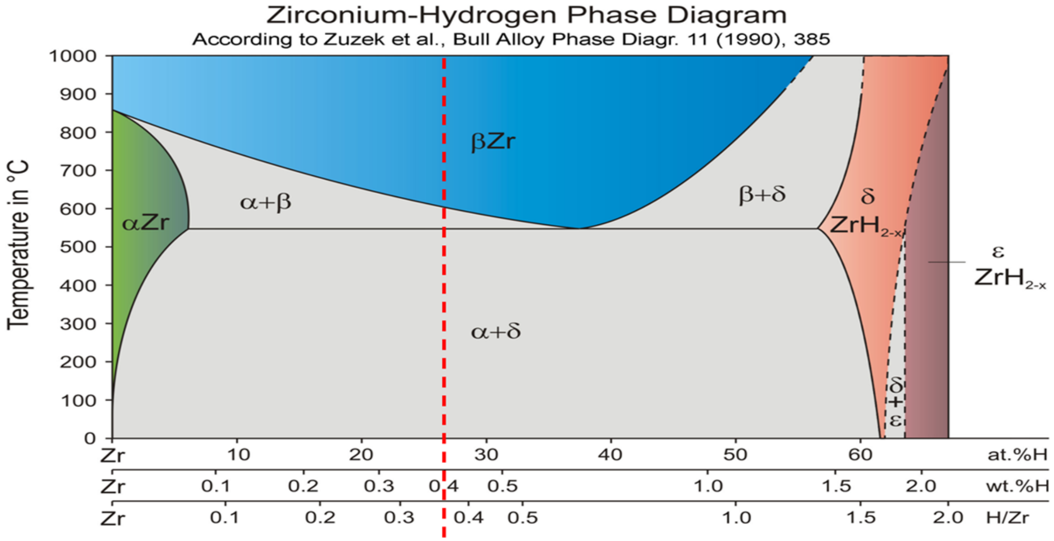
Karlsruhe Institute of Technology

KIT modelling activities of hydrogen uptake/ release of solid and molten Zr alloys

H. Muscher, J. Stuckert, M. Wozniak

16th International QUENCH Workshop, Karlsruhe, 17. November 2010

Institute of Materials Research, Programme NUKLEAR



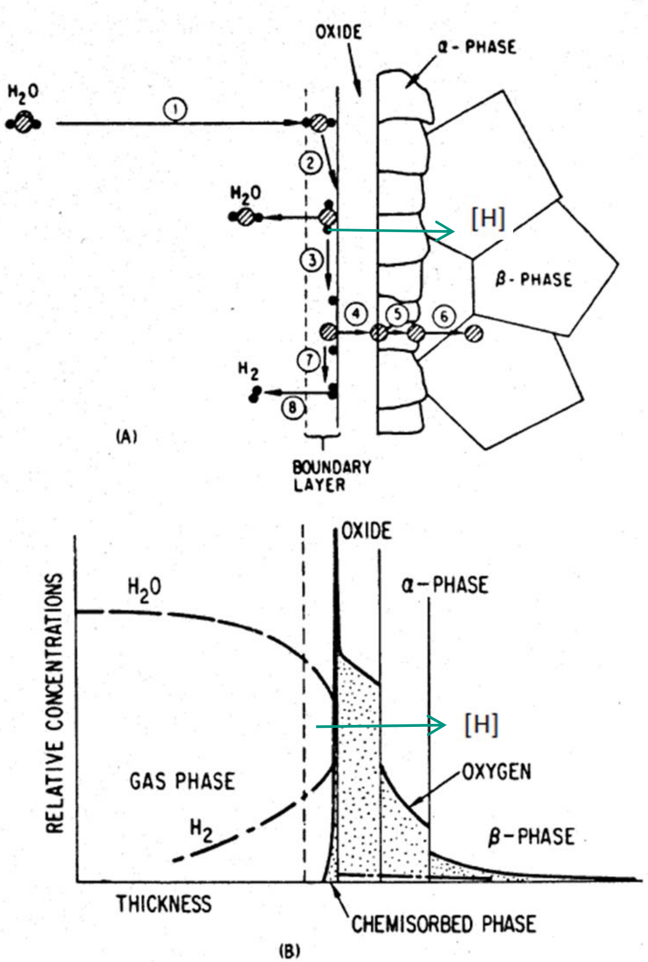
Introduction

- Motivation
- SVECHA 10.0 code
- ASTEC 2.0 rev.1
- Modelling / Quench; CORA-13 -*first runs*
- Conclusions, outlook -*future prospects*

→Validation against NR and SFPR

-code to data, code to code-

→Training course at IRSN 1/2011



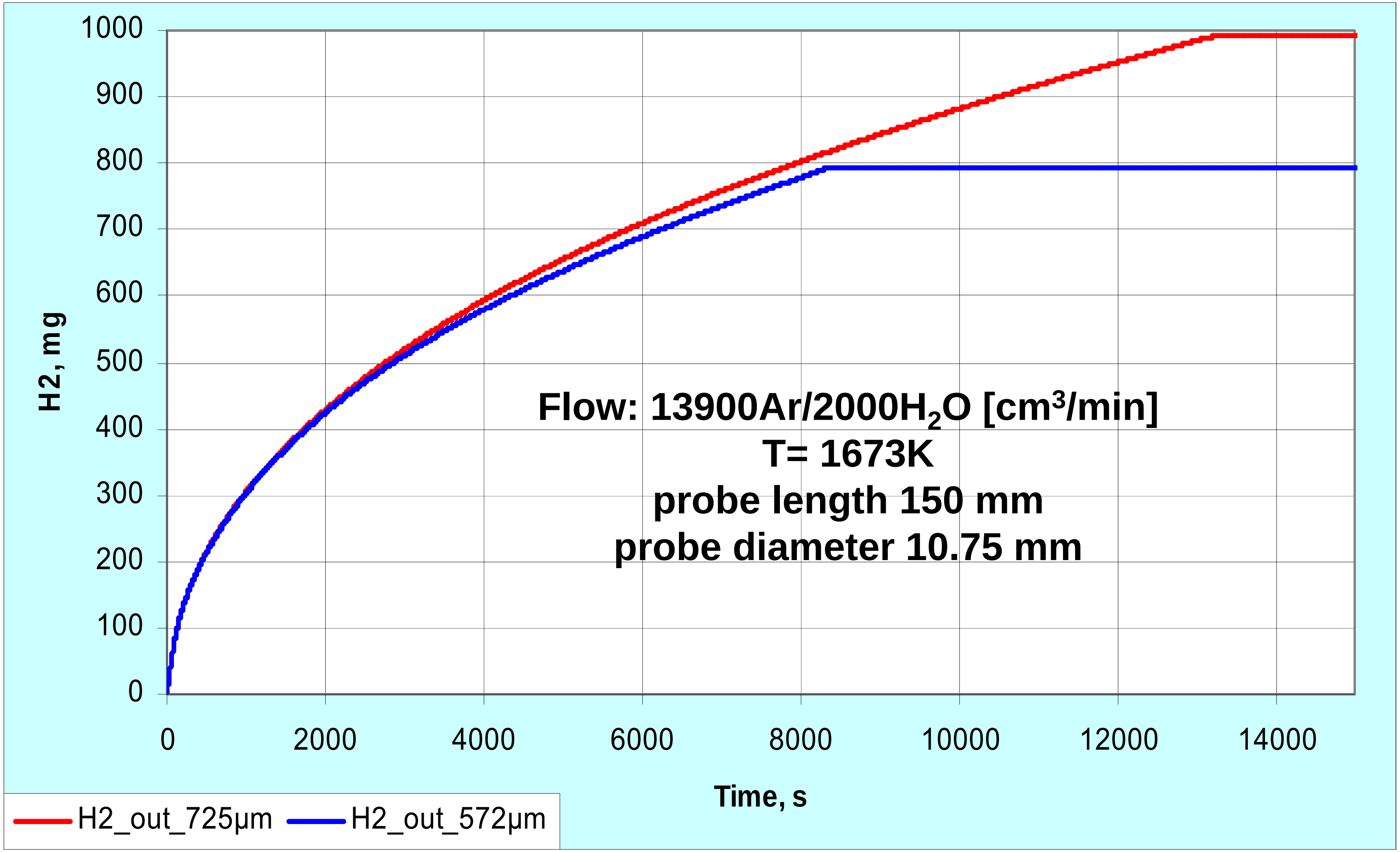
➡ *QUENCH* *<u>experiments</u>* *provide data*

for development of models & codes:

➡ Application of ASTEC on Quench problems/ Zry-4, M5®, E110

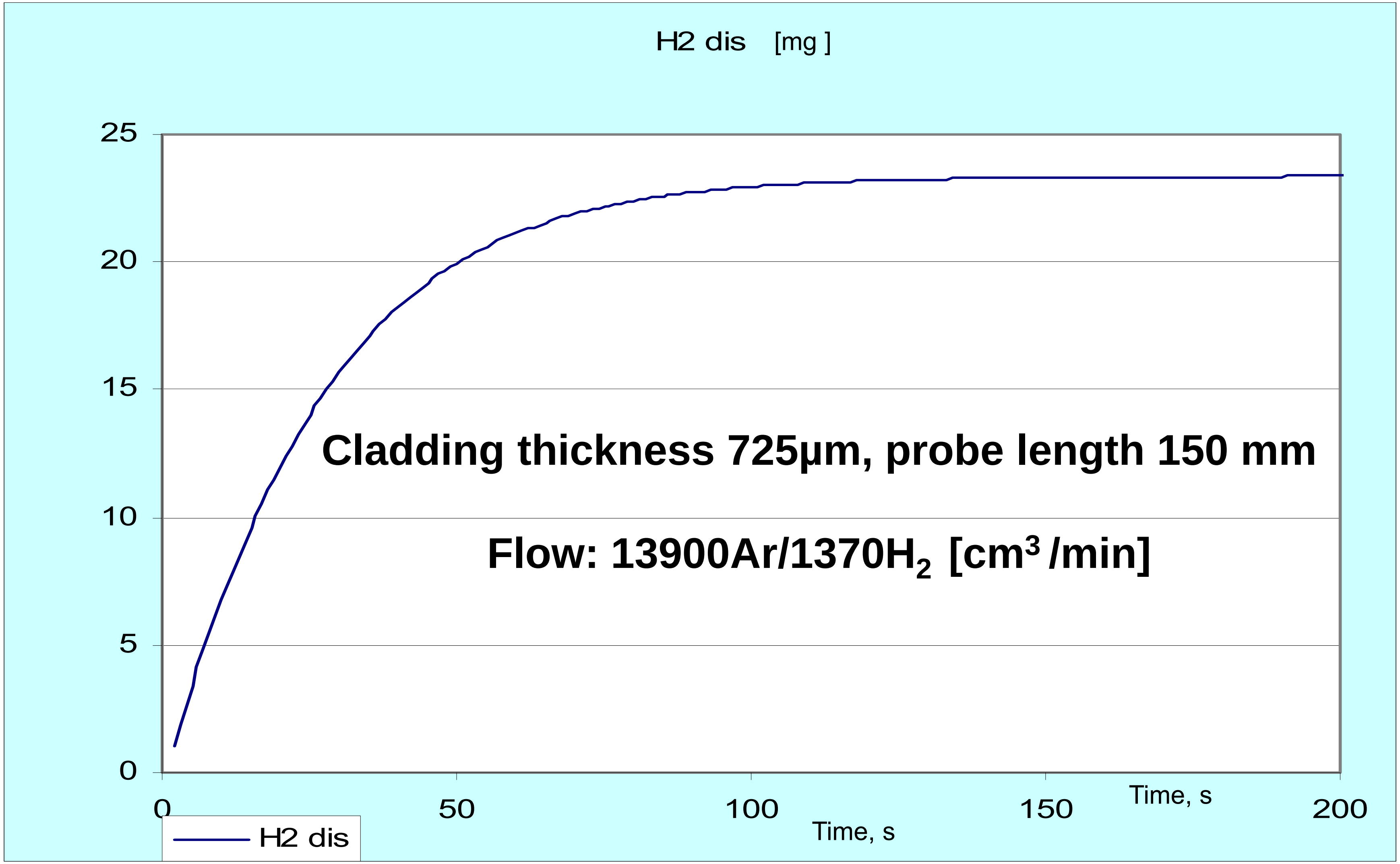
➡ At first only ICARE, ODESSA and MDB use

SVECHA results for [H] total production for two standard cladding geometries: influence of finite systems



Flow: 13900Ar/2000H_2O [cm^3/min]
T= 1673K
probe length 150 mm
probe diameter 10.75 mm

Hydrogen uptake on Zry-4 under hydrogen starvation; SVECHA results



Cladding thickness 725µm, probe length 150 mm

Flow: 13900Ar/1370H_2 [cm^3 /min]

Characteristic time τ for surface concentration change of hydrogen according M. Veshchunov

- **H uptake and release occur in different ways**. The H **release obeys a slow <u>hyperbolic</u>** , whereas the **uptake** a **rapid <u>exponential</u> time law.**
- the hyperbolic time law is valid only in one particular case, namely, when the p_{H2} **drops exactly to zero**; **otherwise**, the system during H **desorption is described with a non-zero value** and **relaxes to the new eq. state exponentially**. Hence, the **model predicts** that **in** possible **tests with the** p_{H2} **drop to a non-zero value, the kinetics of both H absorption and release will obey the same exponential time law.**
- → RTK_s^2 is not "purely" dimensionless.

$$\frac{dC_H(s)}{dt} = -\frac{4k_{H_2}}{LRT}\frac{C_H^2(s)}{k_s^2}$$

$$C_H(s) = \frac{C_{H,0}}{1+\gamma t}$$

$$\gamma = 2\left(k_{H_2}/L\right)\left(P_{H_2}^{1/2}(b)/RTK_S\right)$$

$$K_S = 1.4 \cdot 10^{-3} \cdot \exp(8102.7/T[\mathrm{K}]) \text{ atom ratio/atm}^{1/2}$$

not $\gamma = 4\left(k_{H_2}/L\right)\left(1/RTK_S^2\right)$

$k_{H_2} = 4$ cm/s fitting to the experimental data

-mass transfer coefficient-

$$\frac{L}{2}\frac{dC_H(s)}{dt} = \frac{2k_{H_2}}{RT}\left[P_{H_2}(b) - \frac{C_H^2(s)}{k_s^2}\right]$$

