Hydrogenation of claddings in the new developed HOKI oven and performance of the long-term bundle test under dry storage conditions in the framework of the SPIZWURZ project

J. Stuckert, C. Rössger, J. Moch, M. Grosse, S. Weick

Abstract

During the dry storage of spent nuclear fuel, the initially dissolved hydrogen precipitates as hydrides in the metallic matrix. The orientation of hydrides influences the crack propagation and depends mainly on the hoop stress. In the frame of the SPIZWURZ project, the reorientation of zirconium hydrides in cladding tubes is being investigated under conditions similar to dry storage. For the long-term SPIZWURZ bundle experiment, 21 zirconium alloy tubes were charged with hydrogen to 100 and 300 wppm in the special developed HOKI tube oven as homogeneously as possible along a length of 1.3 m. The developed process allows a stepwise and controlled hydrogen absorption through the specially treated inner surface of claddings placed in the oven heated to 450 °C. The hydrogenation was carried out by successively supplying fixed masses of hydrogen, initially increasing the pressure in the tube sample from the achieved vacuum level to about 0.5 bar. Because of absorption, this pressure dropped to a predetermined vacuum level within a few minutes. During hydrogenation and subsequent heat treatment processes, the outer surface of the tube was exposed to a flow of oxygen to create an outer oxide layer more than 1 µm thick, which served as a barrier to hydrogen accumulating in the tube wall. After the hydrogen loading of the samples, the axial distribution of hydrogen was determined by laser scanning profilometry. This method makes it possible to use the correlation between the swelling of the rod diameter and the hydrogen concentration. This correlation was obtained by hot extraction of hydrogen from pre-hydrogenated reference samples. A long-term bundle test with hydrogenated and pressurized cladding tubes began on 12.05.2023 and will last until mid-January 2024. The peak cladding temperature decreased in steps of about 15 K from 400 to 200 °C currently (the average cooling rate is about 0.9 K/day).

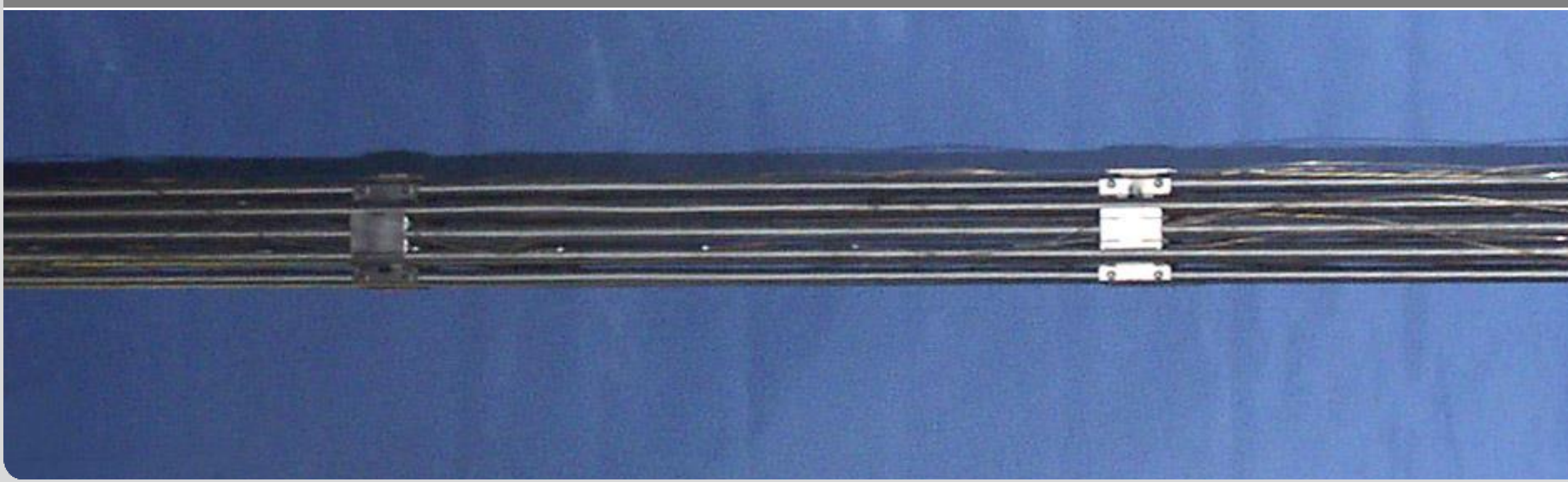
Karlsruhe Institute of Technology

Institute for Applied Materials

Hydrogenation of claddings in the new developed HOKI oven and performance of the long-term bundle test under dry storage conditions in the framework of the SPIZWURZ project

J. Stuckert, C. Rössger, J. Moch, M. Grosse, S. Weick

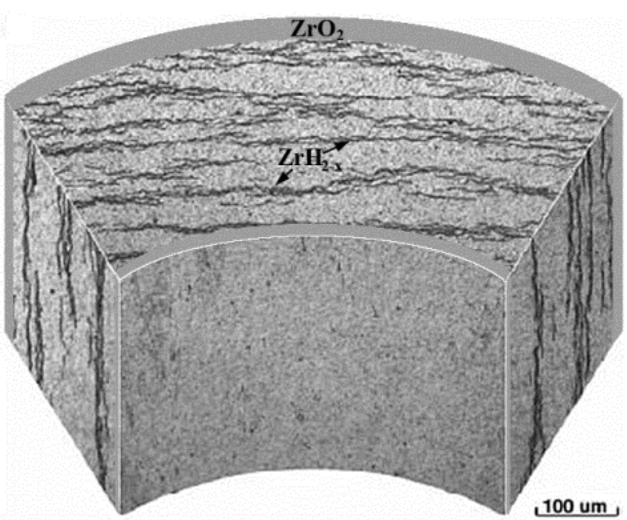
Institute for Applied Materials; Program NUSAFE



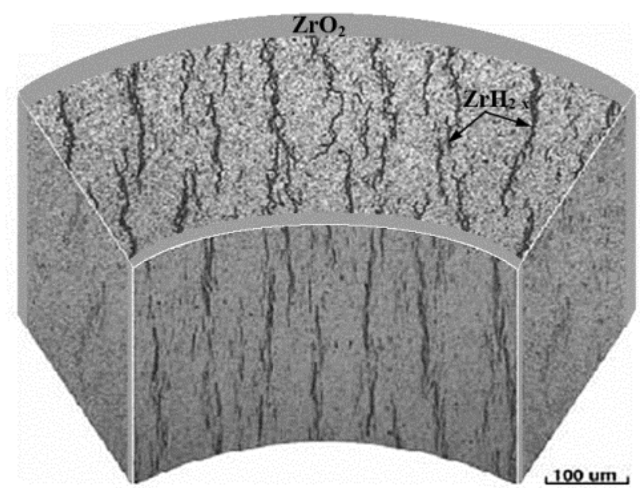
Goal of bundle test:

investigation of behavior of hydrides during the long-time dry storage of spent fuel with

- ***different cladding materials (Zry-4, opt. ZIRLO, DUPLEX)***
- ***different cladding inner pressures (140, 100 bar)***
- ***different hydrogen contents (100, 300 wppm)***
- ***different temperature histories (due to axial T profile in the bundle)***

