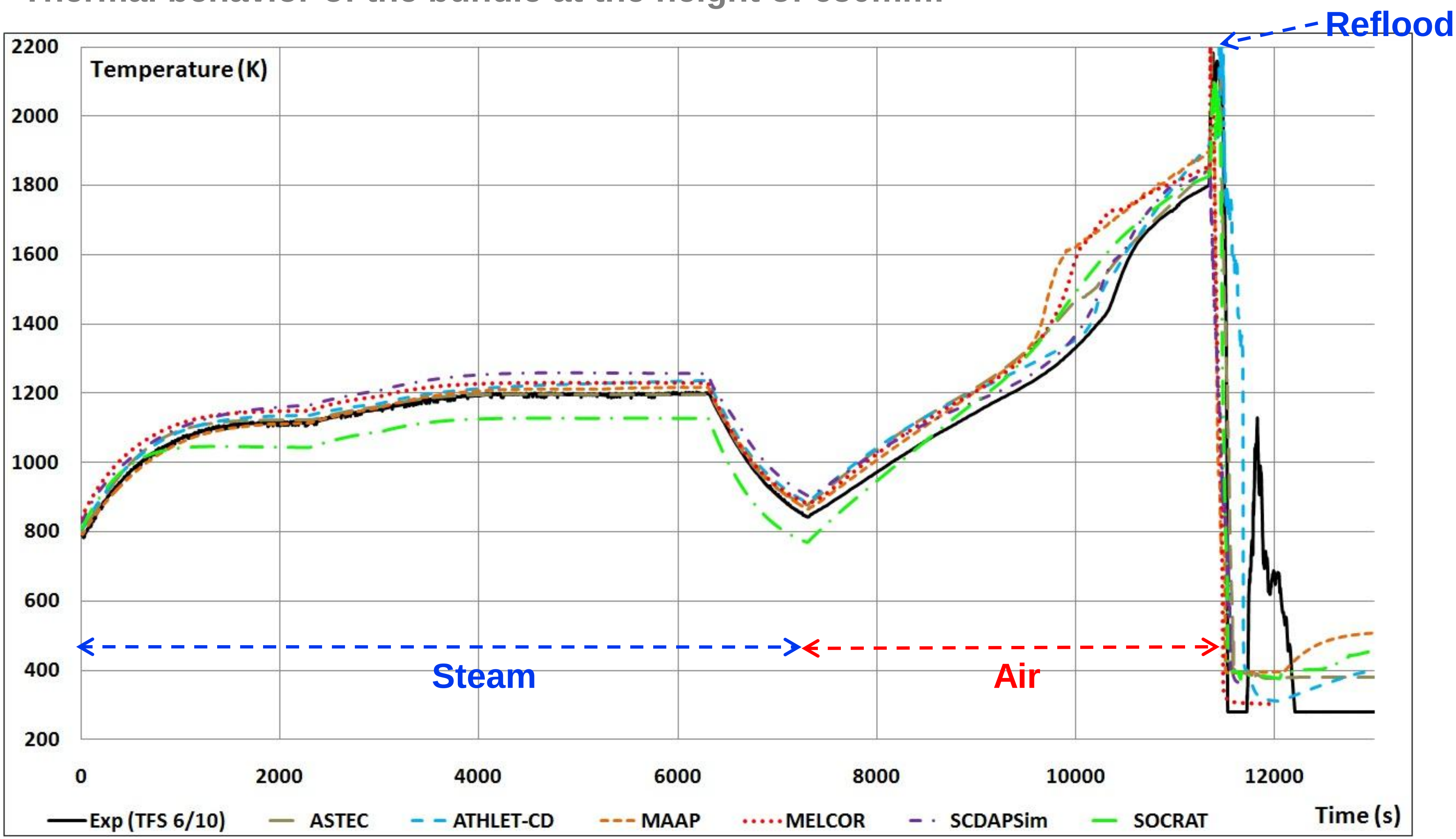
VALIDATION AGAINST QUENCH-16 EXPERIMENT

- **Thermal behavior of the bundle at the height of 250mm:**



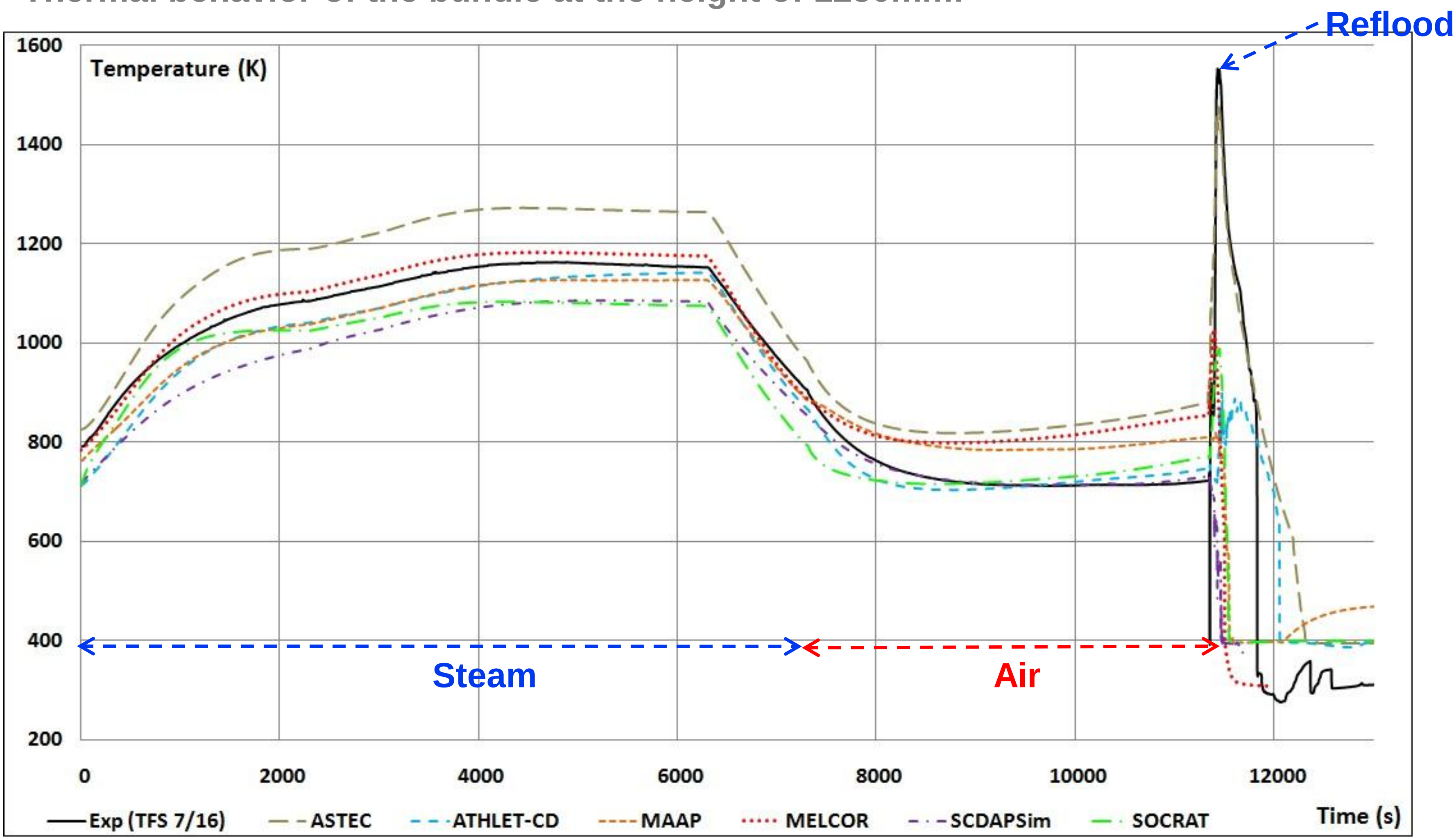
VALIDATION AGAINST QUENCH-16 EXPERIMENT

- **Thermal behavior of the bundle at the height of 650mm:**



VALIDATION AGAINST QUENCH-16 EXPERIMENT

- **Thermal behavior of the bundle at the height of 1250mm:**



VALIDATION AGAINST QUENCH-16 EXPERIMENT

- **Gases behavior → Hydrogen Production:**

	at the end of P-ox phase (g)	at the end of air phase (g)	Total (g)
Experiment	16	17.3	144
ASTEC V2.1	**21**	**21**	**123**
ATHLET-CD	14.9	14.9	53
MAAP	**13.4**	**17.8**	**18.1**
MELCOR	14.5	18.5	27.2
SCDAPSim	**14.5**	**17.8**	**18.7**
SOCRAT	9.6	9.6	106.3

