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Neutron Imaging Investigations of the Secondary Hydriding of Nuclear Fuel Cladding Alloys during Loss of Coolant Accidents

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Abstract

The hydrogen concentration and distribution at both sides of the burst opening of cladding tubes used in three QUENCH-LOCA simulation bundle experiments were investigated by means of neutron radiography and tomography. The quantitative correlation between the total macroscopic neutron cross-section and the atomic number density ratio between hydrogen and zirconium was determined by testing calibration specimens with known hydrogen concentrations. Hydrogen enrichments located at the end of the ballooning zone of the tested tubes were detected in the inner rods of the test bundles. Nearly all of the peripheral claddings exposed to lower temperatures do not show such enrichments. This implies that under the conditions investigated a threshold temperature exists below which no hydrogen enrichments can be formed. In order to understand the hydrogen distribution a model was developed describing the processes occurring during loss of coolant accidents after rod burst. The general shape of the hydrogen distributions with a peak each side of the ballooning region is well predicted by this model whereas the absolute concentrations are underestimated compared to the results of the neutron tomography investigations. The model was also used to discuss the influence of the alloy composition on the secondary hydrogenation. Whereas the relations for the maximal hydrogen concentrations agree well for one and the same alloy, the agreement for tests with different alloys is less satisfying, showing that material parameters such as oxidation kinetics, phase transition temperature for the zirconium oxide, and yield strength and ductility at high temperature have to be taken into account to reproduce the results of neutron imaging investigations correctly.

Keywords: hydrogen in zirconium; quantitative analysis; neutron imaging

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1. Introduction

In order to obtain the license for operation of a nuclear reactor, the safe behaviour during operation and hypothetical accident conditions has to be proved. One of the design basis accident scenarios used for standard safety assessment is the so-called loss of coolant accident (LOCA). A large-break LOCA postulates the rupture of a large pipe of the primary cooling circuit of a PWR. In most of the PWRs, the break of the cold leg is identified as limiting scenario, i.e. the rupture of a pipe connecting a main coolant pump with the reactor pressure vessel. The consequences are an immediate drop of the reactor pressure und a very fast heating of the reactor core. Fig. 1 gives a scheme of this scenario. This LOCA transient is limited and ended by the ECCS (emergency core cooling system) which ensures that the reactor core remains in a coolable geometry during the event and afterwards.

Coolability is achieved if the temperature does not exceed a certain temperature given in the regulations (for instance 1200°C) and the core geometry remains intact even during the thermo-shock occurring during emergency quenching. The basis for the thermo-shock resistivity is the ductile behavior of the fuel cladding tube. The ductility is reduced by oxidation. Therefore, in the past, an oxidation limit was introduced into the licensing rules, the so-called ECR (equivalent cladding reacted) criteria: ECR < 17 %. Below this oxidation ratio, the cladding behavior was assumed to be ductile. Various simulation experiments have shown that, in addition to the existing criteria, hydrogen absorption occurring after the burst of the cladding rods has to be taken into account [1-3].

Nomenclature

LOCA	loss of coolant accident
ECR	equivalent cladding reacted
L/d	ratio between distance between detector and aperture over the diameter of the aperture

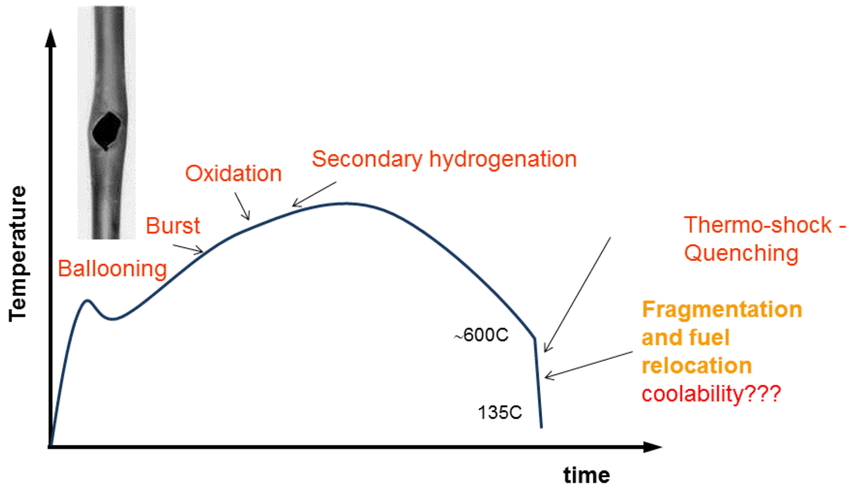

Fig. 1 Scheme of a LOCA scenario

Oxidation of zirconium by steam produces free hydrogen:

$$Zr + 2\,H_2O = ZrO_2 + 4\,H \tag{1}$$

$$4H = (4\text{-}x)\,H_{absorbed} + x/2\,H_2 \tag{2}$$

In particular, the hydrogen produced by the oxidation of the inner surface by steam penetrating through the burst opening after burst is quickly absorbed by the remaining metallic zirconium. Currently, the influence of the hydrogen absorbed during the accident on the mechanical properties is under discussion [4-7]. It was shown, that hydrogen absorption strongly decreases the ductility of zirconium giving an additional effect to the embrittlement caused by oxidation. If a large amount of hydrogen is absorbed (> 500 wt.ppm H), the ECR < 17 % is no longer conservative. However, the results available were obtained with single-rod tests or on small specimens. They cannot be transferred directly to nuclear reactors.

In order to study the hydrogen uptake during LOCA under conditions more prototypic for German pressurized water reactors (PWR´s) and its influence on the mechanical properties including the thermo-shock stability, the QUENCH-LOCA program was launched at the Karlsruhe Institute of Technology [8]. By experimental simulation of the accident at fuel rod bundle scale, the processes occurring during LOCA can be studied. The posttest examinations are focused on the quantitative determination of the hydrogen concentration and distribution in the fuel rod simulator claddings and its effect on the mechanical properties of the cladding. The QUENCH-LOCA program comprises seven tests with different materials and temperature scenarios. Two tests will be performed with claddings preloaded with hydrogen to simulate high burn-up. Up to now, five tests were performed; posttest examinations are finished for three tests.

The QUENCH bundle consists of 21 fuel rod simulators of a length of 2.5 m with original cladding tubes, but electrically heated and with zirconia pellets instead of urania pellets. A scheme of the bundle is given in Fig. 2.

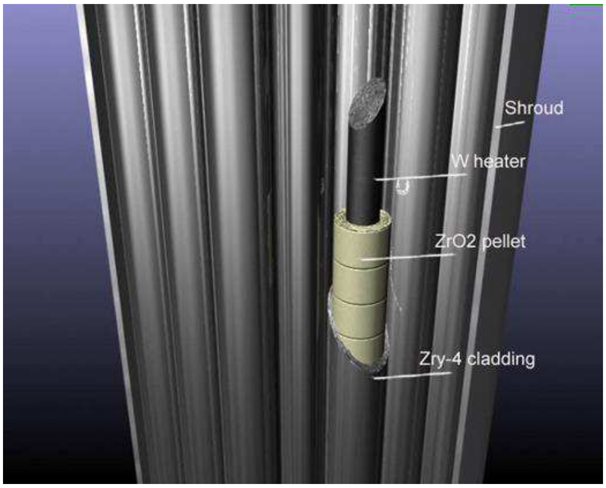

Fig. 2 Scheme of the QUENCH bundle

Details of the QUENCH-LOCA test series are given for instance in [8]. The modern cladding alloys M5™ and optimized ZIRLO™ are compared with the classical Zircaloy-4 (Zry-4). The tests comprise claddings in the as-received state as well as pre-hydrided to simulate high burn-up. Tab. 1 gives an overview on the test parameters.

Fig. 3 compares the temperature scenarios of the first four tests. The temperature scenarios of the QUENCH-L1 .. -L5 tests are prototypic for loss of coolant accidents of German PWRs. Whereas the bundle was quenched from a temperature of about 1350 K in the commissioning test QUENCH-L0, the other scenarios comprise a cool-down phase after reaching maximal temperatures. Quenching was initiated at a maximal cladding temperature of about 1000 K for the tests QUENCH-L1 and -L2 and 1200 K for QUENCH-L3HT, respectively.

After the tests, the bundles were dismounted. The posttest examinations of the rods comprise eddy current measurements of the outer oxide layer thicknesses, metallographic, X-ray and TEM investigations and mechanical testings. A very important part of the posttest examinations are the non-destructive neutron imaging investigations of the rods. This is the only non-destructive method to determine the hydrogen distribution in the cladding tubes quantitatively with sufficient spatial resolution at the whole axial region of interest.

