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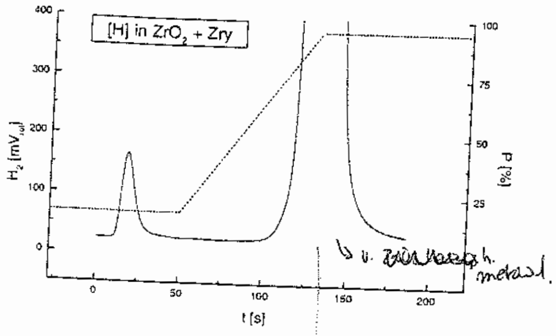
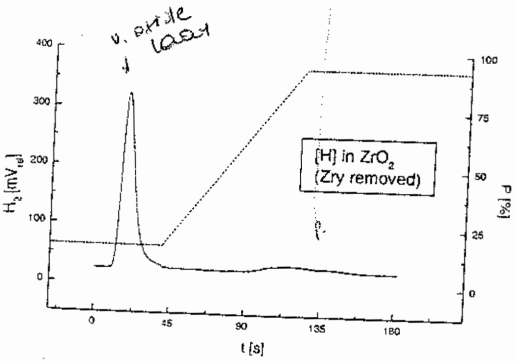
Quantification,

Hydrogen peaks on autoclaved samples: a) Zry + ZrO_2 b) ZrO_2 (Zry removed chemically)





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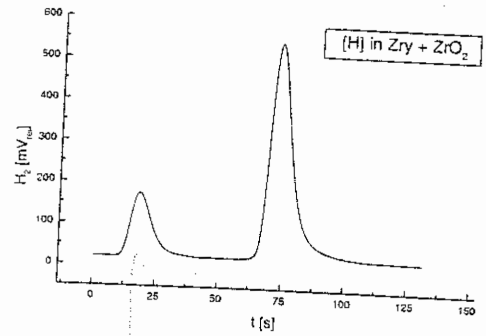
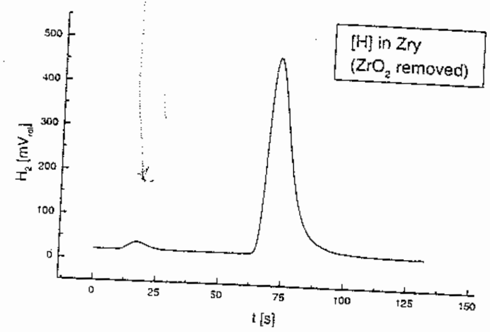
oxide layer grinded off in hot cell.

Hydrogen peaks on irradiated samples: a) Zry + ZrO_2 b) Zry (ZrO_2 removed mechanically)





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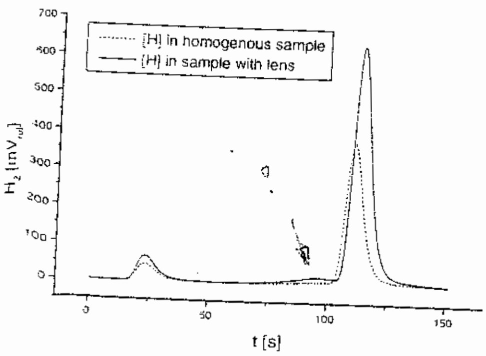
Neutron Radiography



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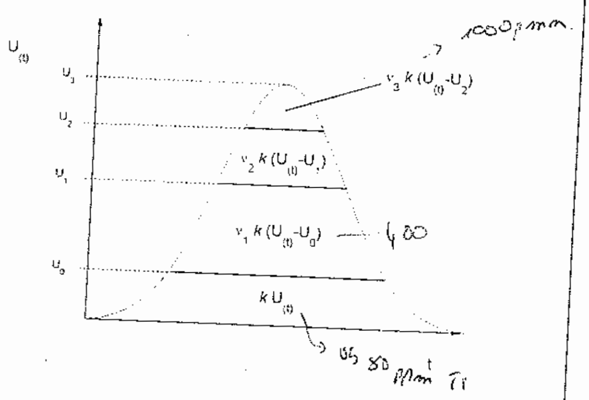
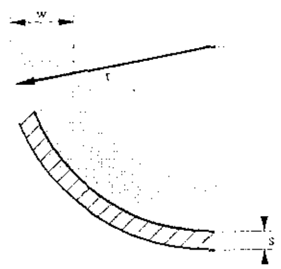
Voltage Intervals for variable calibration



calibration factor k

variable factor v

Calculation of Oxide Thickness



Oxide Thickness *s* (EC-measurements)

Former Wall Thickness *w*

Pilling-Bedworth-ratio

Characteristic Data of Samples

Table 4: Characteristic PIE Data of the Investigated Fuel Rods and Samples

Rod/Sample *Designation*	Liner	Reactor Cycles/ Full Power Days	Burnup [MWd/kg U]	Oxide Thickness [µm]	Diameter [mm]	Wall Thickness [mm]
FR1/H	Zr-alloy 1	5/1656	66.1	66	10.757	0.669
FR2/I	Zr-alloy 1	4/1325	59.4	42	10.747	0.663
FR2/D	Zr-alloy 1	4/1325	59.4	22	10.730	0.676
FR3/G	Zr-alloy 1	1/338	18.9	7	10.672	0.740
FR4/I	Zr-alloy 2	5/1656	66.8	64	10.750	0.675