→ Hydrogen production is in good agreement for most of the codes with the experiment for the pre-oxidation. Final calculated hydrogen production is underestimated as temperatures escalation is not caught for the overall bundle.

VALIDATION AGAINST QUENCH-16 EXPERIMENT

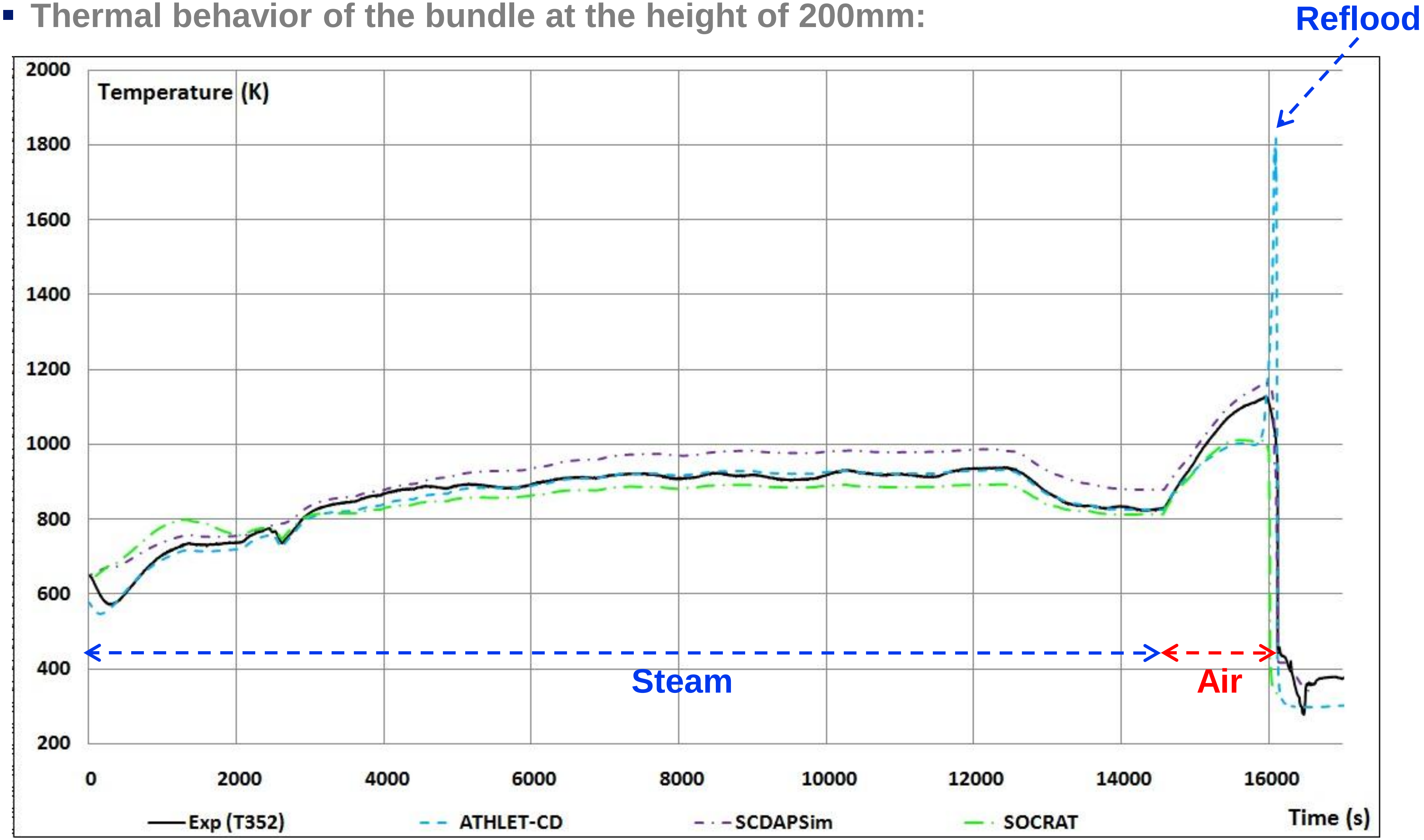
- **Gases behavior → Air:**

	Starvation time (s)	Starvation elevation (mm)	Oxygen consumption (g)	Nitrogen consumption (g)
Experiment	10500	>350	58	29