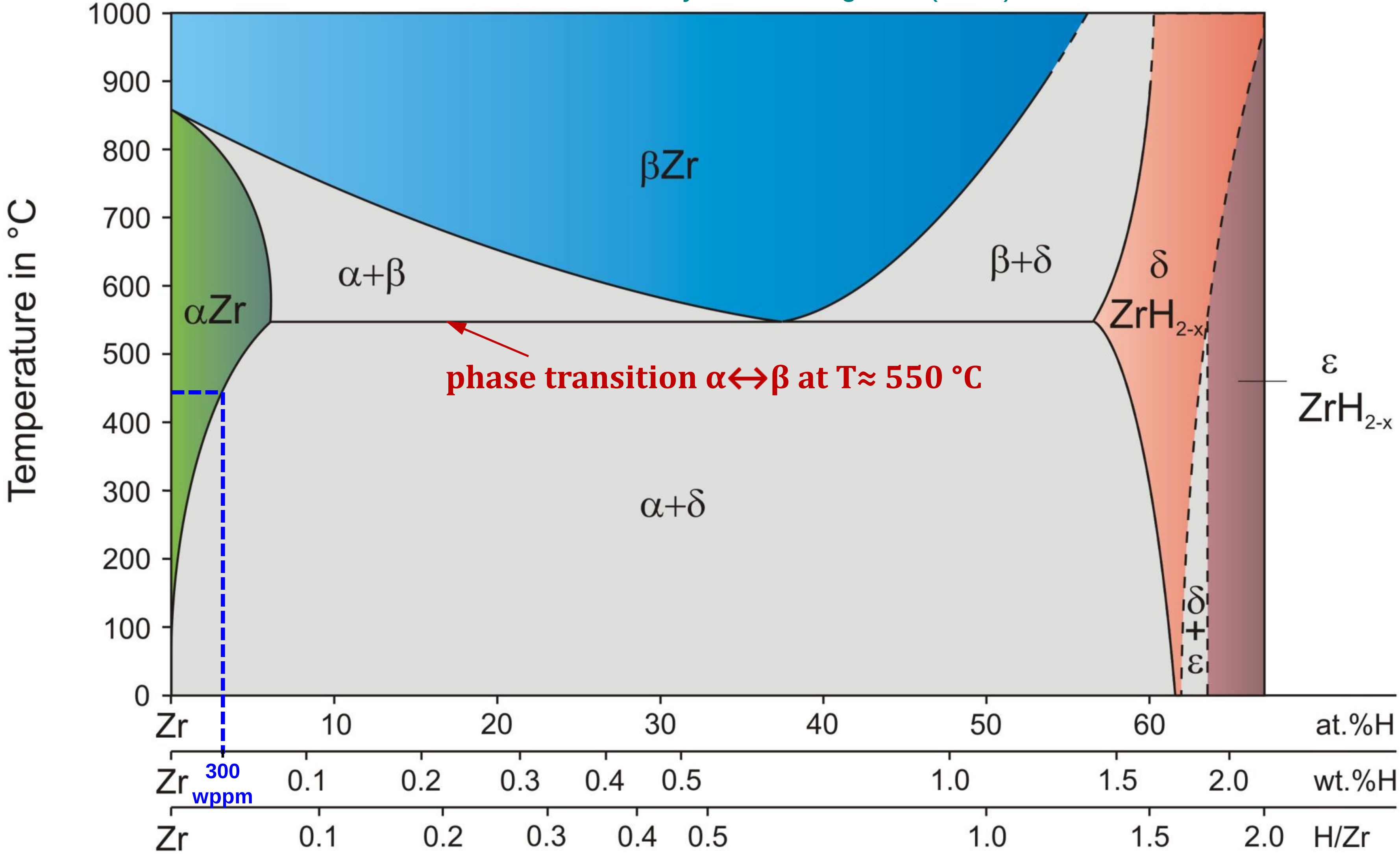


long time cool-down: reorientation of hydrides



Phase diagram Zr-H

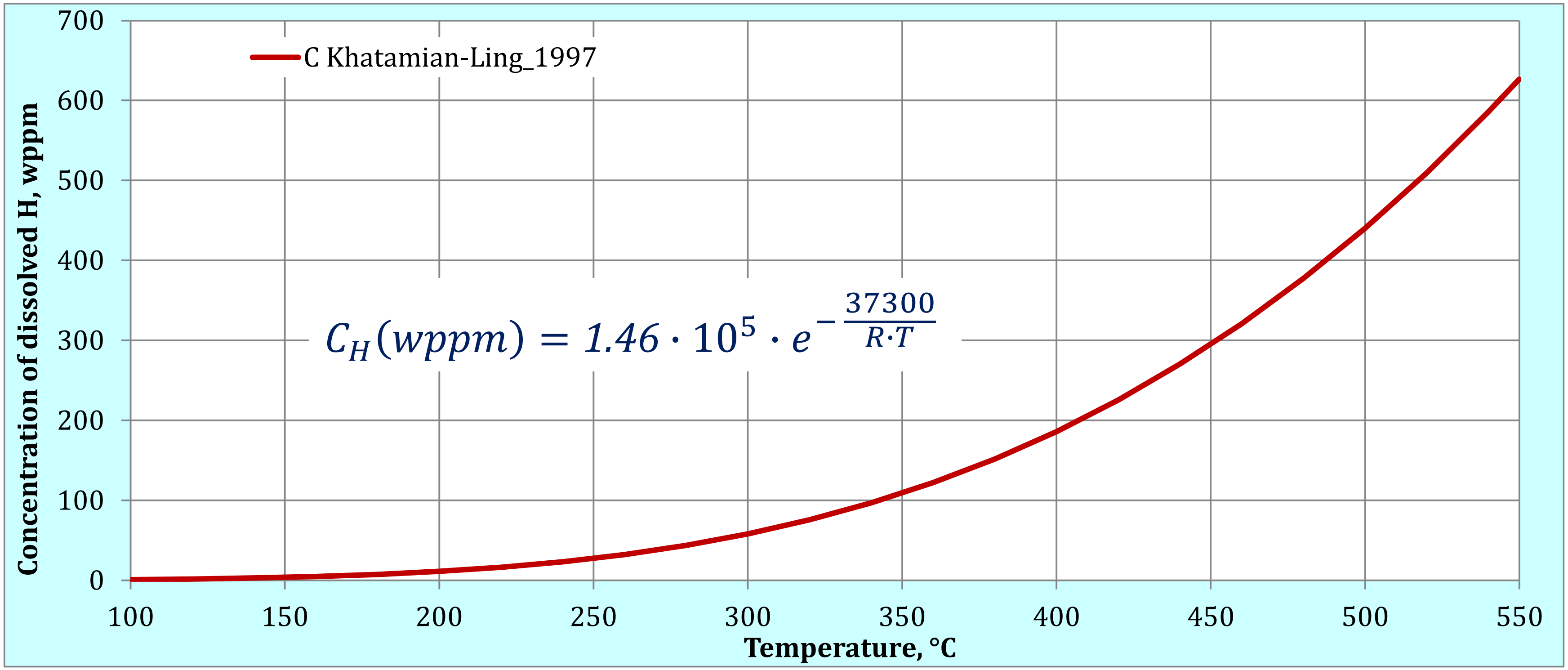
/nach Zuzek et al., Bull Alloy Phase Diagr., 11 (1990), 385/



hydriding of claddings should be performed at T<550 °C to avoid the phase transition

Solubility of hydrogen in α-Zirconium

/D. Khatamian, V.C. Ling, JAC vol.253-254, 1997, https://doi.org/10.1016/S0925-8388(96)02947-7/



$$C_H(wppm) = 1.46 \cdot 10^5 \cdot e^{-\frac{37300}{R \cdot T}}$$

T, °C	175	200	225	250	275	300	325	350	375	400	425	450	475
C_H, wppm	**7**	**11**	18	27	41	58	81	109	144	186	236	**295**	363

dissolved hydrogen at the end of the bundle test (175, 200 °C)

dissolved hydrogen at the beginning of the bundle test (400 °C)

dissolved hydrogen after hydriding in oven (450 °C)

Pre-hydrogenation of claddings in tube oven through the inner cladding surface with simultaneous oxidation of outer cladding surface

Karlsruhe Institute of Technology

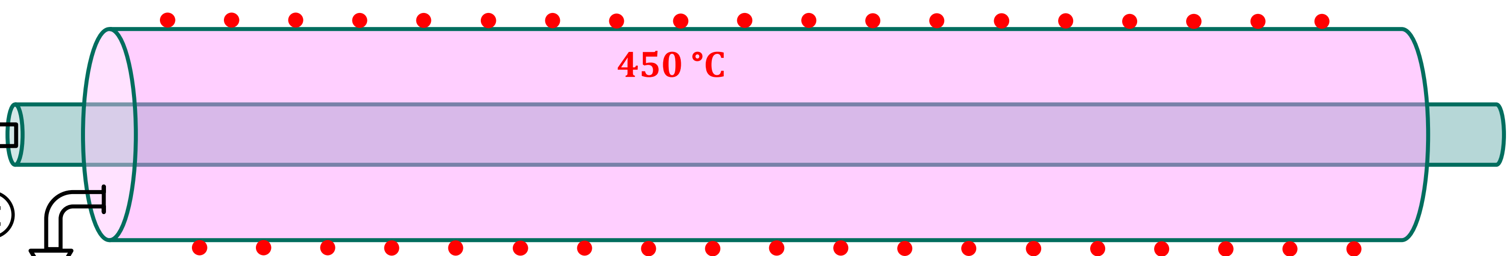
For hydriding to 300 wppm:
1) evacuation of cladding tube,
2) filling of cladding tube with H_2 to **8.4 bar** at T=450 °C,
3) p decrease to ≈**0 bar,**
4) annealing (T=450°C) during 3 h to homogenization of H distribution

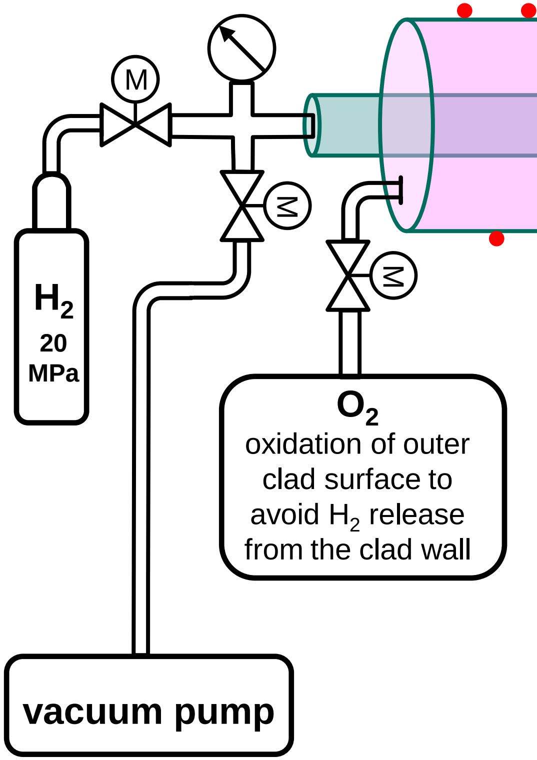
Duration of hydrogen absorption depends on the diffusion coefficient

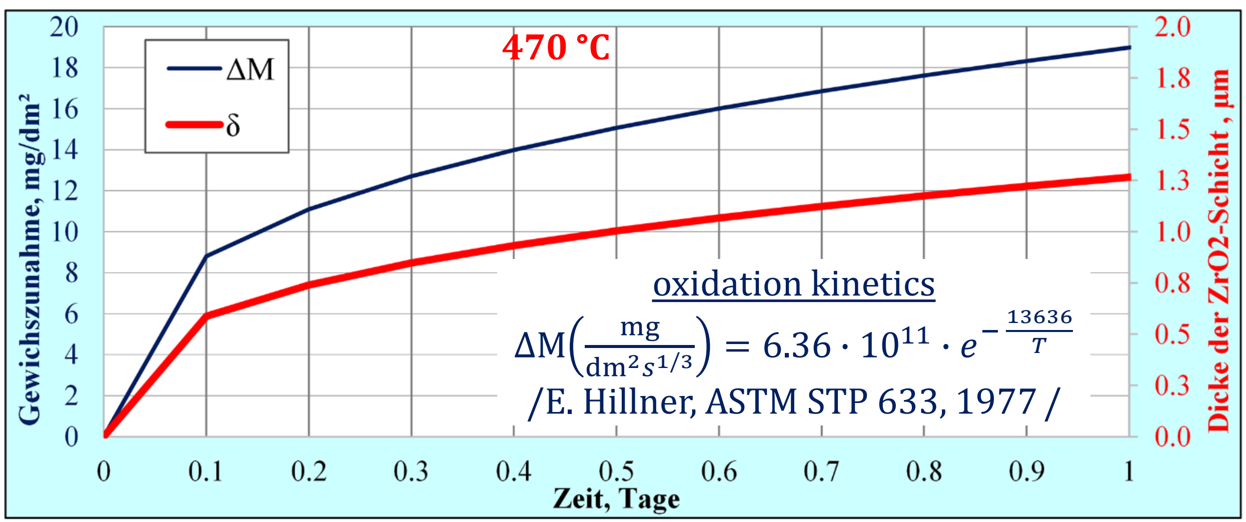
$$D_H^{Zr}\left(\mathrm{cm}^2/\mathrm{s}\right) = 7 \cdot 10^{-3} \cdot e^{-\frac{44560}{R \cdot T}}$$

/J.J. Kearns, JNM vol. 43, 1972, https://doi.org/10.1016/0022-3115(72)90065-7 /

and is therefore $t \approx \delta_{Zr}^2 / D_H^{Zr} \approx$ **1250 s** for clad thickness δ_{Zr}=725 µm, T=450 °C



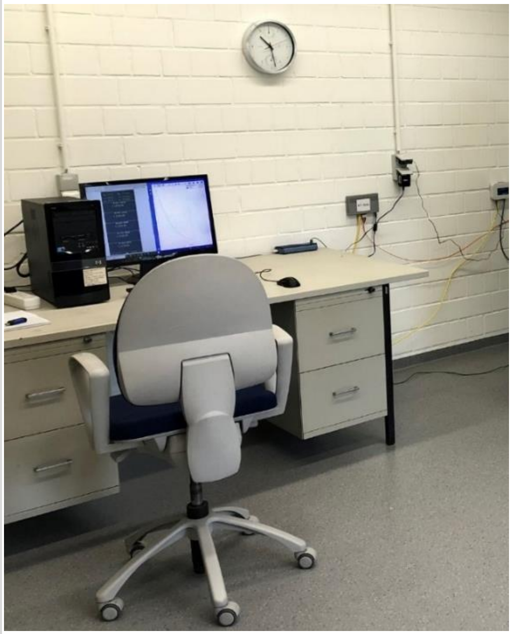




IAM Institute for Applied Materials

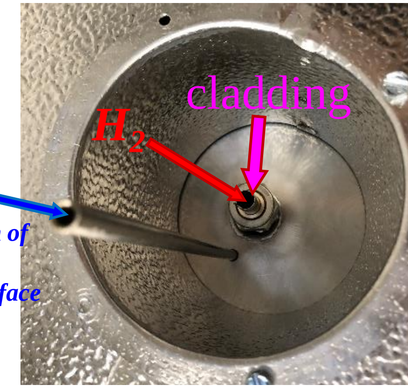
HOKI-facility: hydrogenation of single claddings through the inner cladding surface