2. Neutron imaging investigations

Neutron radiography and tomography is used worldwide by several groups to investigate the system hydrogen – zirconium [9-18]. The combination of high total neutron cross section of hydrogen and low cross section of zirconium provides the possibility of a non-destructive, quantitative determination of hydrogen concentrations in zirconium based alloys with a spatial resolution up to about 25 µm and a resolution of the hydrogen concentration up to about 50 wt.ppm.

Tab. 1 Overview of the QUENCH-LOCA tests

Test	Cladding material	Description	Test performed due to 10/2014	Post-test examinations performed due to 10/2014
QUENCH-L0	Zircaloy-4	Commisioning test	+	+
QUENCH-L1	Zircaloy-4	Reference test	+	+
QUENCH-L2	M5™ (AREVA)		+	+
QUENCH-L3	opt. ZIRLO™ (Westinghouse)		-	-
QUENCH-L3HT	opt. ZIRLO™ (Westinghouse)	Temperature higher than prototypic temperatures for German PWRs	+	-
QUENCH-L4	M5™ (AREVA) pre-hydrided	Simulation of high burn up	+	-
QUENCH-L5	opt. ZIRLO™ (Westinghouse) pre-hydrided	Simulation of high burn up	-	-

Some authors correlate the neutron transmission T and hydrogen concentration c_H or number density N_H, respectively [10, 12, 18-20]. However, a theoretical view on the total macroscopic neutron cross.section Σ_{total} shows that this value depends linearly on the number density of hydrogen:

$$\Sigma_{total} = \frac{-\ln(T)}{s} = \sum_i N_i \sigma_i = \underbrace{N_{Zr}\sigma_{Zr} + \ldots}_{\Sigma_{Zry}} + N_H \sigma_H + N_O \sigma_O \tag{3}$$

where s is the path length of the neutrons through the material, and N and σ are the number density and the total microscopic neutron cross section of the isotope i, respectively. The term $N_O\sigma_O$ can be neglected because only very thin oxide layers (~ 25 µm) are formed during the LOCA scenarios studied. A linear dependence of Σ_{total} on N_H can be expected if no additional effects like multiple scattering or beam hardening occur in a significant amount. σ_H is the slope and Σ_{Zry} (the total macroscopic neutron cross section of the as-received state) is the absolute part of the linear equation.

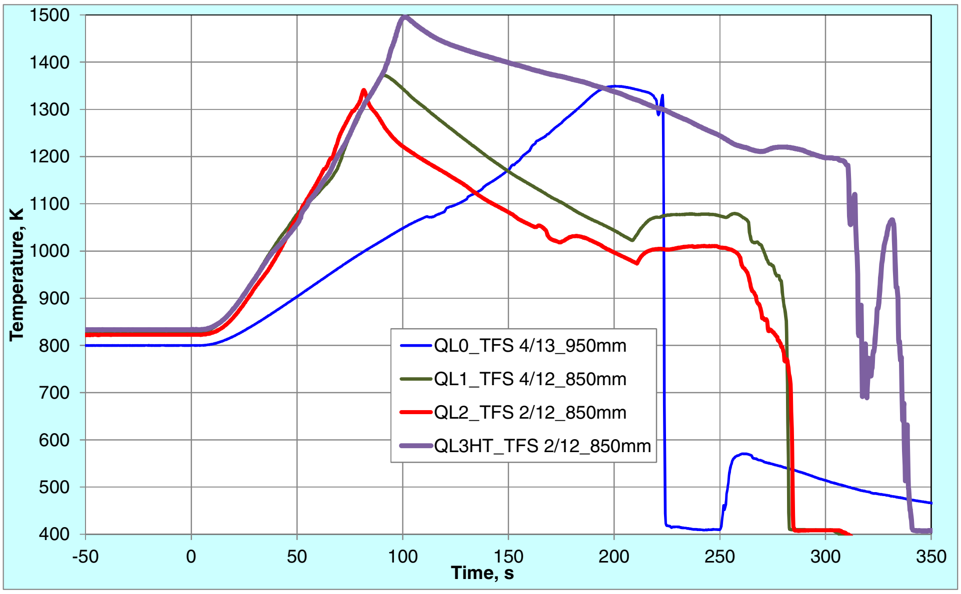

Fig. 3 Temperature scenarios of the tests QUENCH-L0, -L1, -L2 and -L3HT

Most of the investigations presented here were performed at the ICON facility at SINQ (PSI Villigen, Switzerland). The neutron tomography investigations at selected rods of the QUENCH-L1 test were performed at the CONRAD facility at the Berlin Neutron Scattering Center (Germany). Neutron tomography measurements of all rods of the QUENCH-L2 test were performed at the ANTARES facility (FRM-2, TU Munich, Germany). Tab. 2 gives parameters of the experimental setups.