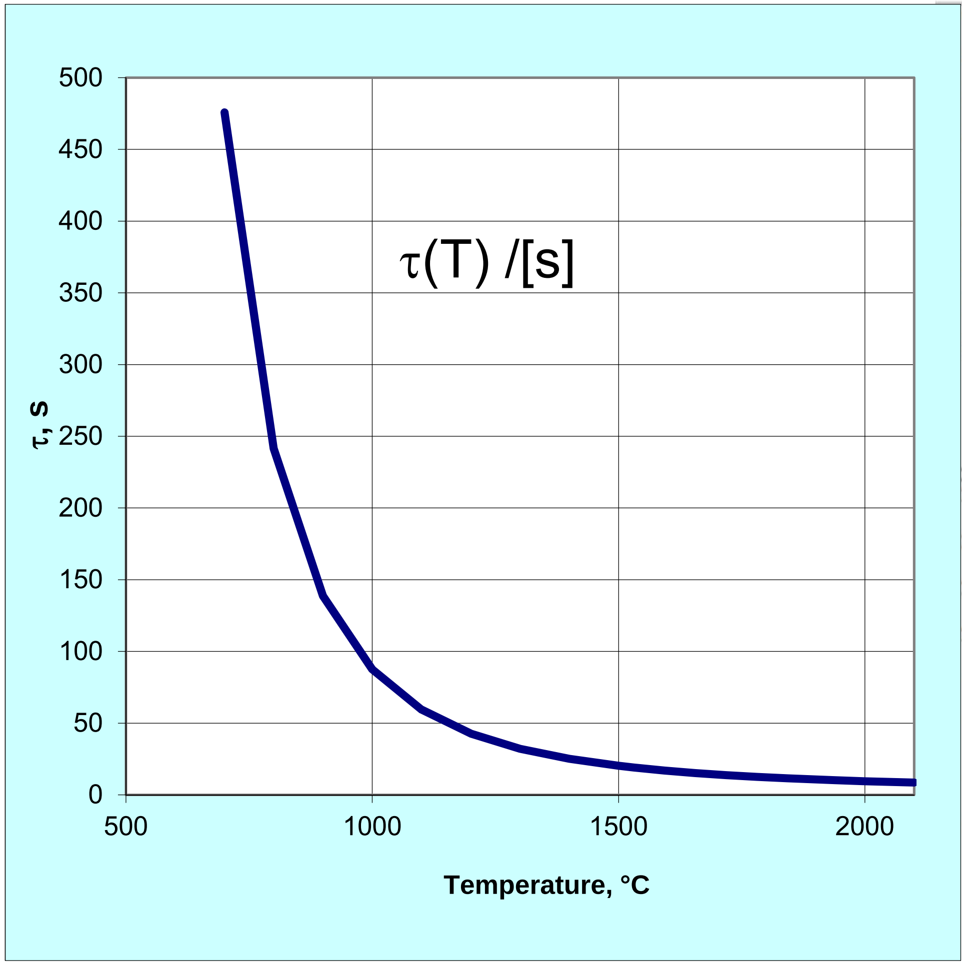
1/e = 0,368 vs. (e-1)/(e+1) = 0,462

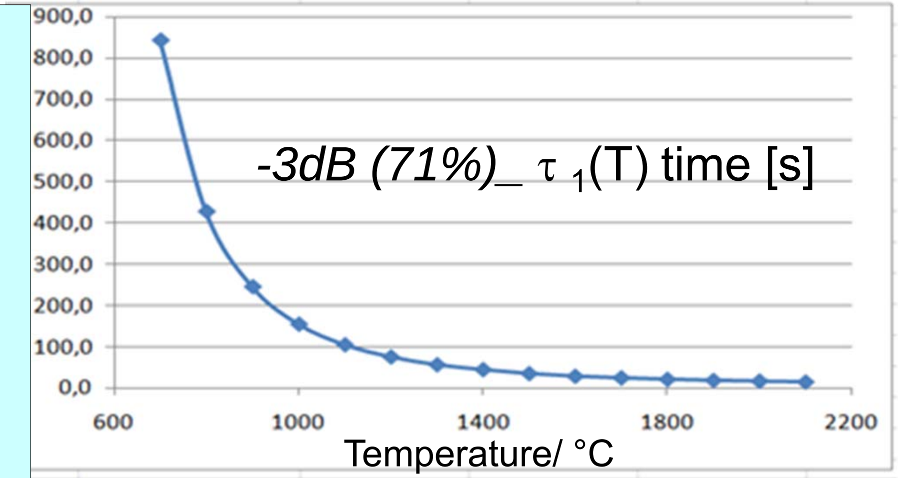
$\tau = 1/2\gamma$

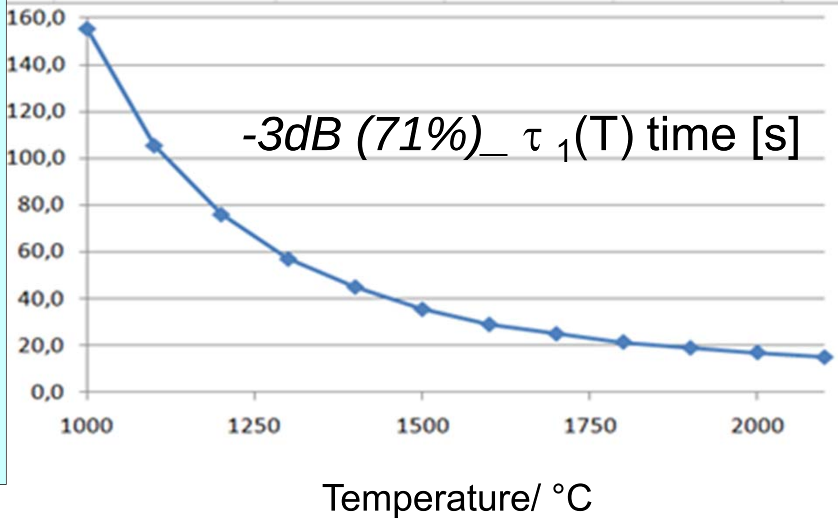
$$C_H(s) = K_S P_{H_2}^{1/2}(b)\frac{1-\exp(-2t\gamma)}{1+\exp(-2t\gamma)}$$

Characteristic time τ [s] vs. H-uptake temperature

cladding δ= 725µm; 13900Ar/2000$H_2O_{(g)}$ [cm^3/min]