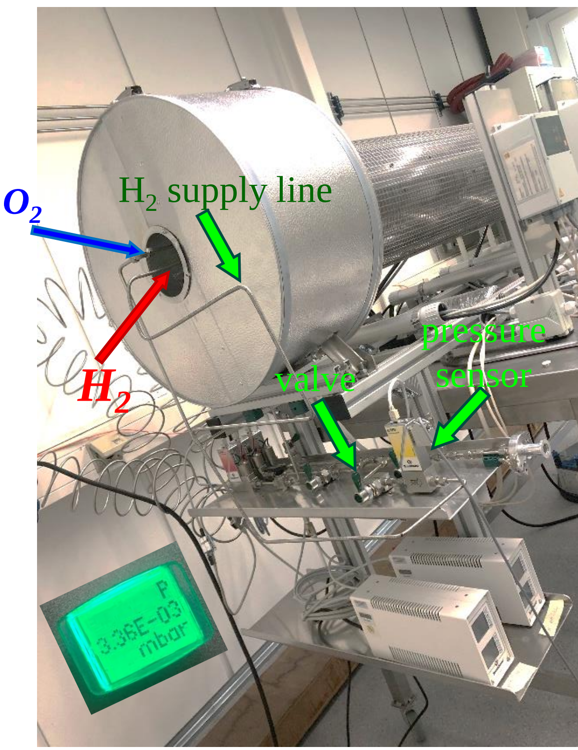
and oxidation of the outer cladding surface



control and recording system

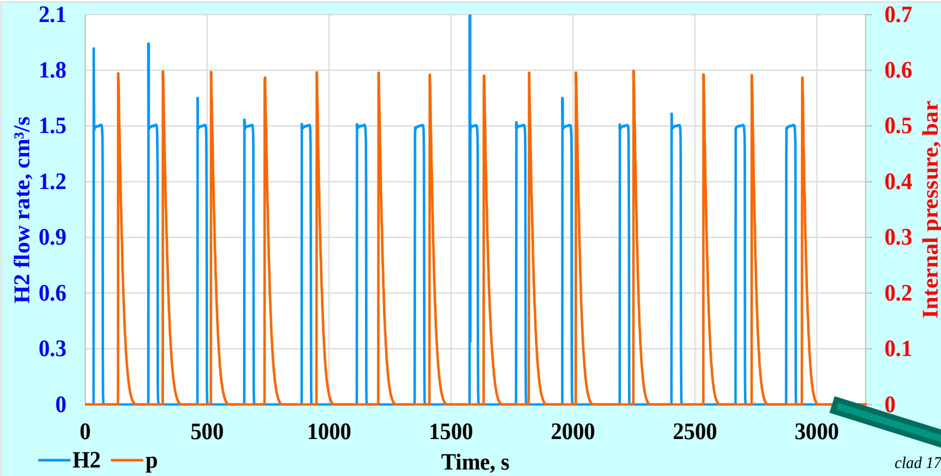
HOKI oven with 5 heated zones and connected gas system





$V_{H2} = V_{hot\ clad} + V_{cold\ supply} = 133\ cm^3 + 20\ cm^3$

Hydrogenation of each cladding in extended pulse mode to prevent rapid formation of hydrides near to the inner cladding surface



pulse filling of the internal cladding volume after special treatment of the inner cladding surface and evacuation of the cladding tube: repeated depressurization of inner cladding volume due to H_2 absorption

1) stepwise hydriding of cladding to 300 wppm H

14 injections *with* ***p_{max}=0.6 bar*** →

$$\text{total } m_{H2} = 14 \times \left(\frac{\mu p_{max} V_{hot}}{R T_{hot}} + \frac{\mu p_{max} V_{cold}}{R T_{cold}}\right) = 0.05\ g$$

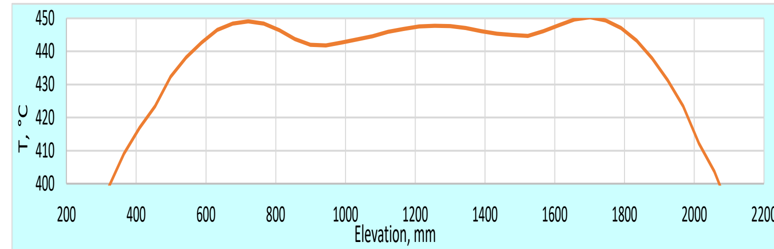
$M_{clad\ 125\ cm}$ = 170 g C_H = 0.05/170 ≈ **300 wppm**

2) stepwise hydriding of cladding to 100 wppm H

5 injections *with* ***p_{max}=0.6 bar*** →

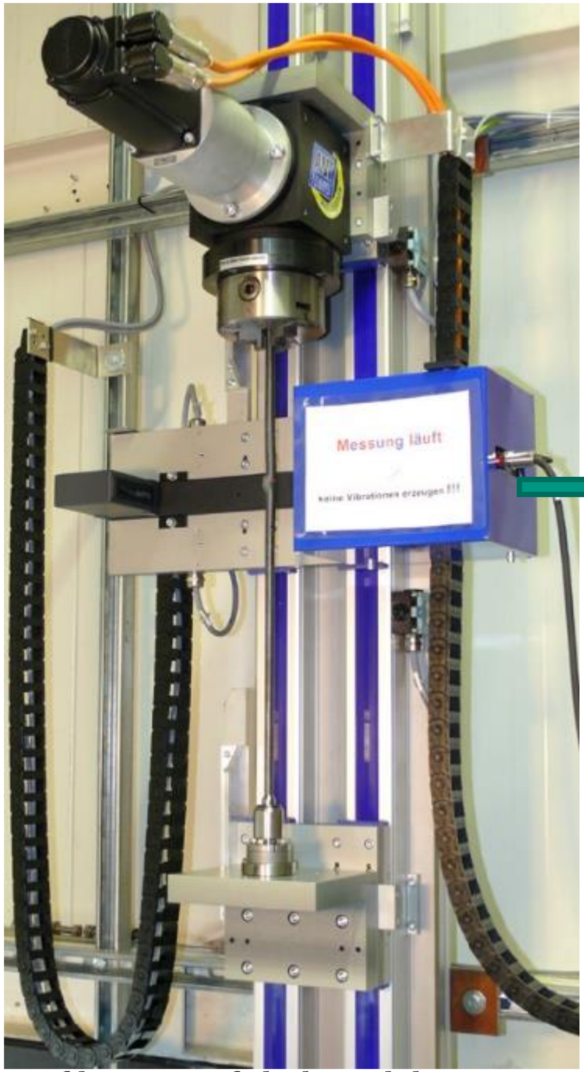
$$\text{total } m_{H2} = 5 \times \left(\frac{\mu p_{max} V_{hot}}{R T_{hot}} + \frac{\mu p_{max} V_{cold}}{R T_{cold}}\right) = 0.0179\ g$$

$M_{clad\ 125\ cm}$ = 170 g C_H = 0.0179/170 ≈ **100 wppm**

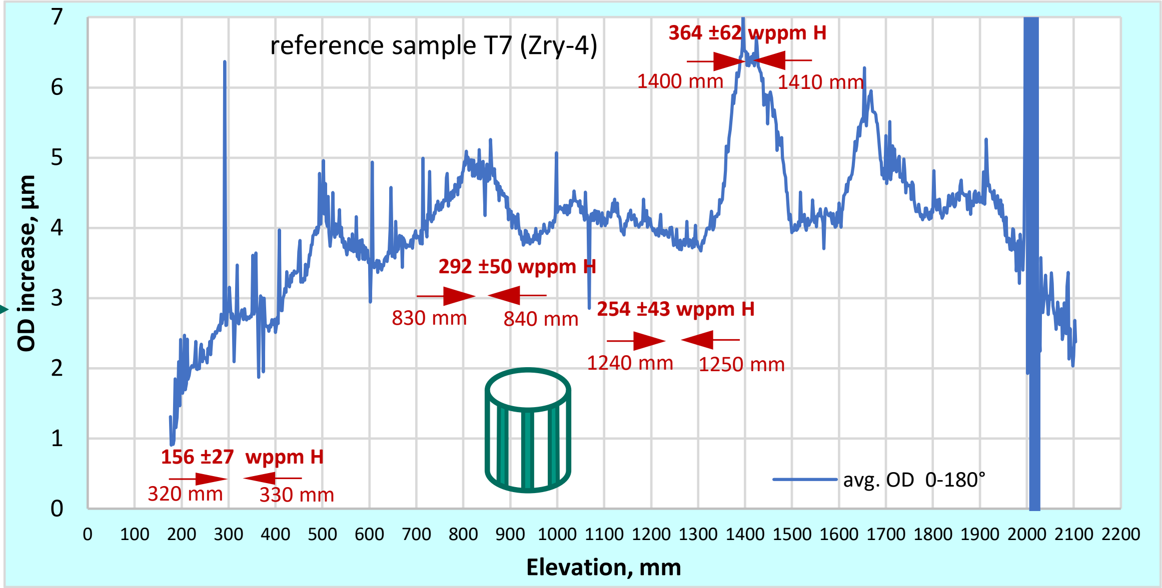


HOKI oven with axial temperature profile: T ≈ 450 °C along the length of ≈ 1250 mm

Determination of axial distribution of hydrogen concentration by increase of circumferential strain at each elevation



profilometry of clads with laser scanner
(thermal expansion ±0.3 µm for ±5 °C)

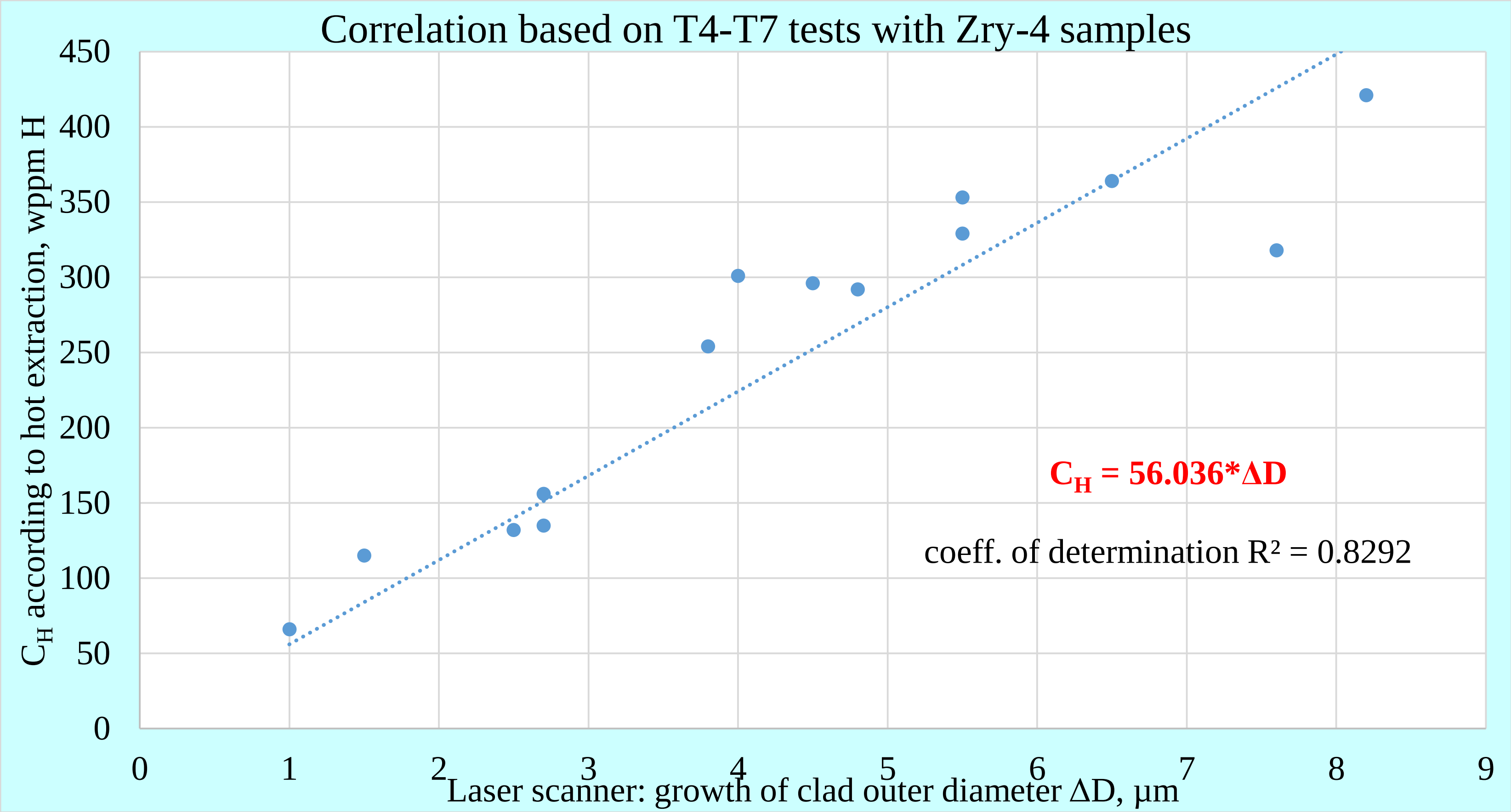


axial profile of cladding diameter increase (laser scanner)

and corresponded hydrogen concentrations
(hot extraction from 3 lamellas 10x1 mm)