ASTEC V2.1	**10000**	**500**	**83**	**40**
ATHLET-CD	10300	≥ 350	58.8	33.1
MAAP	**9600**	**>250**	**82.5**	**9.3**
MELCOR	9850	750	85.40	-
SCDAPSim	**10220**	**750**	**72.96**	**-**
SOCRAT	10110	750	61	0

➔ Starvation time and location are well predicted by most of the codes. Oxygen consumption tends to be overestimated by all the codes (in good agreement for ATHLET-CD and SOCRAT).

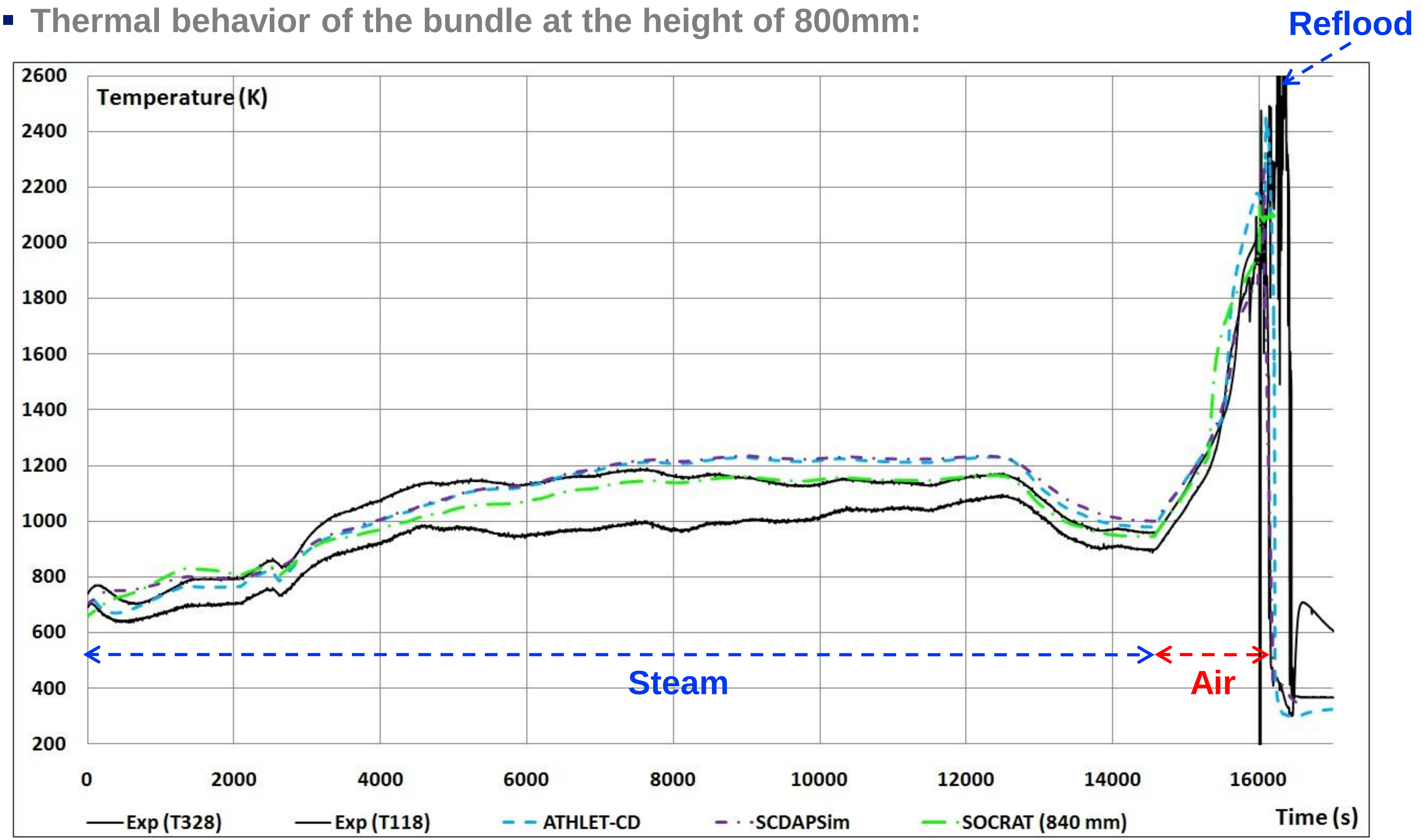
VALIDATION AGAINST PARAMETER-SF4 EXPERIMENT