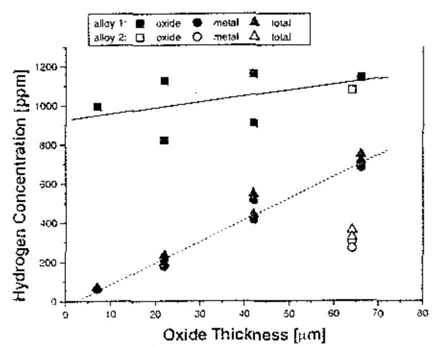
Results of Fractionated Hydrogen Determination

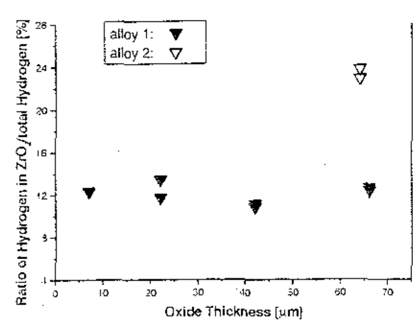
Results of Fractionated Hydrogen Determination of Fuel Cladding Samples

Sample Designation	Weight [g]	Mass Ratio Oxide/Metal	Fraction	Calculated Weight [g]	Hydrogen [wt.-ppm]
FR1/H-H1/H2	0.4993/0.4373	0.0867	oxide metal	0.0398/0.0348 0.4595	1140/1144 682/702
FR1/H-H3*	0.2758		metal*		651
FR2/I-H1/H2	0.4342/0.4184	0.0554	oxide metal	0.0228/0.0220 0.4114/0.3964	907/1158 415/514
FR2/I-H3*	0.2585		metal*		526
FR2/D-H1/H2	0.4519/0.4089	0.0284	oxide metal	0.0125/0.0113 0.4394/0.3976	821/1125 176/207
*FR2/D-H3**	*0.3124*		*metal**		192
FR3/G-H1	0.2999	0.0084	oxide metal	0.0025 0.2974	993 60
FR4/I-H1/H2	0.4208/0.3965	0.0832	oxide metal	0.0323/0.0305 0.3885/0.3660	1077/1008 *303/270*
FR4/I-H3*	0.3878		metal*		262

* oxide removed by grinding

Results of Fractionated Analysis





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DEVELOPING A METHOD FOR FRACTIONATED HYDROGEN DETERMINATION IN FUEL CLADDING SAMPLES

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Introduction

- Hydrogen pick up, an important aspect of cladding corrosion and life limiting criterion of fuel rods for high burnup
- Some hydrogen picked up by ZrO_2
- [H]-determination normally on cladding samples including ZrO_2
- Attempts for separation of [H]-metal vs. [H]-oxide by mechanical removal of ZrO_2
- Development of fractionated hot gas extraction technique at PSI for distinction between [H]-metal and [H]-oxide

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Principle of Hydrogen hot gas extraction technique at PSI

- After NDT in hot cells, fuel cladding cut into ring samples, fuel removed, samples UT-cleaned
- Sample transfer to a shielded box with an remote handled LECO-RH-402 Hydrogen Determinator installed
- Cladding rings fed into graphite crucibles
- Crucibles heated to 2100°C by RF-induction heating
- Cladding molten together with fluxing agent (Sn)
- N_2 carrier gas used for transportation of hydrogen through heat conductance measuring cell outside of the shielding