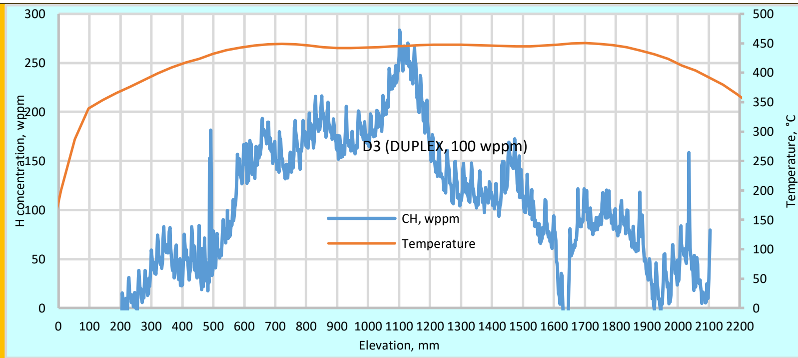
Correlation between hydrogen content and cladding diameter increase

sample	T4			T5			T6				T7			
axial position, mm	750	1250	1650	750	1250	1650	405	755	1155	1455	325	835	1245	1405
OD increase, µm (laser scanner)	**7.6**	**4**	**5.5**	**8.2**	**5.5**	**4.5**	**1**	**2.5**	**2.7**	**1.5**	**2.7**	**4.8**	**3.8**	**6.5**
hot extraction, wppm	**318**	**301**	**329**	**421**	**353**	**296**	**66**	**132**	**135**	**115**	**156**	**292**	**254**	**364**
± wppm	48	45	49	105	88	74	17	33	34	29	27	50	43	62
SD				25	3	2	27	2	1	5	4	13	6	3

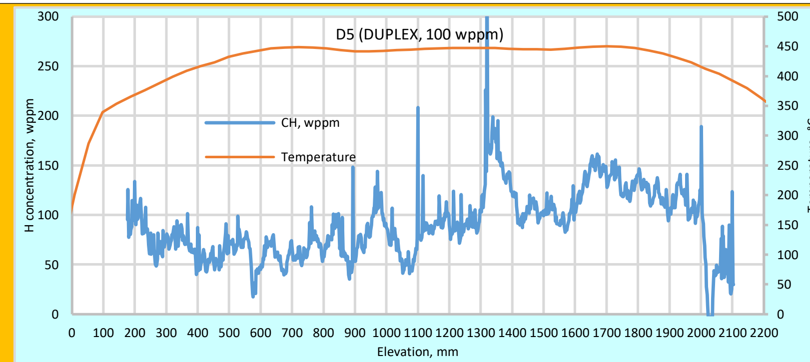


Axial hydrogen distribution for claddings hydrogenated to 100 wppm H

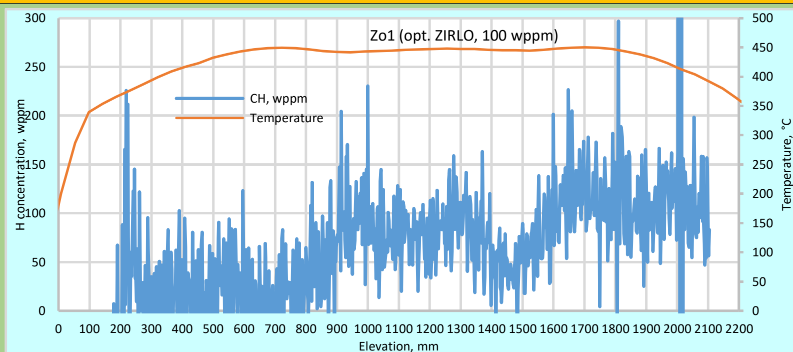
Karlsruhe Institute of Technology



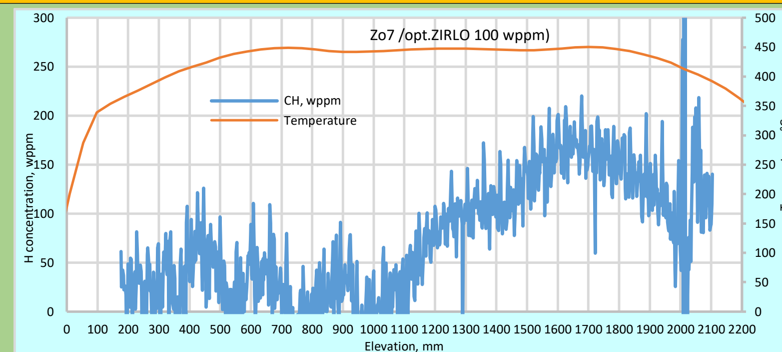
rod 19: **DUPLEX**



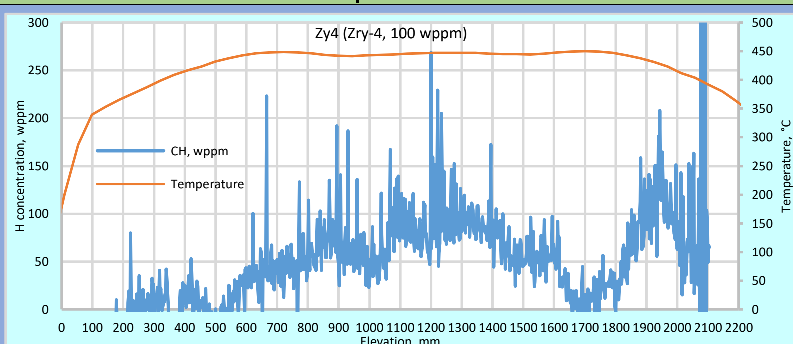
rod 21: **DUPLEX**



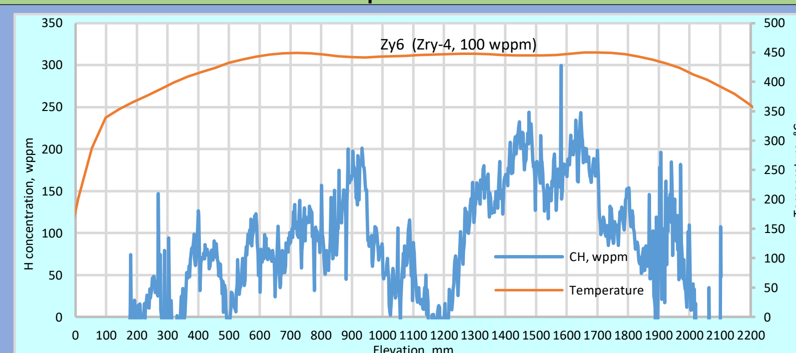
rod 3: **optimized ZIRLO**



rod 15: **optimized ZIRLO**

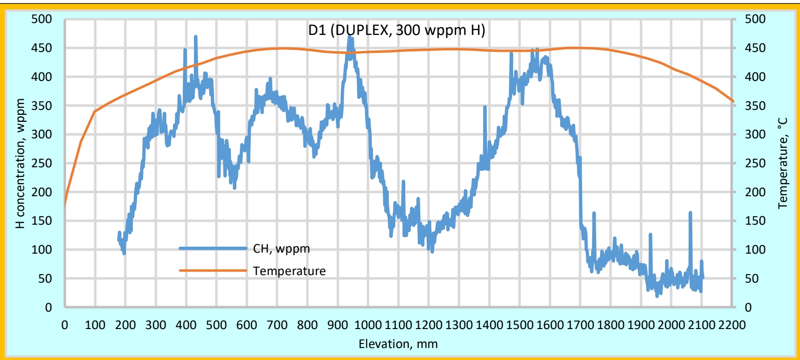


rod 8: **Zircaloy-4**

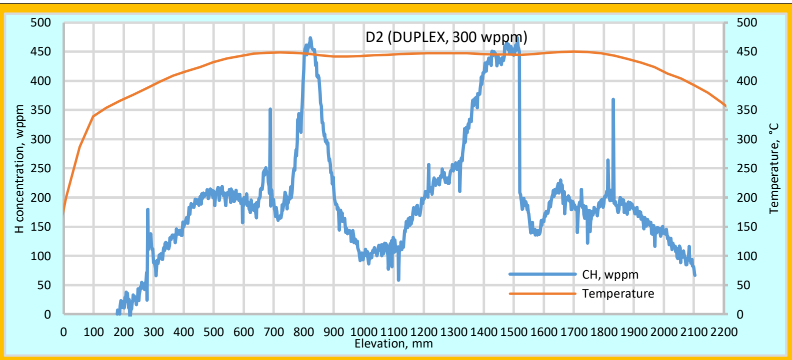


rod 14: **Zircaloy-4**

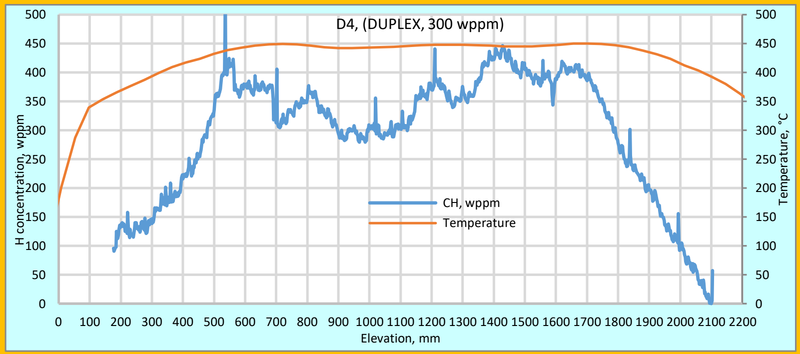
Axial hydrogen distribution for claddings hydrogenated to 300 wppm H