- **Thermal behavior of the bundle at the height of 200mm:**



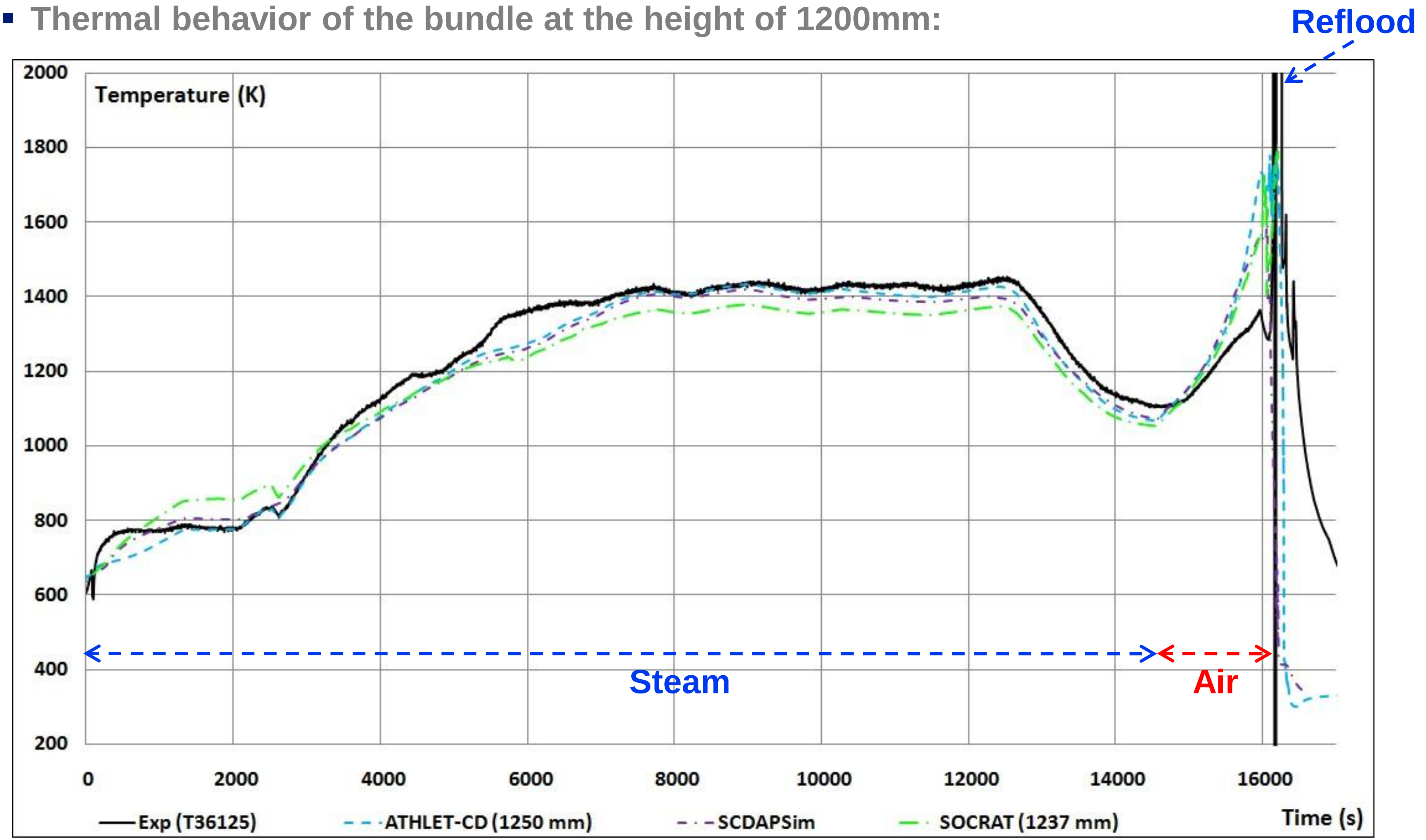
VALIDATION AGAINST PARAMETER-SF4 EXPERIMENT