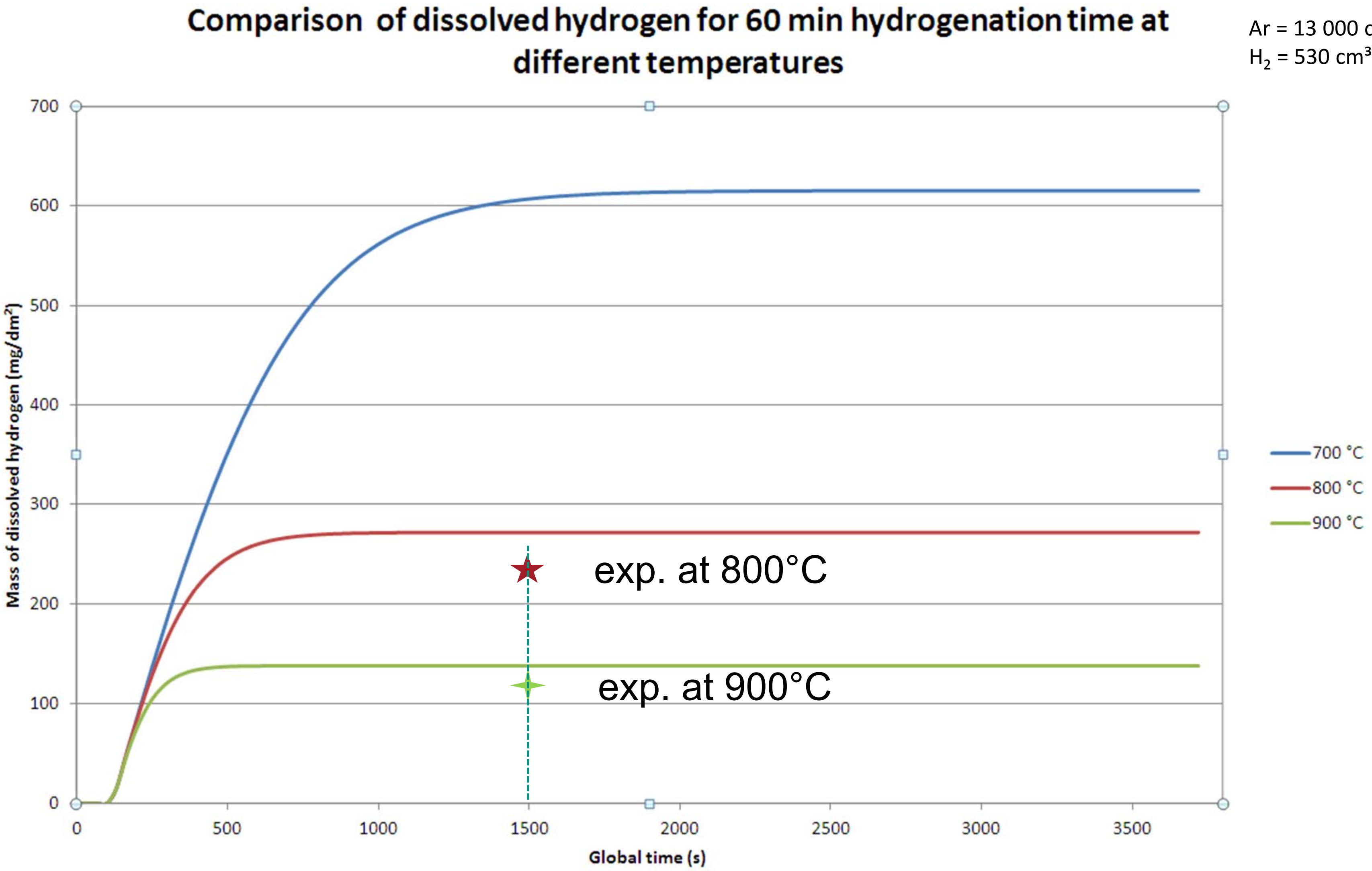




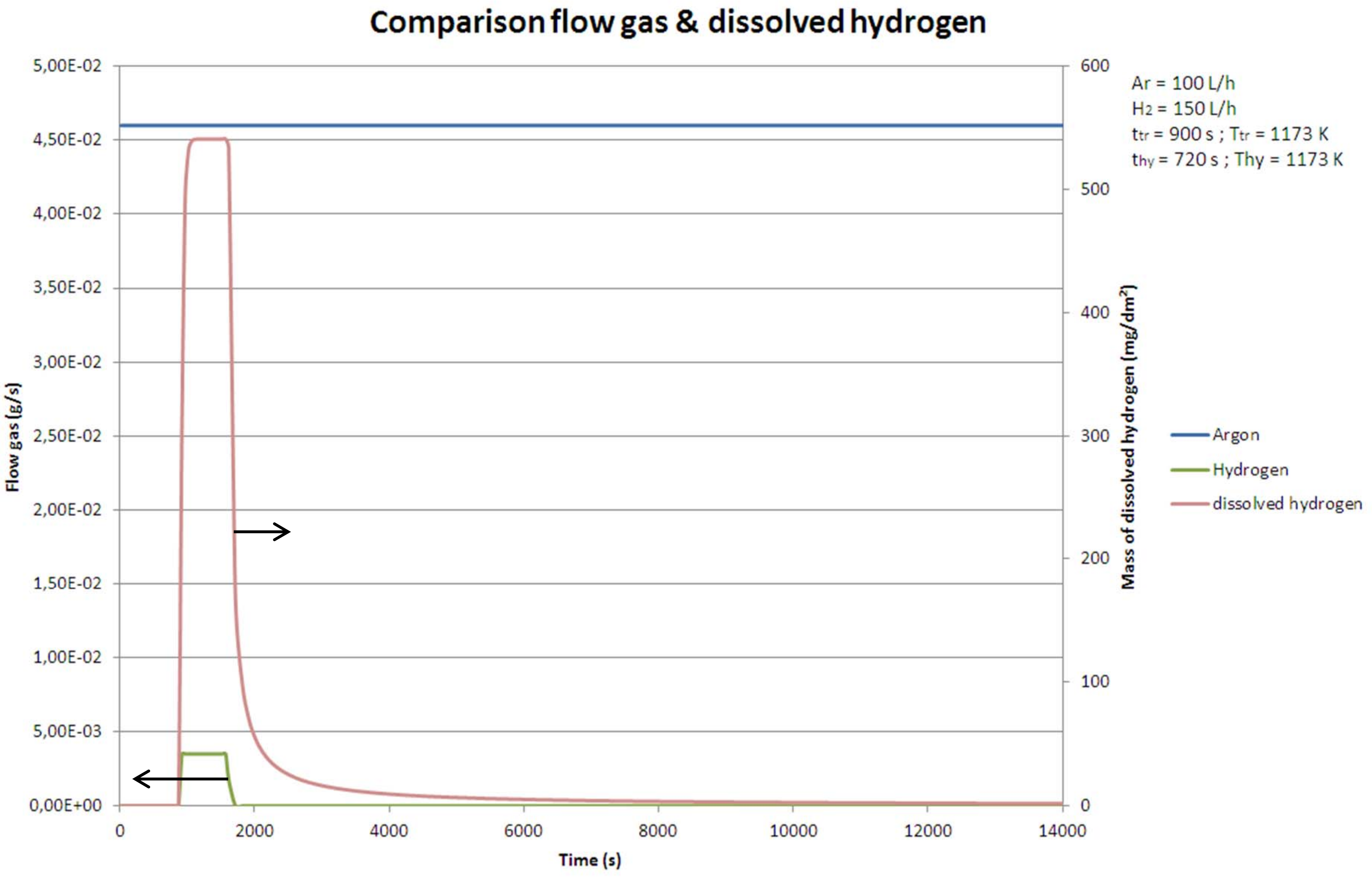


Hydrogenation on temperature for Zry-4: SVECHA 10 simulations

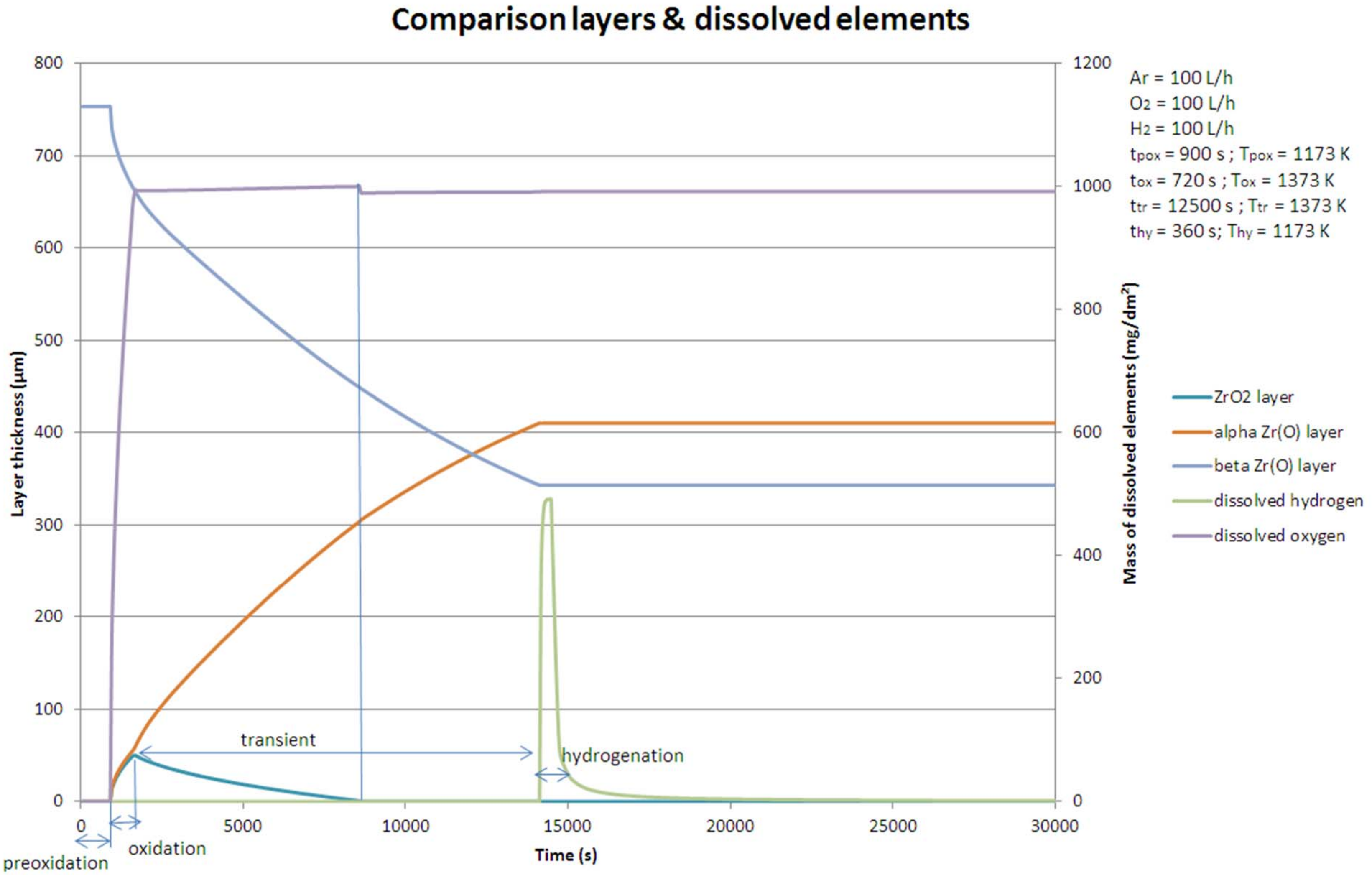
Ar = 13 000 cm³/min
H_2 = 530 cm³/min



LORA-hydrogenation *calculated* with SVECHA 10



SVECHA 10 results for oxide layer dissolution in Ar at 1100°C with following hydrogenation in H_2 at 900°C



For the oxidation-hydrogenation, the beginning is the same as the simple oxidation. After the oxidation, the sample is cooled down to the hydrogenation temperature and then the procedure t is the same as in case of simple hydrogenation.

SVECHA 2000 / SVECHA 2010: discussion of case with switch-off of hydrogen in the gas mix

- using step value of Δt = 50 s for SVECHA 2000 we obtained expected result: a very steep decrease to C_H=0 in metal. HOWEVER:
- surprisingly for Δt = 10 s the result was a multi-step decrease to a non-zero value. The same "phenomenon" was especially well pronounced in the case of Δt = 1 s.

This problem was corrected by code developer in new version SVECHA 2010:

→"Non-zero values are connected with a coupling between H abs. module and the gas kinetics module (GKM) of the SVECHA code. GKM calculates the gas phase content with some accuracy, and when H_2 in reality is absent (reduced after injection), calculated $\mathbf{c}_{H2}$ is very small but non-zero. The criterion for $\mathbf{p}_{H2}$ in the H-absorption module was changed. Result: a modified version of SVECHA 10 code"

- [H]- **spatial distribution** in the Me as a **constant** $\boldsymbol{C_H(t)}$**:** integration on the spatial coordinate across the Me phase and substitution of the BC, lead to **an ODE/ not PDE.** For the case of H abs, when H p_{H2} in the gas changes **stepwise from zero to a terminal value** and Zr is initially free of [H], $\boldsymbol{C_H(t=0)= 0}$
- The kinetics of [H]-**release** is considered for a Zr sample which is initially in an **equil.** with the gas mix. with $p_{H2} \neq 0$, hence, **contains some [H]** / (Sieverts law).

Svecha Q 10/ discussion (2)

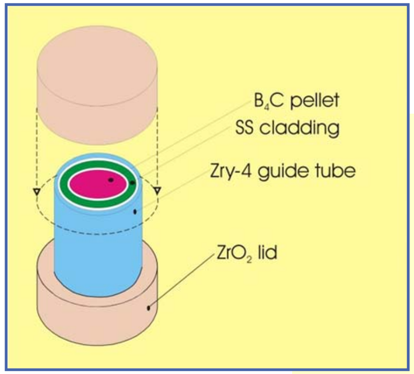
- H-distribution in cladding calculated by the Zr oxidation in steam and simultaneous H_{abs} model: in the S/Q code only total $C_{[H]}$ was available. $C_{[H]}$ in the layers (uniform in both metal layers of oxidized cladding) are not directly given. When ZrO_2 interacts with H_2/Ar mix, H- distribution in the cladding is constant. Modelling: see the IBRAE transactions.