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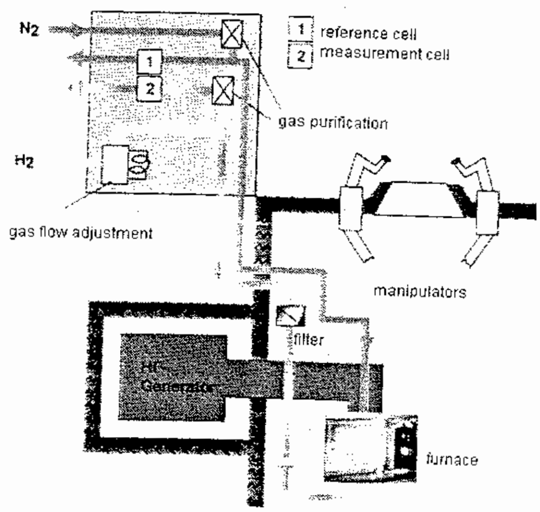
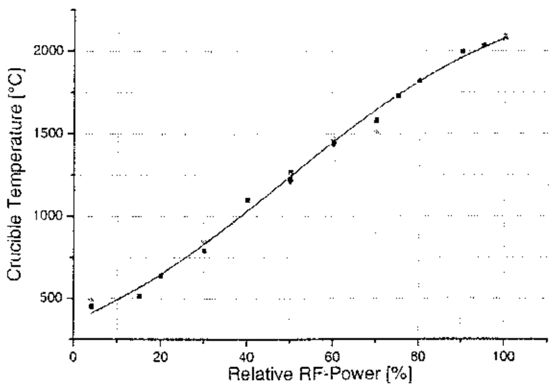
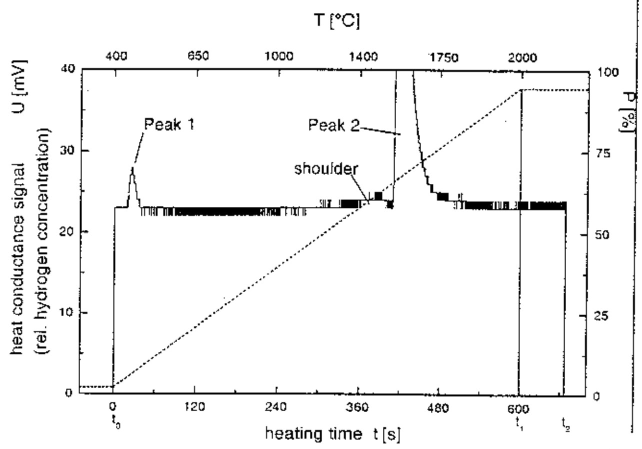
Schematic of Modified Hydrogen Analyzer



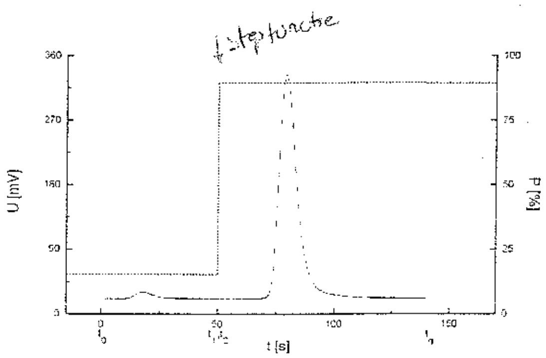
RF-Power versus (steady state) Crucible Temperature

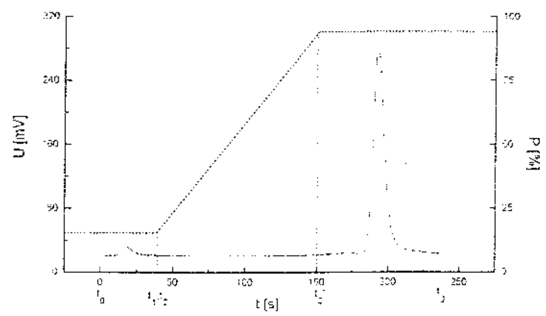


RF-Power Sweep indicating Hydrogen Pulses from several Reservoirs



Time-Power/Voltage Diagrams P1 and P2





Details of Time-Power Programs P1 and P2

Time [timescale, s]	Step	Power P [%] P1	P2
t_A [-120]	outgassing	100	100
t_T [-30]	stand-by (cooling)	0	0
t_0 [0]*	start, step 1	15	15
t_1 [45]	stop, step 1	15	15
t_2 [46]	start, step 2	90	15
t_3 [136]	end, step 2	90	**
t_2' [166]	switch to P=const.		95
t_3 [186]	end, step 2		95

*start of analysis with sample; **linear power increase up to 95%

Conclusions

- A hot gas extraction method was developed to quantify in one step the fraction of hydrogen present in ZrO_2 layers versus the fraction dissolved/precipitated in the Zry metal phase
- The correlation of the respective hydrogen reservoirs (H_{ZrO2} and H_{Zry}) to the extraction signals was reached by separate analysis of samples with metal phase only and samples of separated ZrO_2
- Exact measuring of the different masses of hydrogen within the oxide and the metal was achieved by a variable calibration procedure using several certified hydrogen standards
- Water traces as contamination is excluded in the analysis by careful drying of the samples prior to the hot gas extraction process. Moreover the LECO-analyzer is equipped with a water trap of $Mg(ClO_4)_2$

Conclusions, continued

- The analyzed samples, increasing in burn up and oxide thickness, show a nearly constant (saturated?) hydrogen concentration within the ZrO_2 layer of about 1000 wtppm
- Samples of the same cladding alloy show a constant ratio of mass of hydrogen stored in the oxide to the total mass of hydrogen
- Applying the common hot gas extraction technique without differentiation of H_{ZrO2} from H_{Zry} leads to a hydrogen concentration overestimation in the metal phase of 5-20%

Reference:
A. Hermann, H. Wiese, R. Bühner, M. Steinemann, G. Bart; Hydrogen distribution between fuel cladding metal and overlying corrosion layers; Proc. Int. Topical Meeting on Light-Water-Reactor-Performance; April 10-13, 2000; Park City, Utah; 372