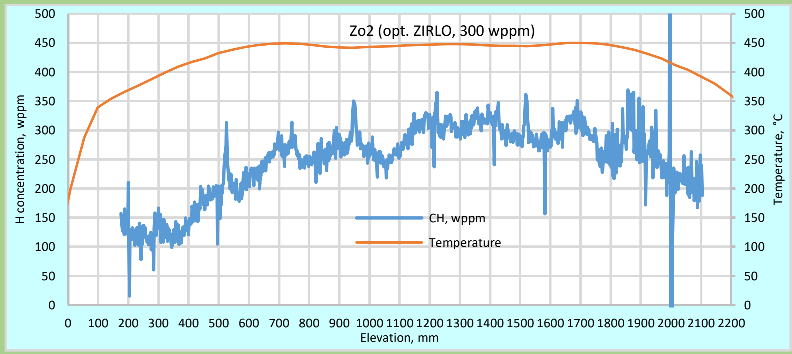
rod 1: **DUPLEX**



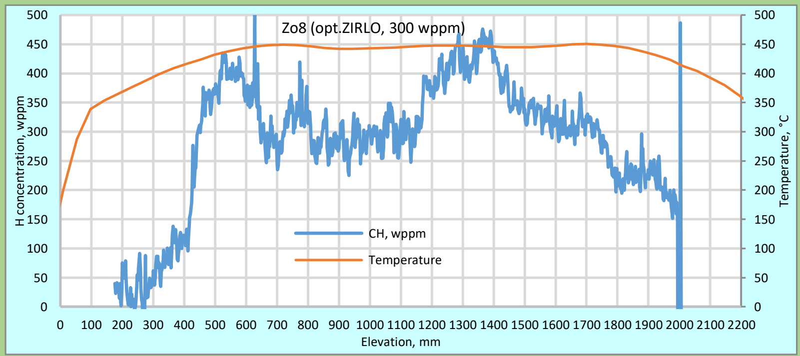
rod 9: **DUPLEX**



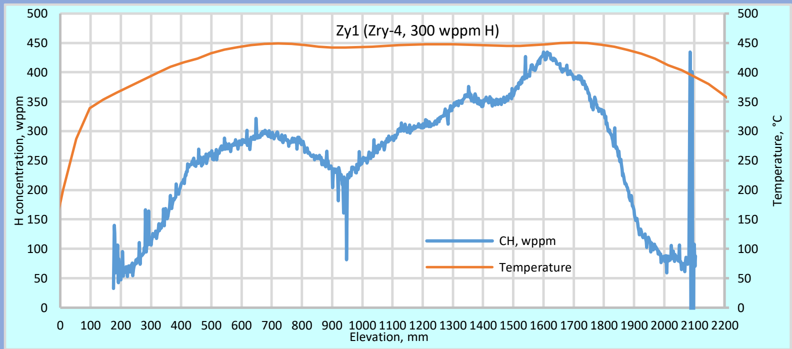
rod 20: **DUPLEX**



rod 5: **optimized ZIRLO**



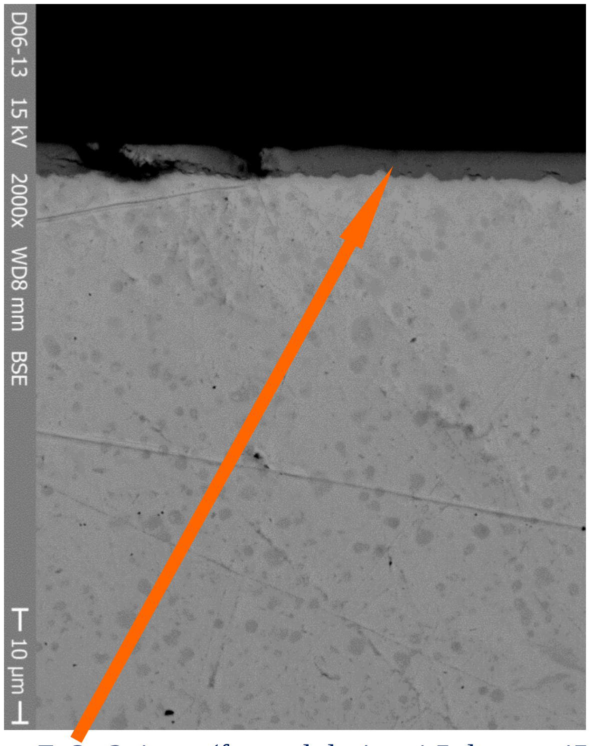
rod 16: **optimized ZIRLO**



rod 2: **Zry-4**

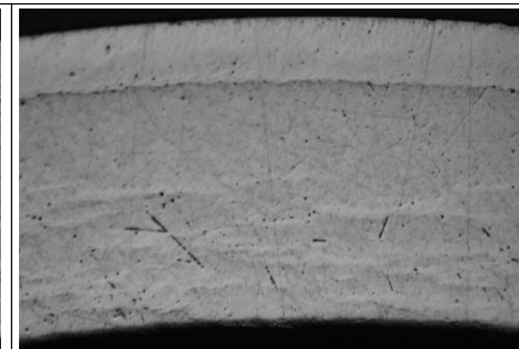
Metallography of the reference sample D6 (DUPLEX with outer 150 µm liner)

not etched cladding cross-sections



outer ZrO_2 2.4 µm (formed during 4.5 days at 450 °C)
corresponds 0.3% O in whole sample,
what was confirmed also by hot extraction

300 wppm



170 wppm

200 wppm

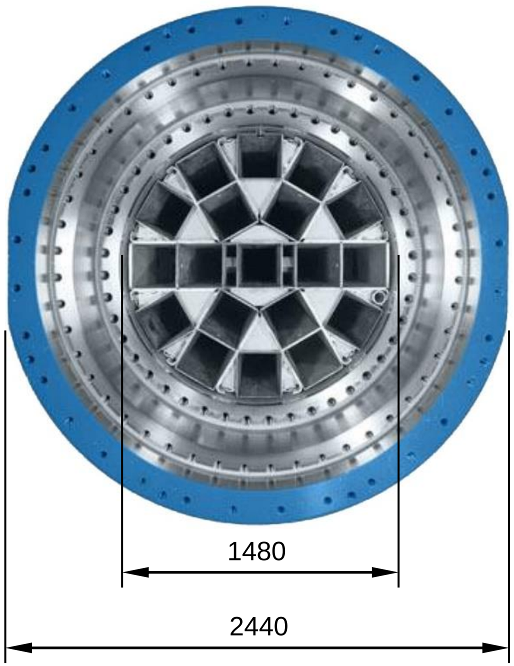
SEM: 170 wppm

hydrides

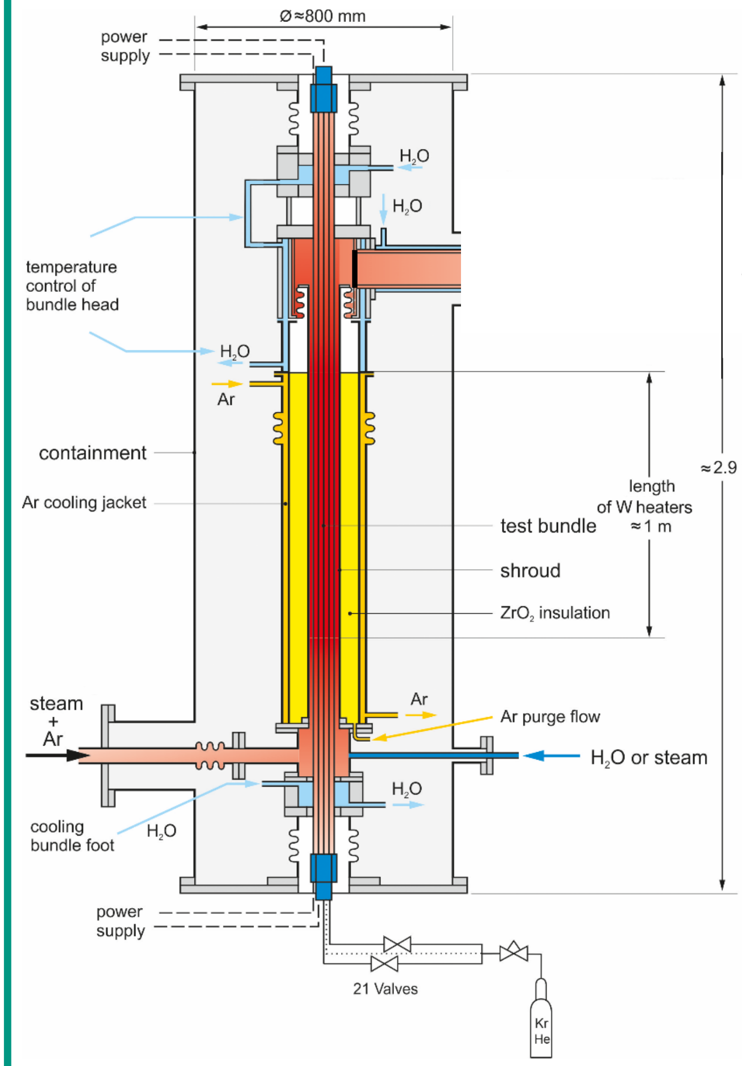
Relationship between the CASTOR-V/19 container (PWR) and the QUENCH bundle simulator

Karlsruhe Institute of Technology

Trockenlager

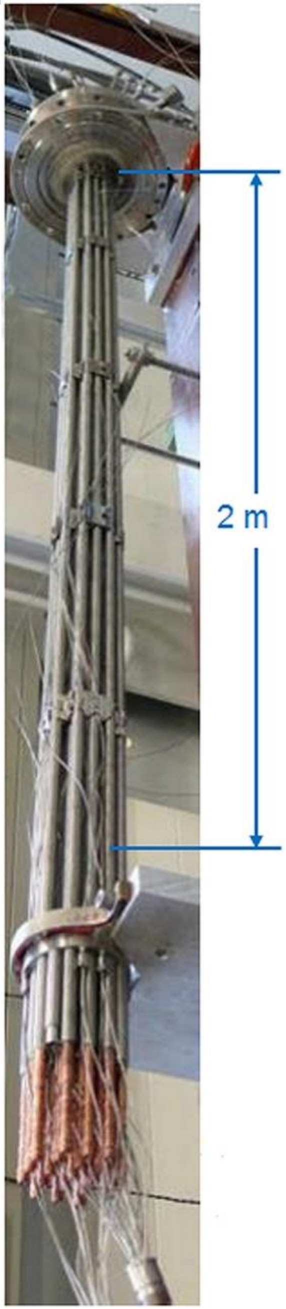


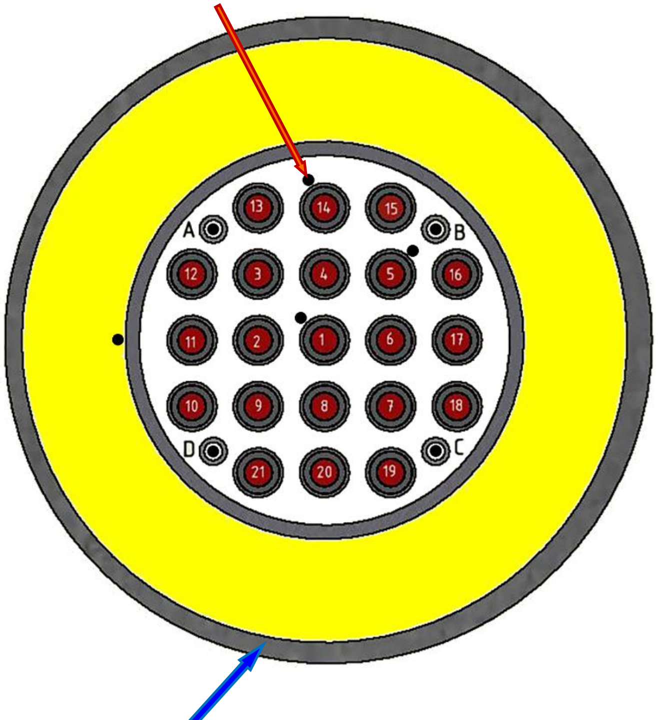
Container for 19 fuel elements
with a maximum height of 4950 mm and a total heat output of 39 kW