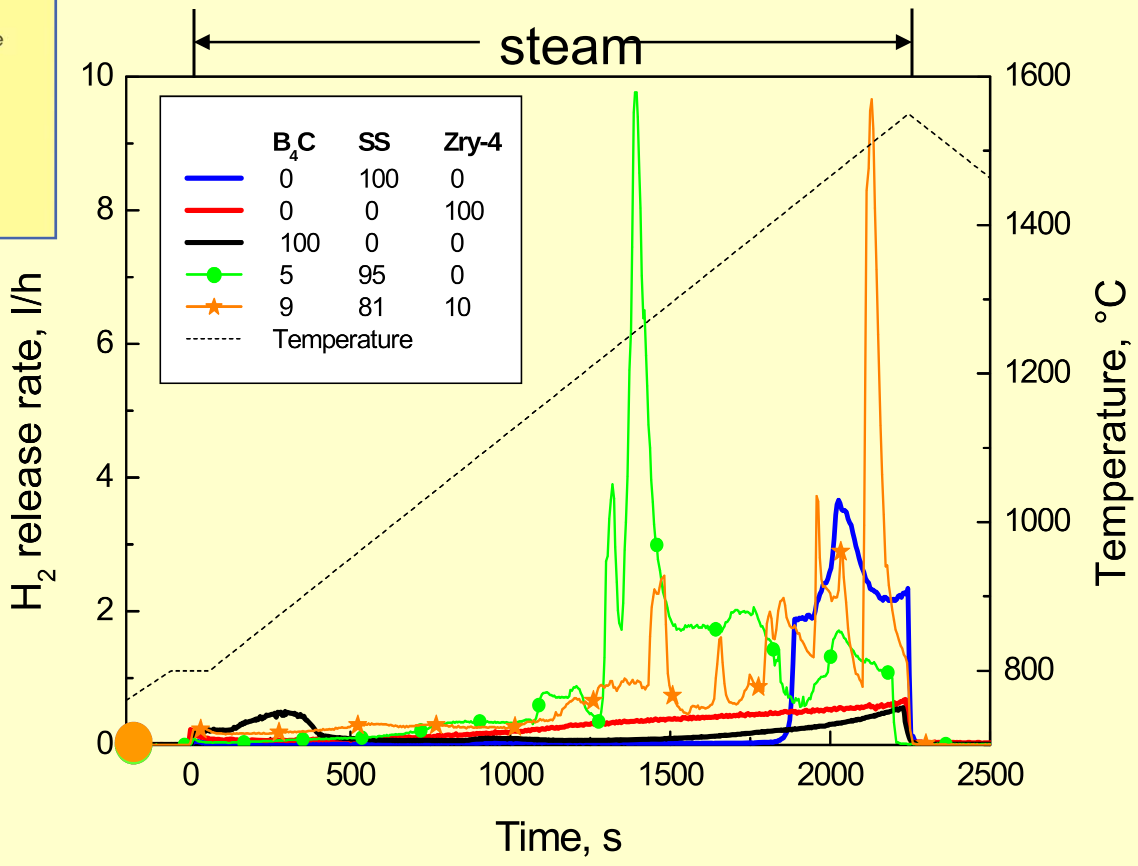
- Gas flow under **const., homogeneous Δp** is described by a model within an approximation that the homogenization process is the most rapid transfer in the system: the characteristic time $\tau_p \sim d/v_S \sim 10^{-4}$ **s** ($d \sim 1$ cm is the hydraulic diameter; $v_S \sim 10^4$ cm/s is the sound vel. in the gas mix). Since considerable H absorption or release take place, hence, in order to afford constant total gas **Δp** an additional **convective flow across the** gas **hydraulic channel (Stefan flow)** occurs. Therefore, mass fluxes of **H_2 and Ar** in the diffusion **Boundary Layer** of the gas phase near the Me surface take the form described by **M. Veshchunov**:

→ v_{St} of the Stefan convection flow as well as the **k_{H2}** value are needed for the calculation

$$J^{(H_2)} = J_D^{(H_2)} + J_{St}^{(H_2)} = k_{H_2}(c_{H_2}(s) - c_{H_2}(b)) - v_{St} c_{H_2}(s)$$

H_2 release during oxidation of absorber melts and pure CR components: solid/ liquid differences





Zry-4

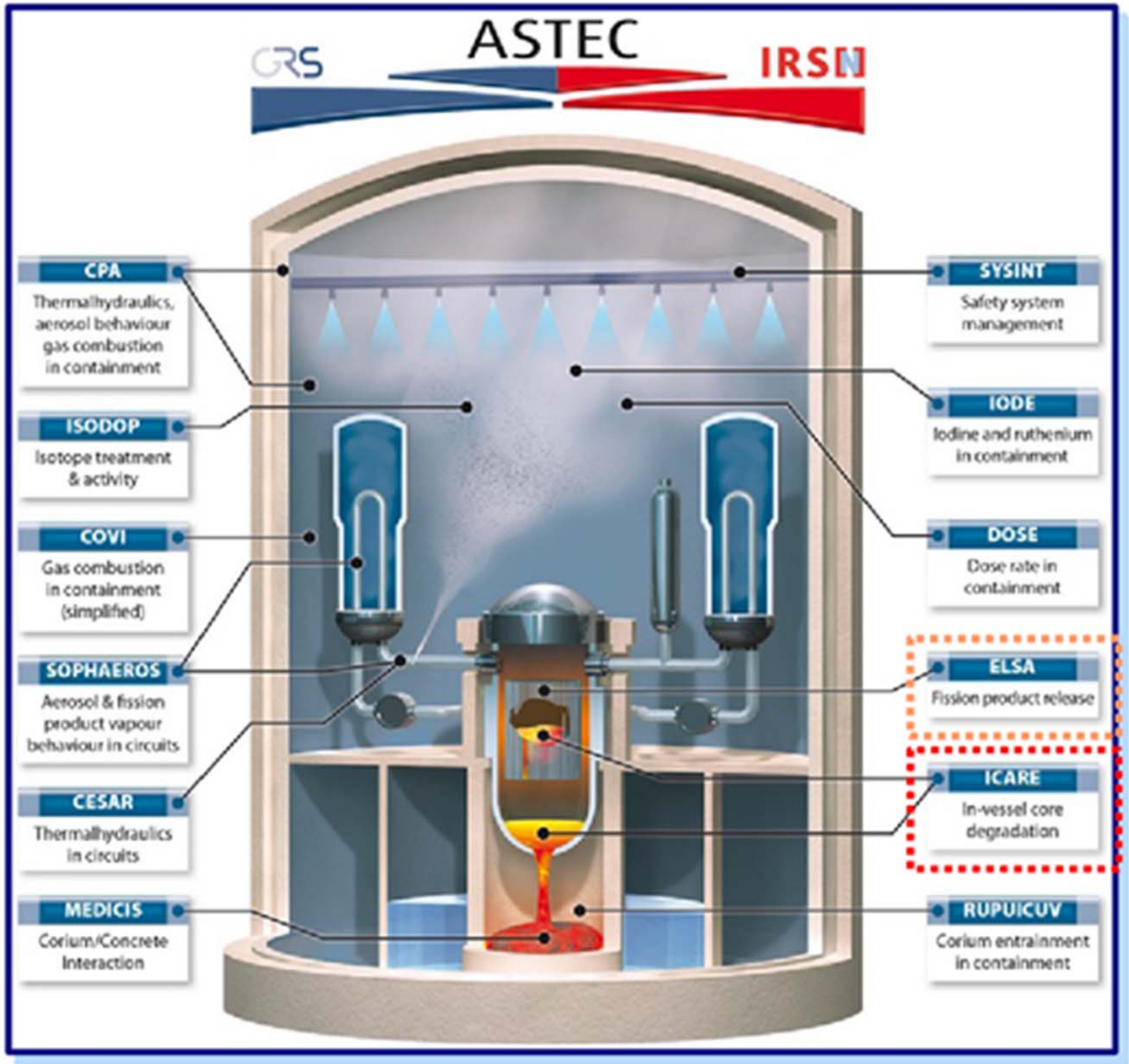
B_4C

SS

B_4C-SS

B_4C-SS-Zry

ASTEC general description



ASTEC MODULES USED:

ICARE

Describes phenomena that occur during the core degradation phase: fuel rods heat-up, clad oxidation, melting, corium behavior and others.

First steps in ASTEC v.2.1

- contract between GRS and KIT on ASTEC 2.1 usage signed 28.10.2010
- **"Overview of** the integral code **ASTEC v2.0**“
- **"Evolution of ASTEC v2.0-rev1 with respect to the original v2.0**”
- **principles** and **general modeling features** of v. 2.0-**rev1**
- focus on the **ICARE** module
- **ICARE** part within **"2009 Training Course material“**
- detailed **ICARE user's manual; guidelines; MARCUS (web)**
- To understand the **contents of "quench05.dat“ input deck**
  in the context of the KIT- **QUENCH** facility **real design**
  →**2011 Training course** to be held at IRSN, **1/2011**

- **best-estimate ASTEC-ICARE input deck** for QUENCH tests : work is underway: Stabilization/ Heat up/ Pre-ox/ Transient heat up/ Quenching