- **Thermal behavior of the bundle at the height of 800mm:**



VALIDATION AGAINST PARAMETER-SF4 EXPERIMENT

- **Thermal behavior of the bundle at the height of 1200mm:**



VALIDATION AGAINST PARAMETER-SF4 EXPERIMENT

- **Gases behavior → Hydrogen Production:**

	at the end of P-ox phase (g)	at the end of air phase (g)	Total (g)
Experiment	21.8	21.8	~108
ATHLET-CD	**21.0**	**21.0**	**92.6**
SCDAPSim	22.86	22.86	45.06
SOCRAT	**8.9**	**8.9**	**170**

➔ Hydrogen production is in good agreement for most of the codes with the experiment for the pre-oxidation phase.

Final calculated hydrogen production is scattered.

VALIDATION AGAINST PARAMETER-SF4 EXPERIMENT

- **Gases behavior → Air:**

	Starvation time (s)	**Starvation elevation (mm)**	**Oxygen consumption (g)**	**Nitrogen consumption (g)**
Experiment	15648	>500	unknown	unknown
ATHLET-CD	**15648**	**≥ 400**	**57.3**	**20.3**
SCDAPSim	15608	500	47.29	-
SOCRAT	**15748**	**800**	**28**	**0**

→ Starvation time and location are well predicted by most of the codes.

OUTLINE

1. **Experiments on air:**
    1. Separate effect tests
    2. Bundle experiments
2. **Synthesis of modelling results:**
    1. Overview of the code matrix
    2. Validation against QUENCH-10experiment
    3. Validation against QUENCH-16 experiment
    4. Validation against PARAMETER-SF4 experiment
3. **Conclusions and Perspectives**

CONCLUSIONS AND PERSPECTIVES

- **Conclusions:**

  - **From the experimental part , the main underlined points are:**
    - The different studied scales showed **very complex processes of air** on cladding degradation.
    - Main reason = **formation of zirconium nitrides** due to interaction of nitrogen with α-Zr(O) which leads to a **very porous and fragile structure** at the outer cladding surface.
    - **Nitrides** can be **exothermically re-oxidised in steam**, accelerating the cladding degradation.

  - **From the simulation part, the main underlined points are:**
    - **Well predicted pre-oxidation phase**
    - **Underestimation of the air effect**
    - Global **difficulties** to catch temperature escalation **during reflood** and the associated hydrogen production

CONCLUSIONS AND PERSPECTIVES

- **Perspectives:**
  - **From the experimental part** and since single effect tests showed **strong cladding degradation also in steam-nitrogen mixtures,** it would be very reasonable to **perform bundle tests under corresponding conditions.**

  - **From the simulation part, improvements are needed on phenomena such as**:
    - **Modelling of porous nitride-oxide layer** formation during air ingress,
    - **Calculation of the penetration of steam** through the porous superficial layer accomplished by nitrides re-oxidation and intensive cladding oxidation during reflood

- **General viewpoint:**
  - A **strong relationship is present in this scientific community**: much collaboration between experimental and modelling people, between public research and industrial research
  - **Proposition of a new QUENCH test,** in the frame of **SAFEST** call for proposal, with an air phase composed of a mixed atmosphere (steam + air) instead of pure air (proposed by EDF, IBRAE, IRSN, GRS, PSI and LEI)

THANK YOU