QUENCH test section

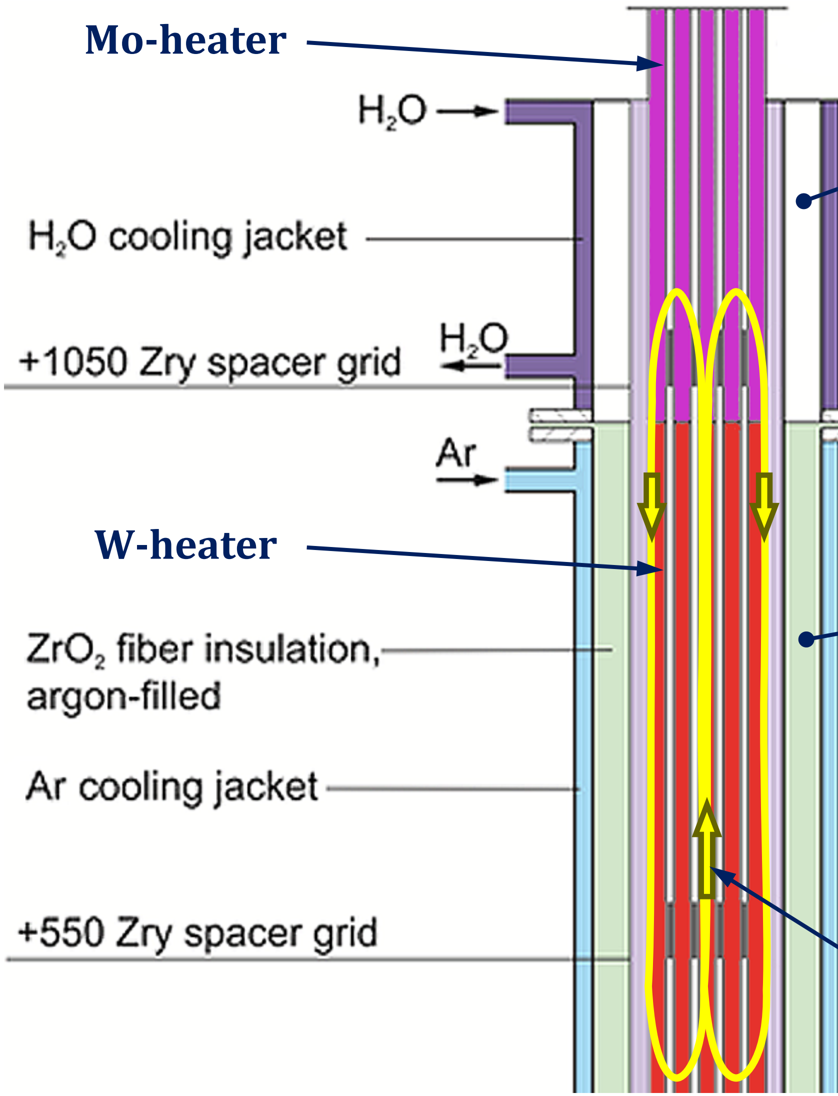
SPIZWURZ bundle





Bundle size		21 heated rods
Pitch		14.3 mm
Corner rod (4)	material	Zircaloy-4
	instrumented (A, B, C, D)	tube ∅ 6x0.5 (bottom: -1140 mm)
Grid spacer	material	Zircaloy-4
	length	42 mm
	sheet thickness	0.5 mm
	elevation of lower edge	Zry: -100, 150, 550, 1050, 1410 mm
Shroud	material	Zirconium 702 (flange: Zry-4)
	wall thickness	3.17 mm
	outside diameter	86.0 mm
	length (extension)	1600 mm (-300 mm to 1300 mm)
Shroud insulation	material	ZrO_2 fiber
	insulation thickness	~ 36 mm
	elevation	-300 to ~1000 mm
Cooling jacket	Material: inner/outer	Inconel 600 (2.4816) / SS (1.4571)
	inner tube	∅ 158.3 / 168.3 mm
	outer tube	∅ 181.7 / 193.7 mm
Thermocouples	at cladding surfaces	rods 1, 5, 9; totally 3x15=45
	inside corner rods	one at each elevation 2-16, totally 15
	at shroud outer surface	one at each elevation 3-15, totally 13

Heat transport in the QUENCH bundle



empty space (δ_{gap}=37 mm) at bundle head field with Ar with heat conductivity λ_{Ar}=0.01772 W/(m·K):

- low bundle head cooling due to conductivity

$$\dot{Q}_{cond} = \lambda \cdot \frac{T_{bundle} - T_{jacket}}{\delta} = 0.01772 \cdot \frac{350-15}{0.037} \approx 160\ W/m^2$$

- ***intensive** bundle head cooling by radiation*

$$\dot{Q}_{rad} = \varepsilon \cdot \sigma \cdot (T^4_{bundle} - T^4_{jacket}) = 0.27 \cdot \sigma \cdot (623^4\text{-}288^4) \approx 2200\ W/m^2$$

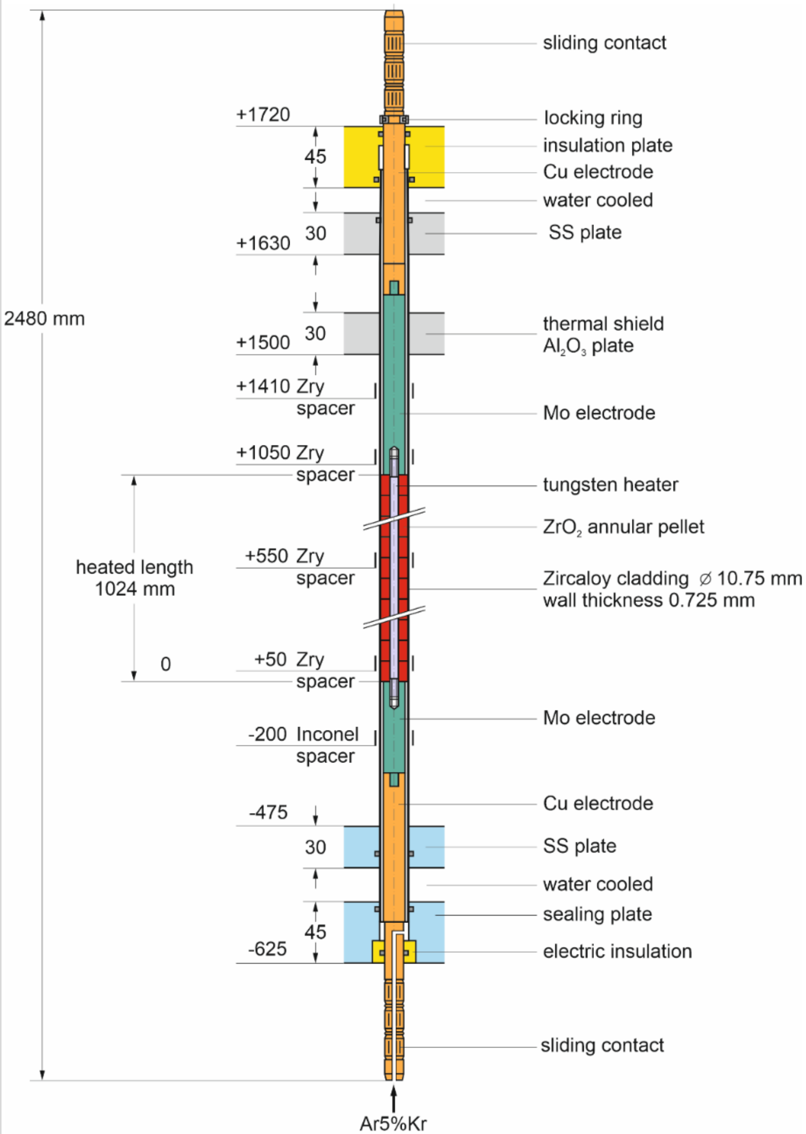
porous ZrO_2 thermal insulation (porosity 92%) with thermal conductivity $\lambda_{porousZrO2}$=0.08 W/(m·K) (673 K)

heat flow:

$$\dot{Q}_{cond} = \lambda \cdot \frac{T_{bundle} - T_{jacket}}{\delta} = 0.08 \cdot \frac{450-15}{0.037} \approx 940\ W/m^2$$

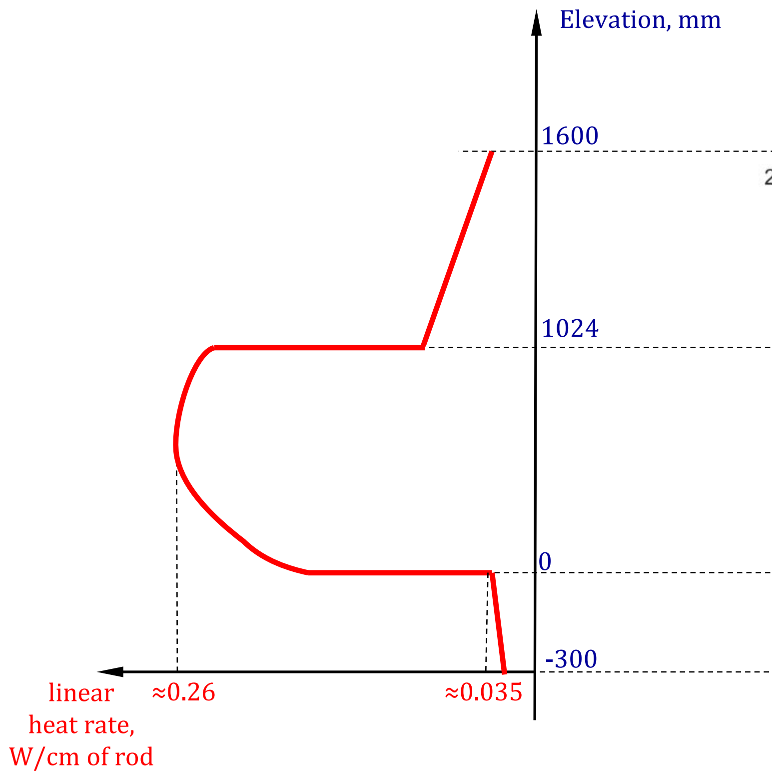
Total QUENCH bundle heat loss ≈630 W

Heated rod



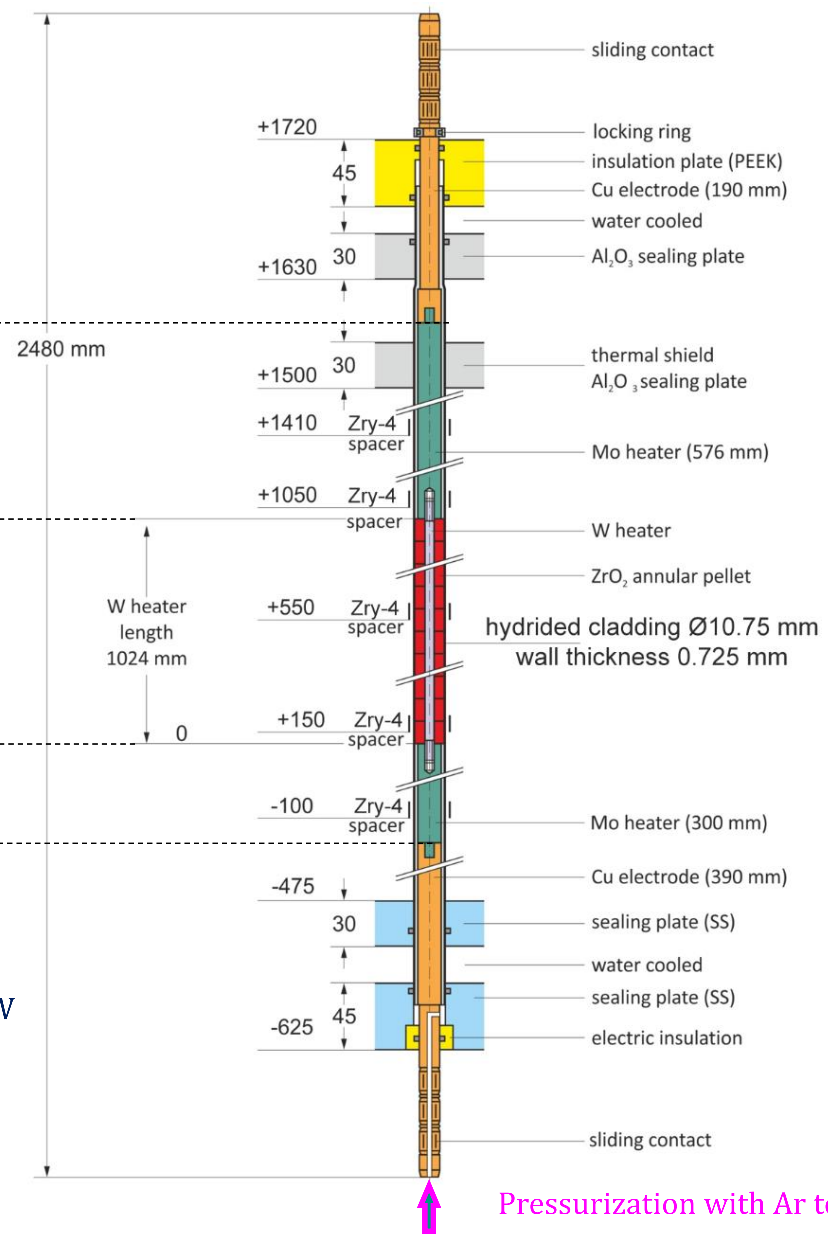
Cladding outside diameter		**10.75 mm**
Cladding thickness		**0.725 mm**
Cladding length	**(position in the bundle)**	**2278 mm (between -593 and 1685 mm)**
Rod length	(elevations)	2480 mm (-690 to 1790 mm)
Internal rod pressure; gas		5.5 MPa abs.; Kr
Material of middle heater 	 surface roughness	Tungsten (W) Ra=1.6 µm
Tungsten heater length		1024 mm (between 0 and 1024 mm)
Tungsten heater diameter		4.6 mm
Annular pellet	material dimensions surface roughness	ZrO_2;Y_2O_3-stabilized ∅ 9.15/4.75 mm; L=11 mm Ra=0.3 µm
Pellet stack		0 mm to ~1020 mm
Molybdenum heaters and copper electrodes	length of upper part length of lower part outer diameter: prior to coating after coating with ZrO_2 coat. surface roughness borehole of Cu-electrodes	766 mm (576 Mo, 190 mm Cu) 690 mm (300 Mo, 390 mm Cu) 8.6 mm 9.0 mm Ra=6-12 µm diameter 2 mm, length 96 mm
Gas volume inside the rod	**heated**	**15 cm³**
Gas volume outside the rod	**not heated (room T)**	**20 cm³**