Tab. 2 Parameters of the experimental setups

Facility	Measurement	L/d	Scintillator	Thickness of the scintillator, µm	Illumination times per frame, s	Number of projections
ICON	radiography	340	Gadox	20	300	-
ICON	tomography	340	Gadox	20	90	625
CONRAD	tomography	300	Gadox	10	75	600
ANTARES	tomography	600	LiF	100	20	400

For the calibration of the dependence of the total macroscopic neutron cross section on the hydrogen number density, cladding tube segments were annealed at various temperatures in Ar/H_2 atmospheres with varying hydrogen partial pressures. The amount of hydrogen was determined by measuring the weight gain of the samples. Fig. 4 compares the calibration curves determined for the facilities applied. The linear dependence of Σ_{total} on N_H expected from Eq. (3) was confirmed. All facilities use cold neutrons. Therefore, the calibration does not differ strongly between the three facilities. The calibration specimens were used to verify the reconstruction of the 3D hydrogen distribution from neutron tomography data [21]. The analysis confirms that the correct CT number was calculated.

3. Results of the neutron imaging measurements at QUENCH-LOCA specimens

A typical neutron radiograph of an inner rod of the QUENCH-L0 test is given in Fig. 5. Darker rings indicate the enrichments of hydrogen in the cladding tube on both sides of the burst opening. Both the model calculations as well the metallographic posttest examination, show that the hydrogen enrichments are located where the inner oxidation ends. Because all steam penetrated into the gap between the inner cladding surface and pellets is completely consumed after several millimeters, the extension of the inner oxide layer is limited.

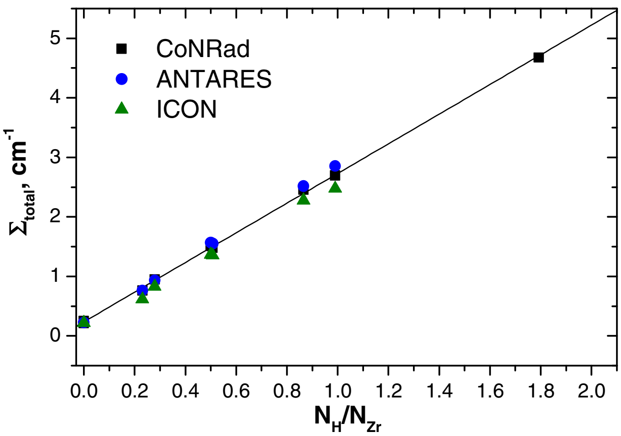

Fig. 4 Calibration of the dependence of the total macroscopic neutron cross section on the hydrogen to zirconium atomic ratio

Hydrogen enrichments were found in the inner rods of the QUENCH-L1 and -L2 bundles. Fig. 6 gives a typical example for it. Compared to QUENCH-L0, the enrichments are more blurred because the bundle was not quenched from the highest temperatures. The hydrogen has time to diffuse in axial direction. No hydrogen enrichments were found in the peripheral rods of these tests.

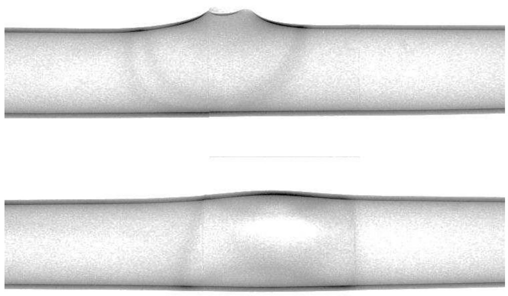

Fig. 5 Neutron radiographs (Side view (top) and frontal view (bottom)) of the ballooned part of rod QUENCH-L0 #06

The hydrogen concentrations were determined by means of neutron tomography investigations. Tab. 3 compares the maximum concentrations found in the bundles QUENCH-L0, -L1 and -L2. In nearly all peripheral rods of the QUENCH-L0 bundle and in all peripheral rods of the QUENCH-L1 and -L2 bundles, no hydrogen enrichments were found. This observation is most likely caused by the temperature gradients in the bundles. The maximum temperatures of the peripheral rods are about 70 K below the maximal temperatures of the inner rods.