ASTEC v1.3 activities for QUENCH tests at KIT

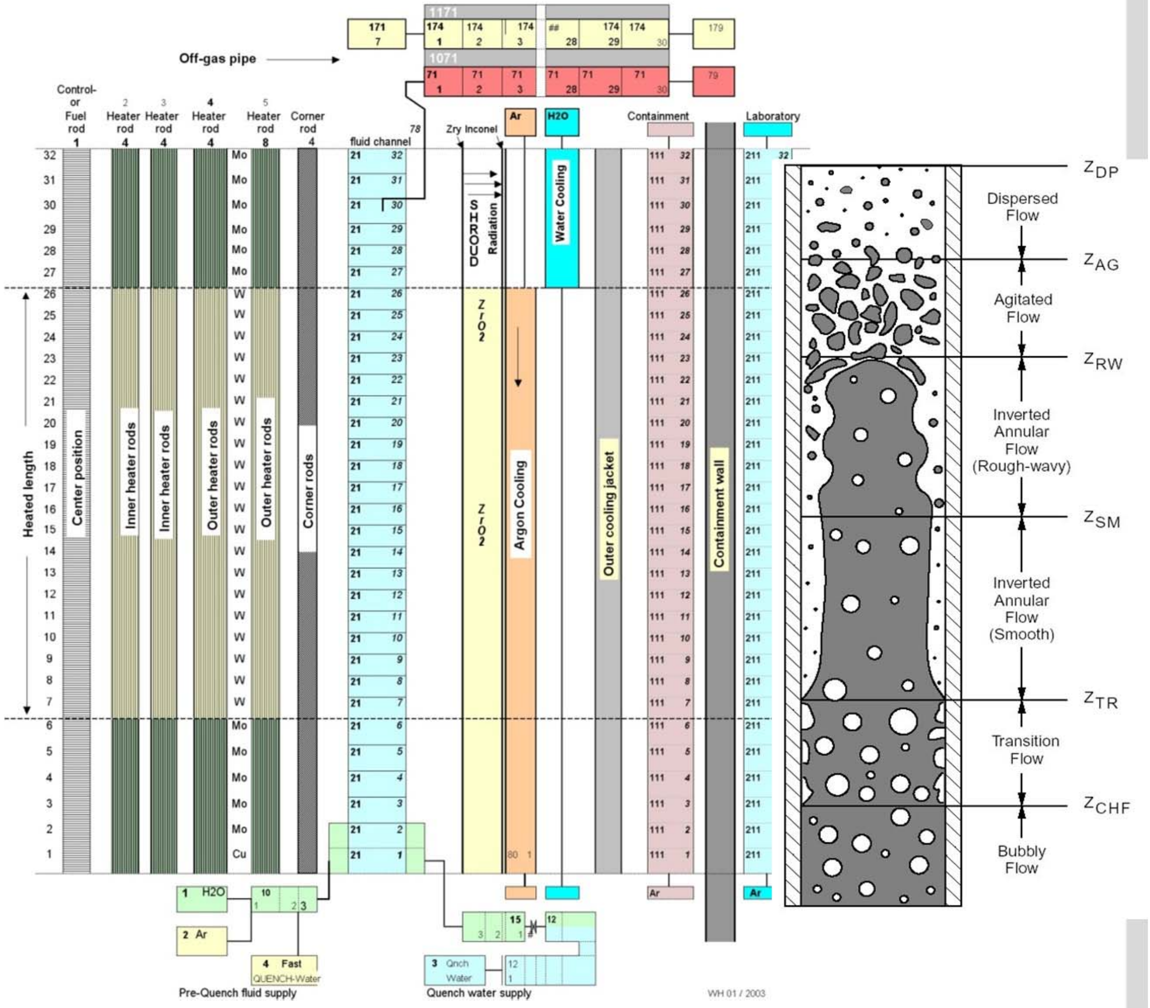
- Q-13 v1.3. input deck created based on optimized Q-11 deck
- Code validation: model qualification for delayed core reflood
- usage of QUENCH database
- Reduce number of Code systems (ICARE2 -> ASTEC V1.x) **at KIT**

- pre-test and post-test calculations done by W. Hering, Ch. Homann
- Application of ASTEC to QUENCH experiments:
  - Water quench: Q-06 (ISP-45) Q-11 (Q-L2)
  - Assessment of core degradation/ delayed core reflood

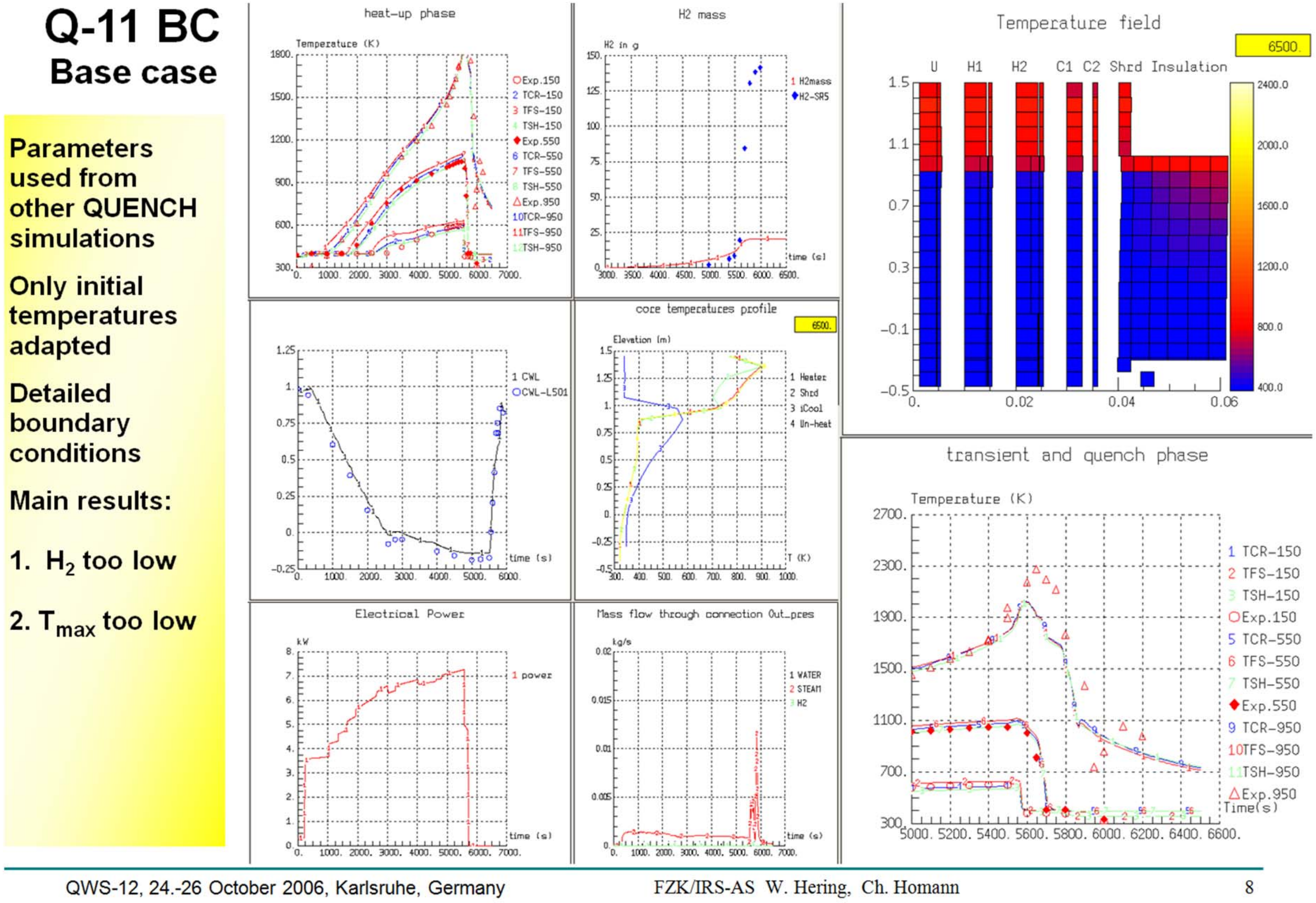
- Preparation of Q-11 and SARNET Code Benchmark

Bundle nodalisation/ reflood physics/ Quench

- Empirical water level tracking
  $z(t) = f(\sigma, \rho_l, \rho_v, u_b, r_b, u_v, T_l, g, \tau)$
  v: vapor, b: bubble
- Reflooding temperature:
  $T_r \sim T_{sat}(p) + 200K + f(p)$
- Prescribed wall T/K profile
- Regimes:
  - Nucleate boiling
    (fixed value for HT)
  - Film boiling (CATHARE)
    $q(t) = f(a, T_W, T_l, s, e, T_W, T_l),$
- Quench front elevation = $z_{(liq)}$
- “Swell” level detected by void



Simulations with ASTEC v.1.3 at KIT (an example)



Q-11 BC
Base case

Parameters used from other QUENCH simulations

Only initial temperatures adapted

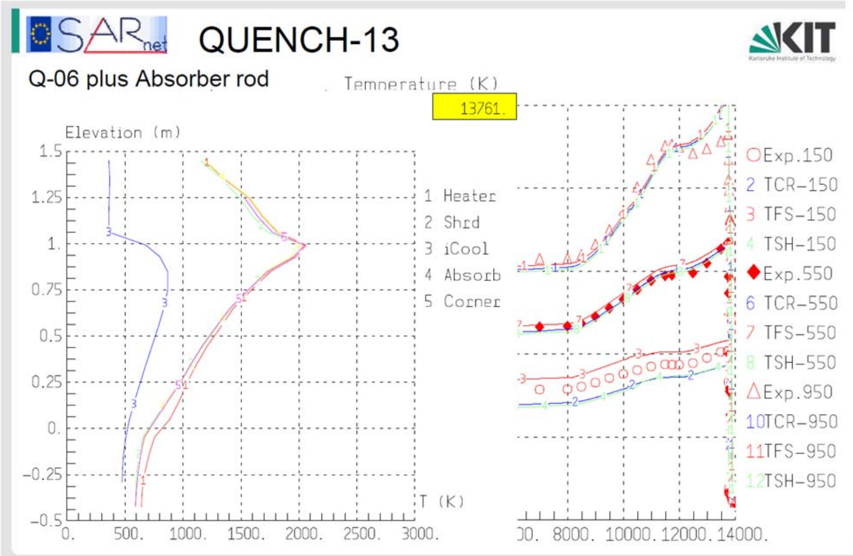
Detailed boundary conditions

Main results:

1. H_2 too low
2. T_{max} too low

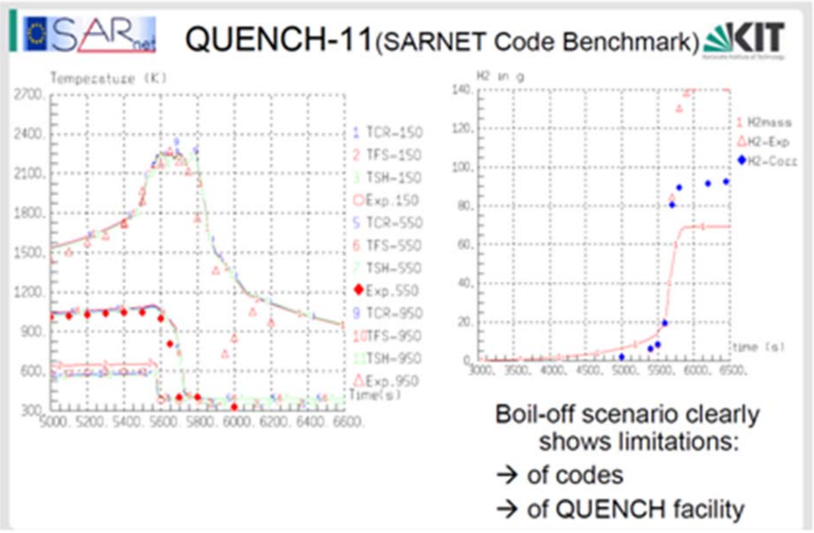
QWS-12, 24.-26 October 2006, Karlsruhe, Germany FZK/IRS-AS W. Hering, Ch. Homann 8

Former ASTEC 1.3 simulations at KIT / SARNET



QUENCH-13

Q-06 plus Absorber rod



QUENCH-11(SARNET Code Benchmark)

Boil-off scenario clearly shows limitations:

→ of codes

→ of QUENCH facility

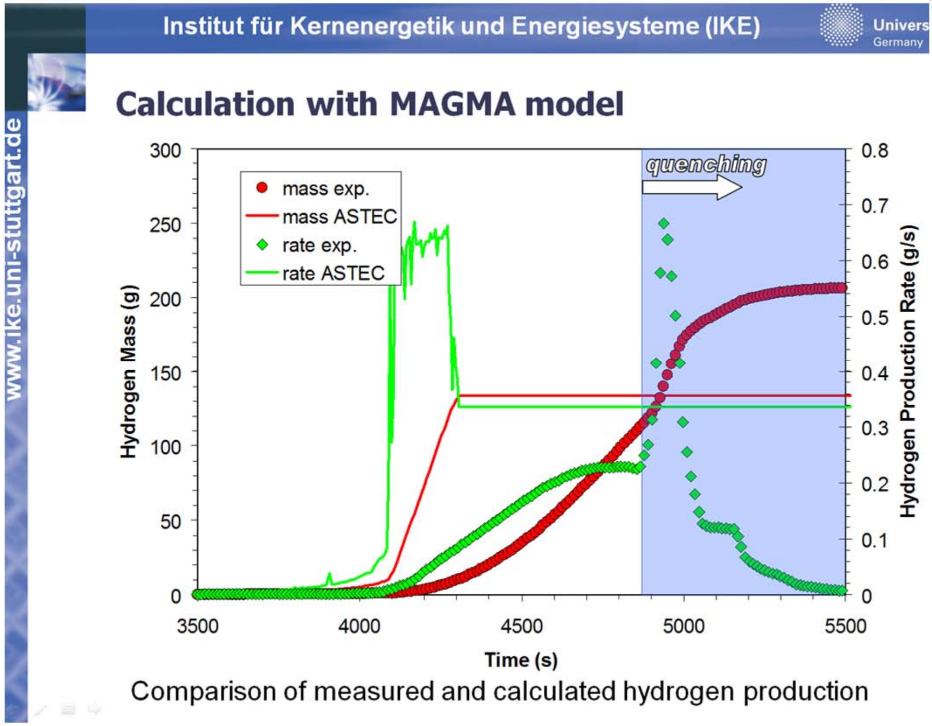
Rewriting of input decks ASTEC 1.3 → 2.0 rev1 needed

(following W. Hering et. al.)

„Q-11 simulation: aux. heater as a Cu-wire
BCs adjustment (heat losses…)
Finer resolution of diagrams (post-processing)
Cut-off water supply when H_2O-level reaches
shroud failure location (Q-11 specific change..)
Incl. delay time of H_2O injection to Q-11 test section“

Newest results on H_2 production adopting MAGMA

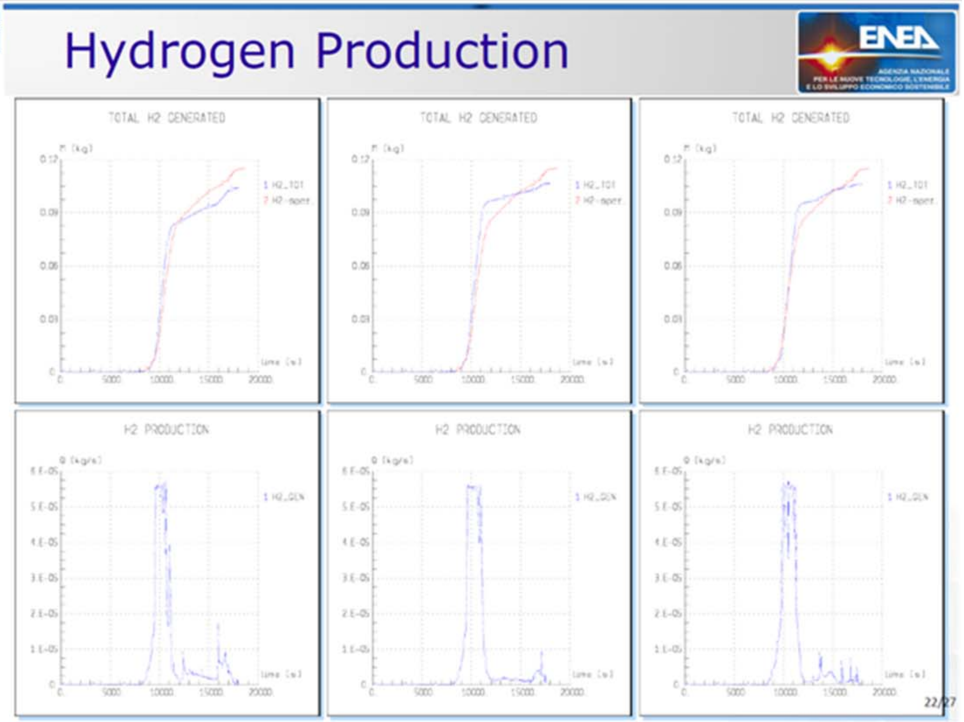
ASTEC v.2.0 rev.1 Release: July 2010



Institut für Kernenergetik und Energiesysteme (IKE)

Calculation with MAGMA model

Comparison of measured and calculated hydrogen production



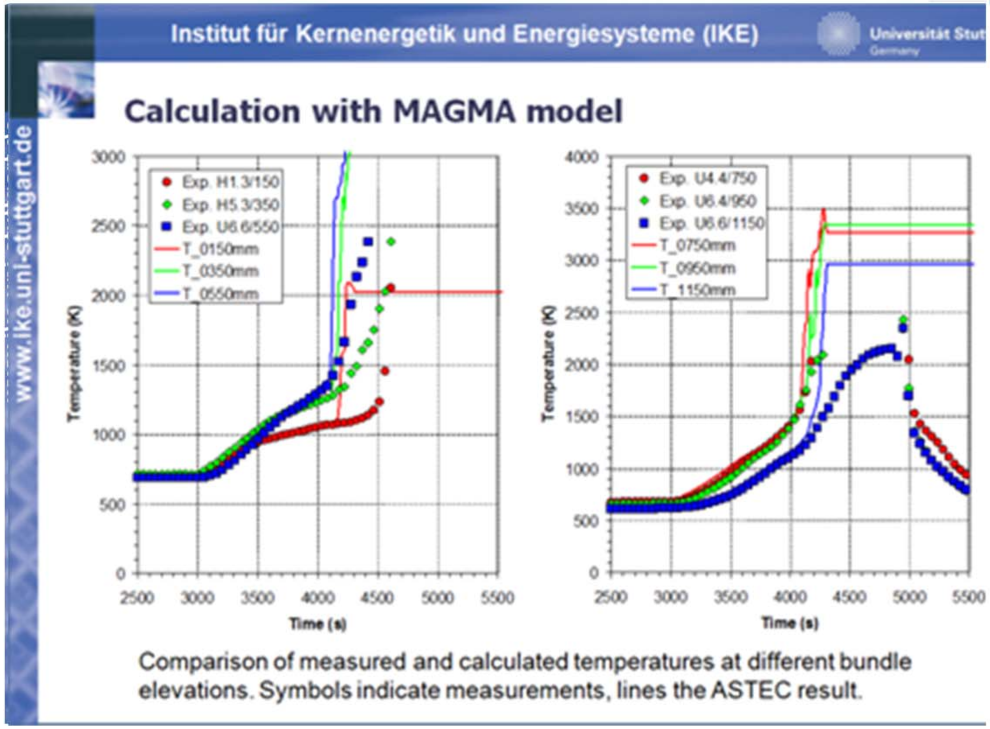
Hydrogen Production

Buck, IKE, 10/2010

Bandini, ENEA, 10/2010

Newest results on T- evolution adopting MAGMA(2)