Fuel rod simulator, electrically heated with W and Mo heaters

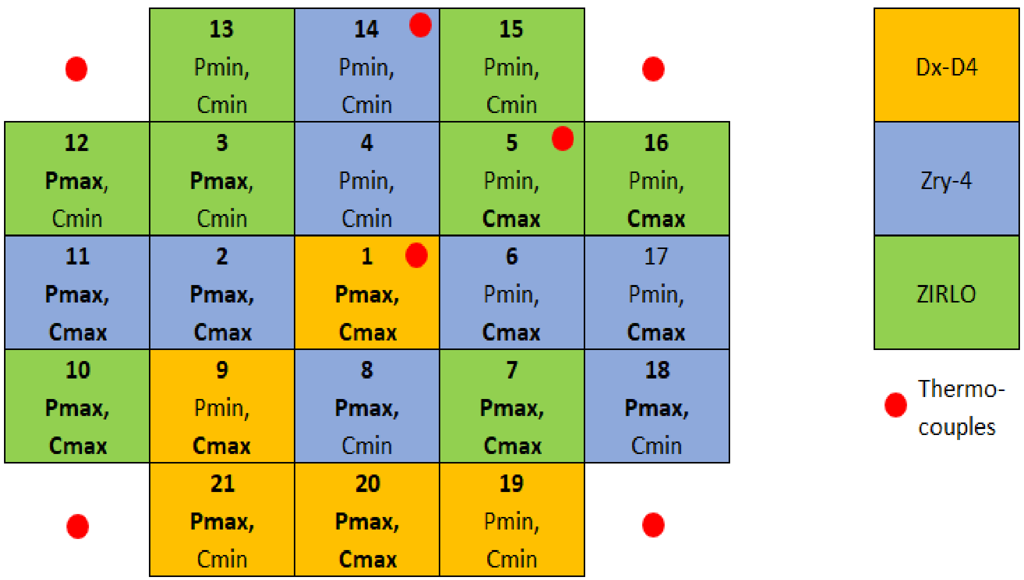


Axial power distribution at a maximum bundle temperature of 400 °C and assumed heat losses of 630 W

To comparison: the average linear heat rate of CASTOR V/19 with a total heat output of 39 kW is ≈0.02 W/cm

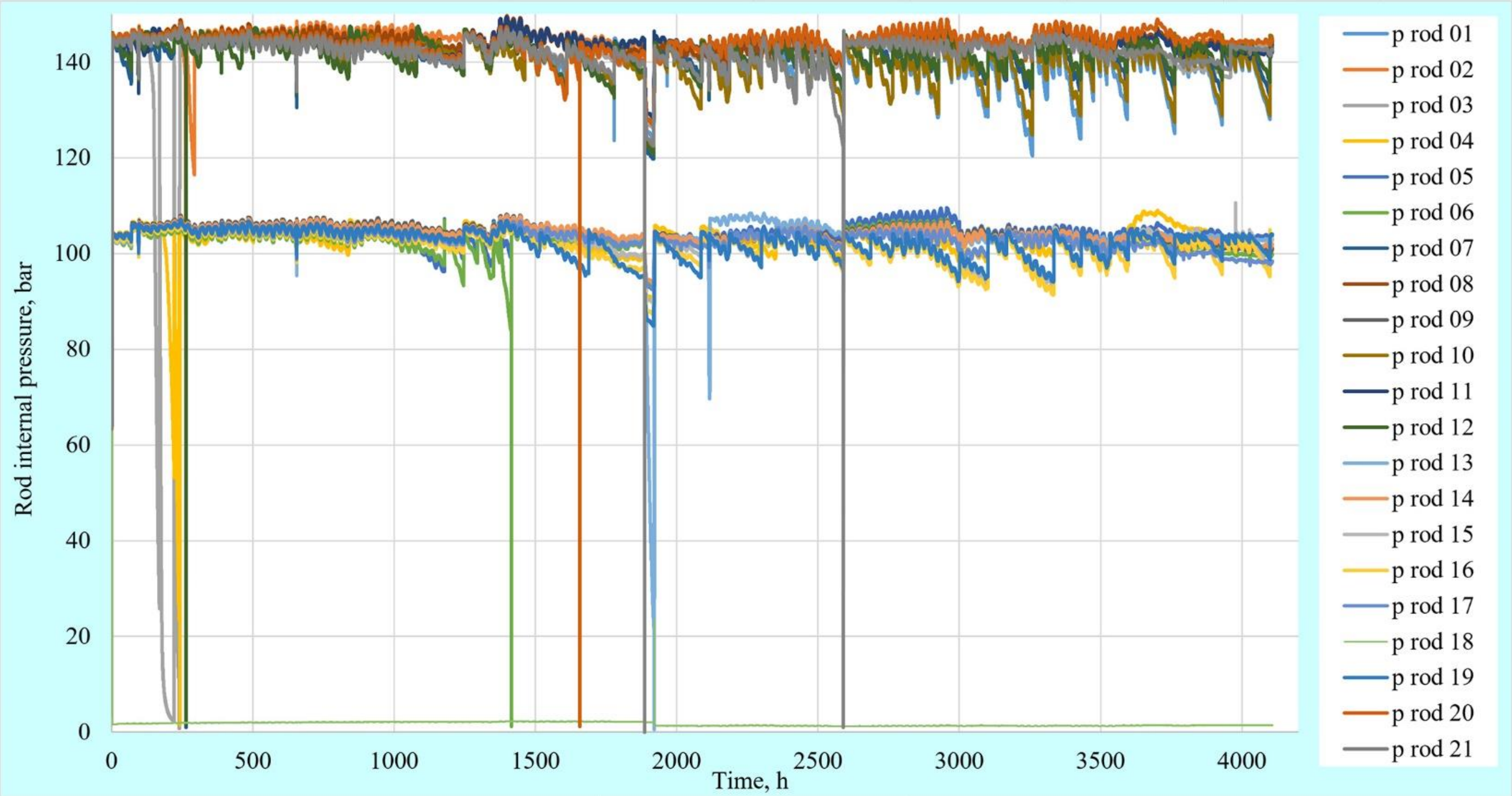


Bundle composition



number	rod	alloy	H conc., wppm	mark
D1	1	***DUPLEX***	**300**	D1
Zry0212	2	***Zry-4***	**300**	Zy1
Zo049	3	***ZIRLO***	**100**	Zo1
Zy31	4	***Zry-4***	**100**	Zy2
Zo087	5	***ZIRLO***	**300**	Zo2
Zy85	6	***Zry-4***	**300**	Zy3
Zo156	7	***ZIRLO***	**300**	Zo3
Zry197	8	***Zry-4***	**100**	Zy4
D2	9	***DUPLEX***	**300**	D2
Zo165	10	***ZIRLO***	**300**	Zo4
Zry199	11	***Zry-4***	**300**	Zy5
Zo220	12	***ZIRLO***	**100**	Zo5
Zo221	13	***ZIRLO***	**100**	Zo6
Zy914	14	***Zry-4***	**100**	Zy6
Zo332	15	***ZIRLO***	**100**	Zo7
Zo351	16	***ZIRLO***	**300**	Zo8
Zry1021	17	***Zry-4***	**300**	Zy7
	18	***Zry-4***	**100**	Zy8
D3	19	***DUPLEX***	**100**	D3
D4	20	***DUPLEX***	**300**	D4
D5	21	***DUPLEX***	**100**	D5

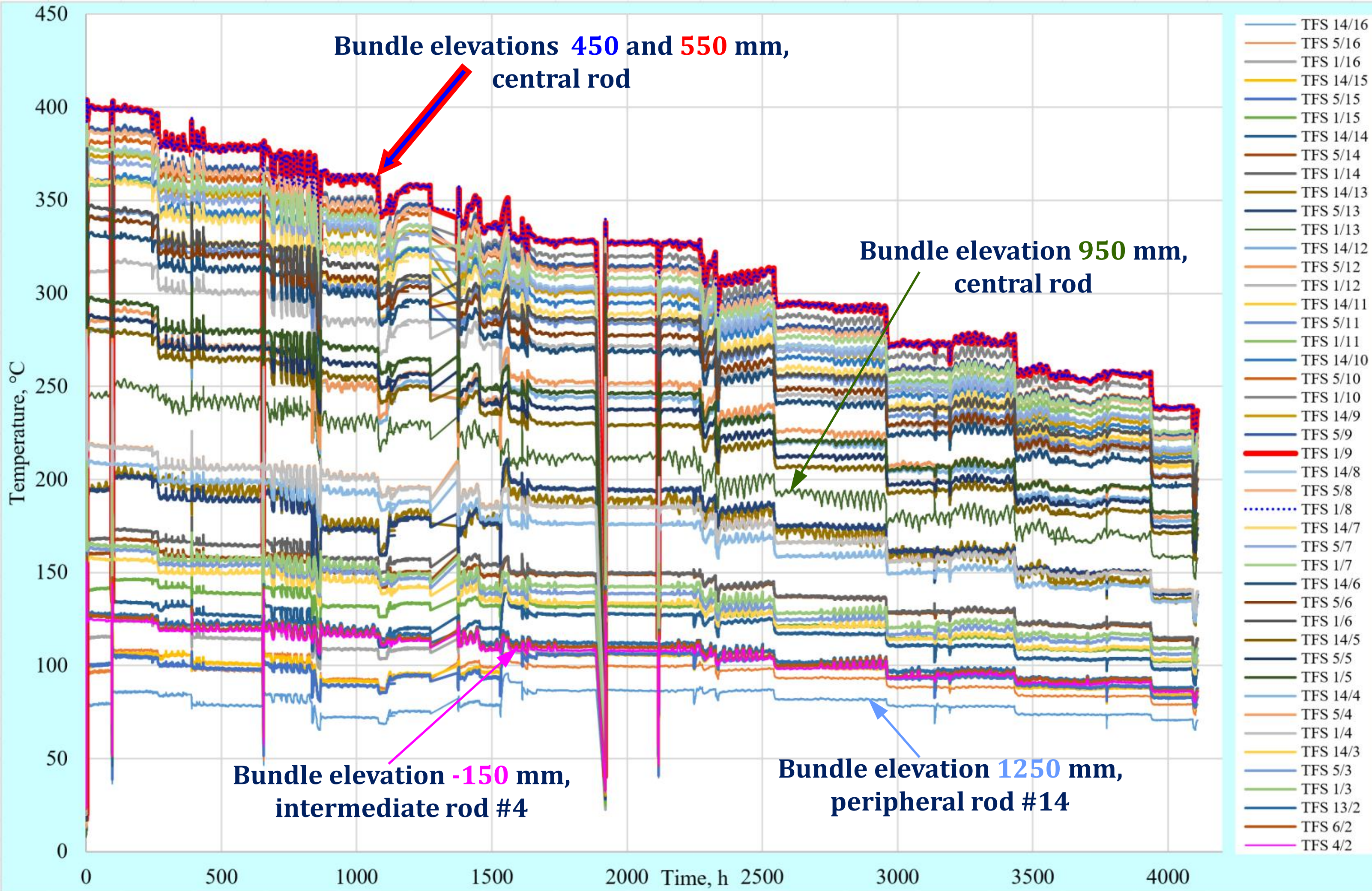
Pressures inside the rods between 12.05 and 30.10.2023