ASTEC v.2.0 rev.1 Release: July 2010

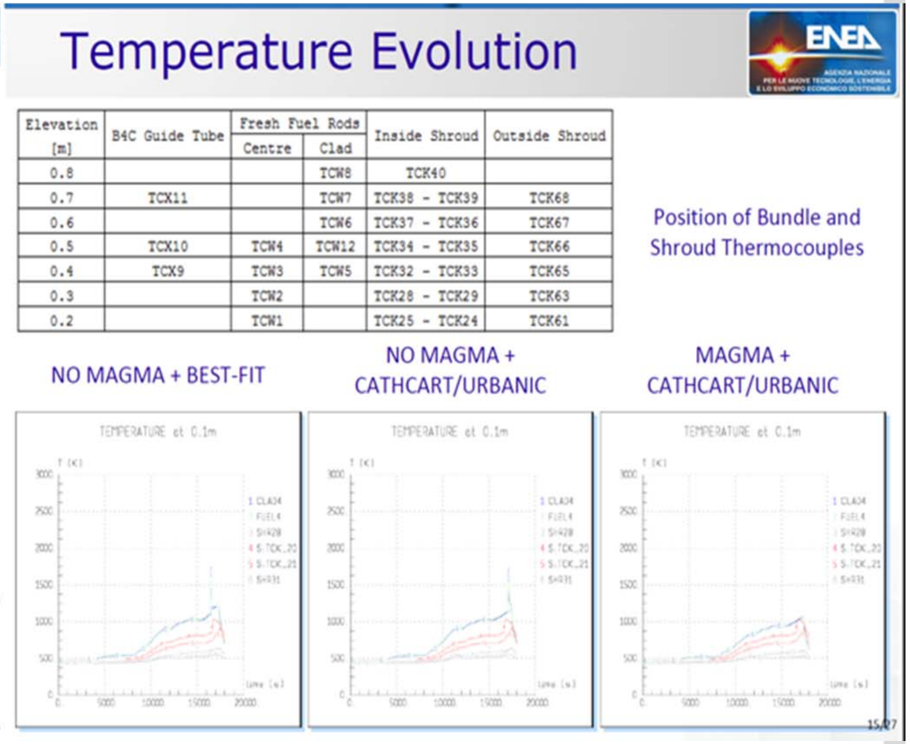


Institut für Kernenergetik und Energiesysteme (IKE)

www.ike.uni-stuttgart.de

Calculation with MAGMA model

Comparison of measured and calculated temperatures at different bundle elevations. Symbols indicate measurements, lines the ASTEC result.



Temperature Evolution

Elevation [m]	B4C Guide Tube	Fresh Fuel Rods		Inside Shroud	Outside Shroud
		Centre	Clad		
0.8			TCW8	TCK40	
0.7	TCX11		TCW7	TCK38 - TCK39	TCK68
0.6			TCW6	TCK37 - TCK36	TCK67
0.5	TCX10	TCW4	TCW12	TCK34 - TCK35	TCK66
0.4	TCX9	TCW3	TCW5	TCK32 - TCK33	TCK65
0.3		TCW2		TCK28 - TCK29	TCK63
0.2		TCW1		TCK25 - TCK24	TCK61

Position of Bundle and Shroud Thermocouples

NO MAGMA + BEST-FIT

NO MAGMA + CATHCART/URBANIC

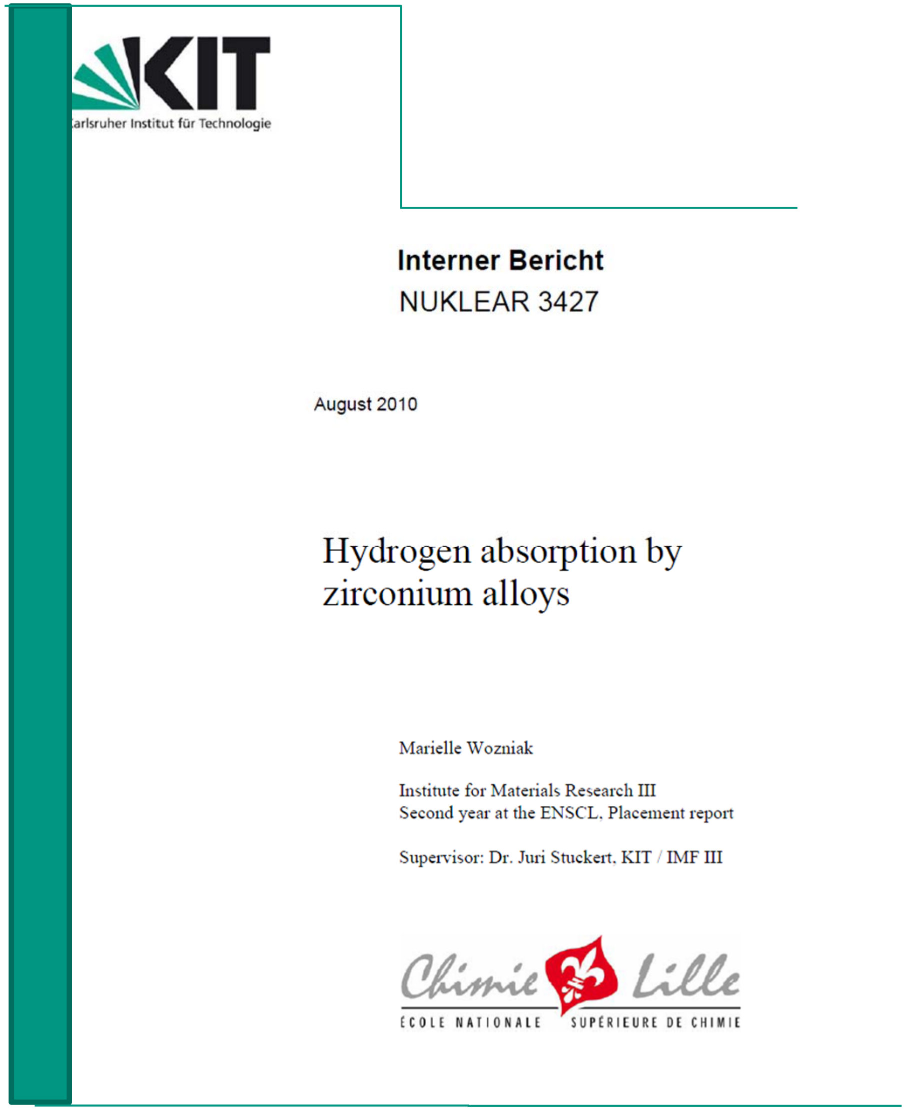
MAGMA + CATHCART/URBANIC

Buck, IKE, 10/2010

Bandini, ENEA, 10/2010

Internal KIT-reports, progress presented monthly

- SVECHA activities: KIT Internal report published 08-2010 available online, Quench web site
- QUENCH-05 /-11 /-15 to be simulated with ASTEC V2.0 rev.1
- QUENCH-L0 to be simulated
- Participation at GRS, ISTC conferences
- KIT-ASTEC 1.3 work done 2006 was presented here (nodalisation schemes, T/K- fields, quench water level etc)
- At KIT new calculations on the Zry-4 cladding /steam interactions using SVECHA 2.0/10.0 tools have been performed - hydrogenation in LORA



arlsruher Institut für Technologie

Interner Bericht
NUKLEAR 3427

August 2010

Hydrogen absorption by
zirconium alloys

Marielle Wozniak

Institute for Materials Research III
Second year at the ENSCL, Placement report

Supervisor: Dr. Juri Stuckert, KIT / IMF III

Chimie Lille
ÉCOLE NATIONALE SUPÉRIEURE DE CHIMIE

Conclusions / Outlook

- Hydriding can proceed via molecular H_2 and- in parallel- via $H_2O_{(g)}$ decomposition during Zr oxidation (which is even more important for reflood). Both mechanisms are implemented in SVECHA Q 2.0/ 10.0. for different temperatures of hydrogenation [H].
- →The [H] content in the experiments does not reach the simulation value for all [H]-times although the [H]-saturation level was reached.

  SVECHA results are always higher than the experimental NR data.

- Simulation of [H]-absorption can also be done using the integrated ASTEC 2.0 rev.1, released 07/2010 by IRSN. Results obtained (LEE/ IKE/ ENEA) show differences in the total H_2 values during the quench phase depending strongly on the oxidation model used.

- The 1D CANDLING model adopted in ASTEC 1.3 produced somehow conflicting results because of an extrapolation of solid-state models to the processes in the liquid phase.
- The modeling of Zr-O **melt** oxidation, being independent of solid state processes,

  needs more consideration.

→Using the 2D-MAGMA tool of ASTEC 2.0 rev1 will probably led to better results in simulating Q- tests.

- KIT ASTEC 1.3 input decks must be rewritten, updated, both for the purposes of the new ASTEC 2.0 rev1 and for finer (i.e. less coarse) nodalisation.