- two pressurization levels of **106 and 146 bar**
- daily refill of 7 rods with $Ar+O_2$ due to small leakages
- short depressurizations of 6 rods due to change of sealing rings

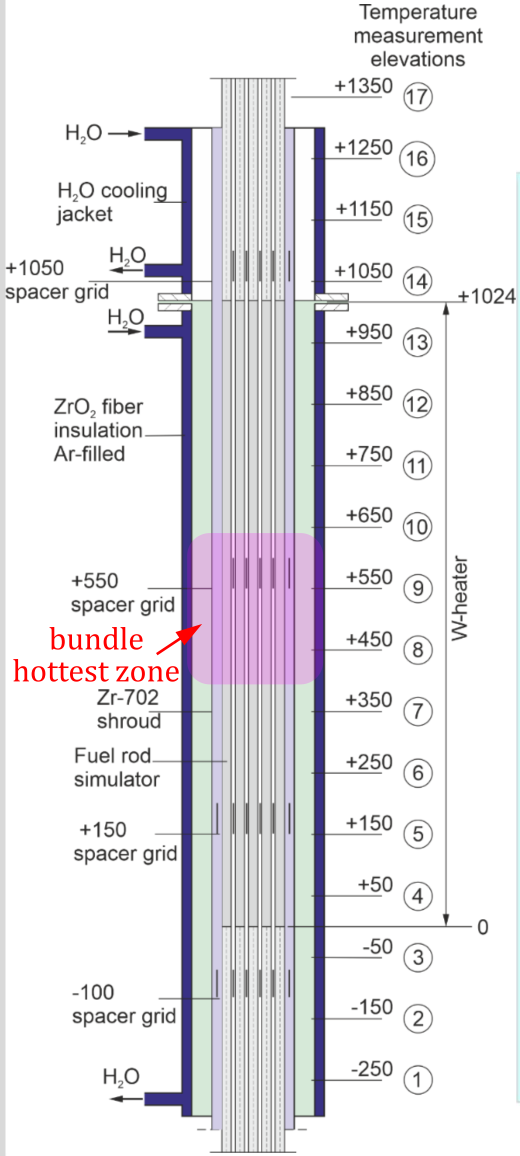
Reading of cladding surface thermocouples (TFS) between 12.05 and 30.10.2023

Karlsruhe Institute of Technology

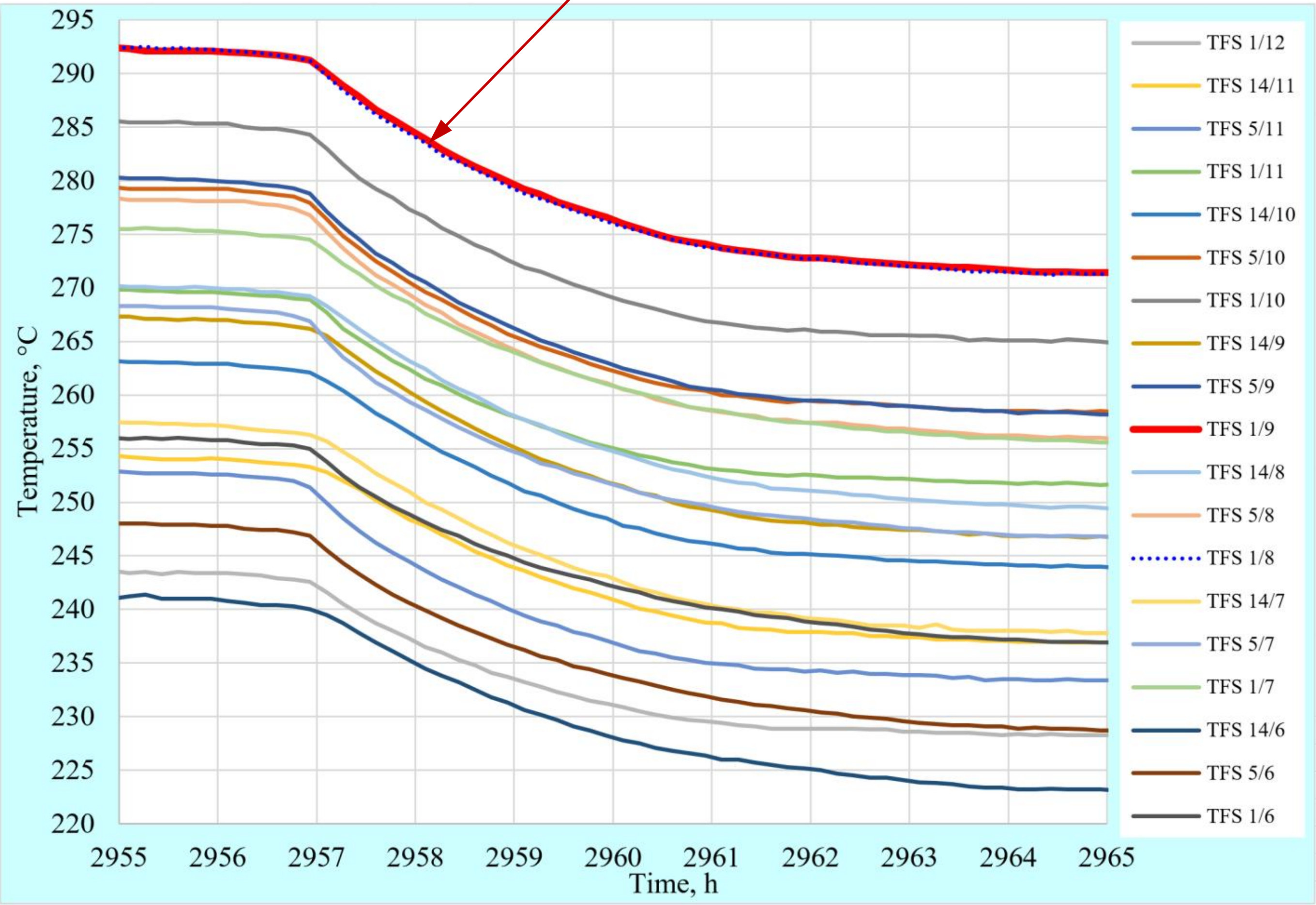


- peak cladding temperature decreased in steps with 15 K decrement and average duration of 400 h, average cooling rate 0.9 K/day
- periodic daily temperature fluctuations ≈±1.5 K for each thermocouple
- 4 el. power breakdowns

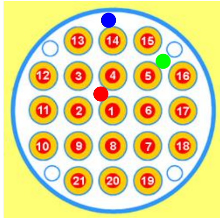
Smooth temperature decrease on the time of the power step reduction

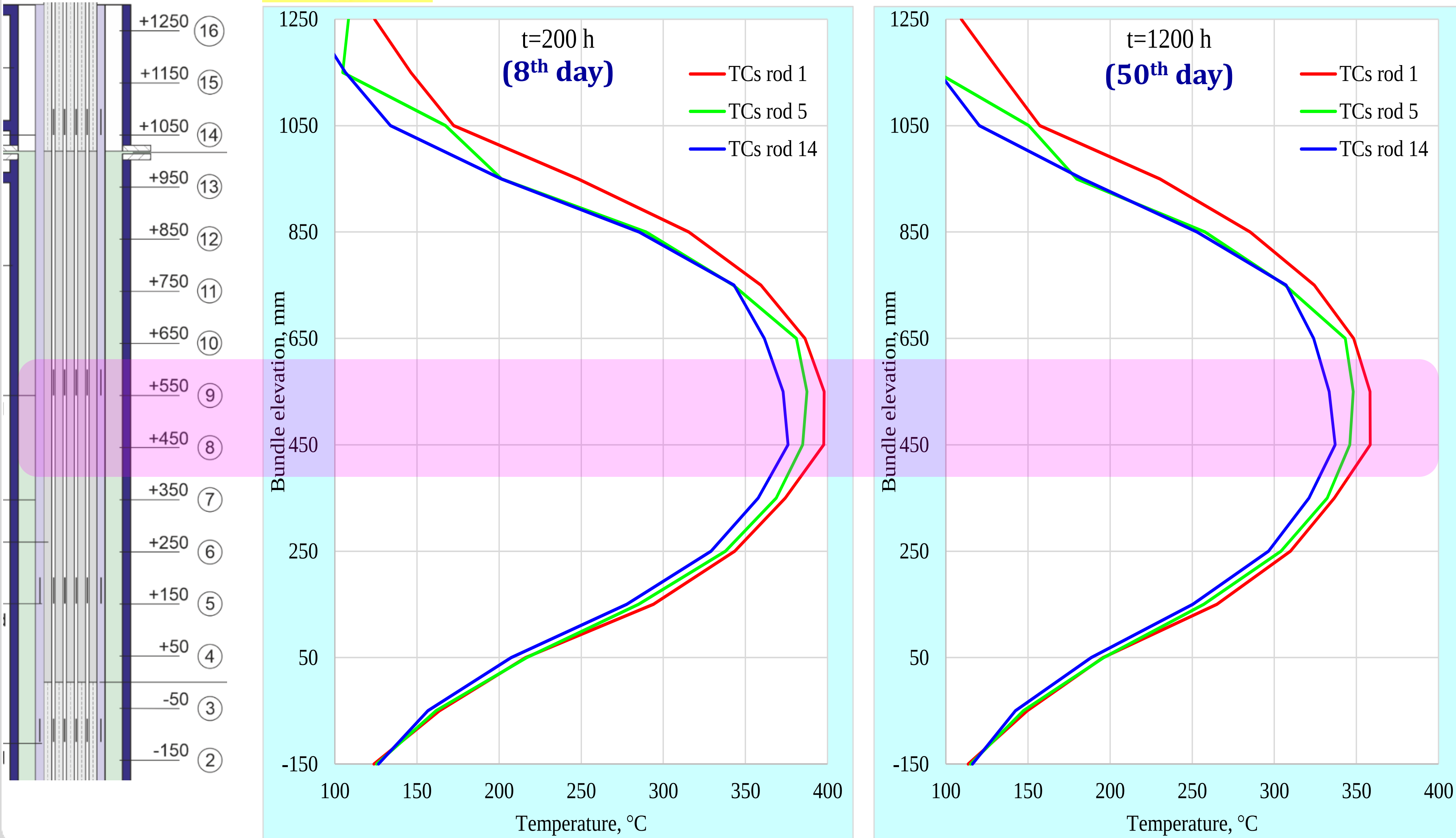


cooling rate decreased from 4 K/day ($5*10^{-5}$ K/s) to 0 K/s during 10 h



Axial temperature distribution for three rod groups





Summary

Karlsruhe Institute of Technology

- For the long-term SPIZWURZ bundle experiment, zirconium alloy tubes were charged with hydrogen to 100 and 300 wppm in the special developed HOKI tube oven as homogeneously as possible along a length of 1.3 m.
- The developed process allows a stepwise and controlled hydrogen absorption through the specially treated **inner** surface of claddings placed in the oven heated to 450 °C.
- The hydrogenation was carried out by successively supplying fixed masses of hydrogen, initially increasing the pressure in the tube sample from the achieved vacuum level to about 0.05 MPa. As a result of absorption, this pressure dropped to a predetermined vacuum level within a few minutes.
- During hydrogenation and subsequent heat treatment processes, the outer surface of the tube was exposed to a flow of oxygen to create an outer oxide layer more than 1 μm thick, which served as a barrier to hydrogen accumulating in the tube wall.
- After the hydrogen loading of the samples, the axial distribution of hydrogen was determined by laser scanning profilometry. This method makes it possible to use the correlation between the swelling of the rod diameter and the hydrogen concentration (verified by hot gas extraction).
- A long-term bundle test with 21 hydrogenated and pressurized cladding tubes began on 12.05.2023 and will last until mid-January 2024. The peak cladding temperature decreased in steps of 15 K from 400 to 200 °C today (average cooling rate ≈0.9 K/day).

Thank you for your attention

http://www.iam.kit.edu/awp/163.php

http://quench.forschung.kit.edu/