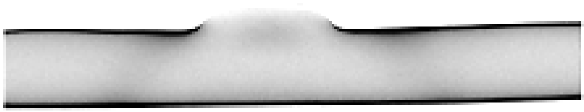

Fig. 6 Neutron radiographs of the ballooned part of rod QUENCH-L1 #08

Tab. 3 Results of the neutron tomography investigations

Test	Maximal hydrogen concentration, wt.ppm
QUENCH-L0	2700
QUENCH-L1	1700
QUENCH-L2	1070

4. Discussion

All rods of the tests already performed survived the quenching which demonstrates that the thermo-shock stability is given for LOCA accidents of German PWRs.

In order to understand the band-shaped hydrogen enrichments at both sides of the ballooning region, a model was developed [22], taking into account the following processes:

- Diffusion of steam into the gap between pellets and the inner cladding surface,
- Oxidation of the inner cladding surface and production of molecular hydrogen,
- Diffusion of the molecular hydrogen in the gap,
- Hydrogen uptake by the cladding, and
- Diffusion of the absorbed hydrogen in radial and axial directions inside the cladding.

In order to investigate the effect of the different alloys, model calculations were performed varying the temperature scenarios measured for the QUENCH-L0, -L1 and -L2 test. All other parameters such as oxidation kinetics, temperatures of phase transformations, and size and shape of the ballooning were kept constant. Fig. 7 compares the hydrogen distributions modelled. The general shapes of the hydrogen distributions including the positions of the maxima are well predicted, whereas the absolute concentrations are strongly underestimated.

In order to compare the modelling results with the results of the neutron tomography investigations, the maximum hydrogen concentrations were referred to the QUENCH-L1 reference test. As Fig. 8 shows, the values agree well for the two tests using Zry-4 as cladding material, but gave significant discrepancies for the QUENCH-L2 test using M5™. This result clearly shows that material parameters such as the oxidation kinetics, the temperature of the monoclinic to tetragonal phase transition in the zirconium oxide, and the yield strength and plasticity at high temperatures have an effect on the hydrogen uptake. For instance, it is known that the Zr-Nb alloy M5™ has a lower oxidation rate than Zry-4 at least at temperatures below 1300°C. Additianlly, the transition temperature between monoclinic and tetragonal zirconia is about 50 K higher for M5™. Both effects result in a lower hydrogen uptake according the model applied.

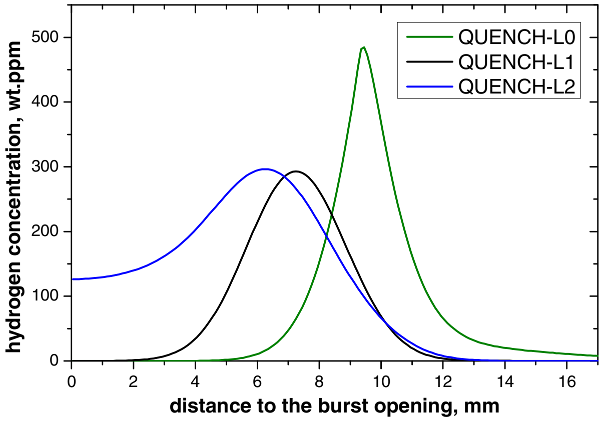

Fig. 7 Modelling results of the secondary hydrogenation during the test QUENCH-L0, -L1 and -L2

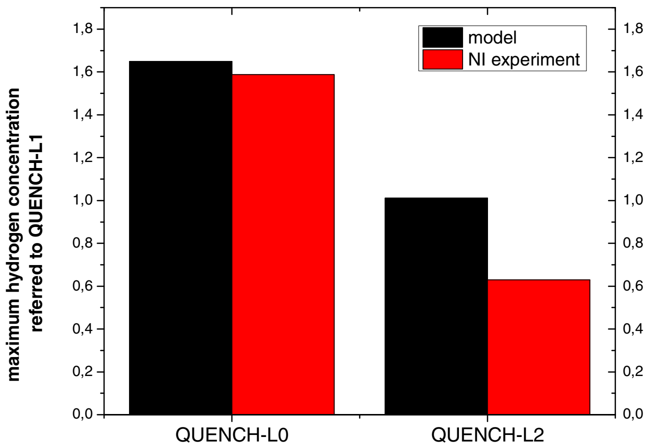

Fig. 8 Comparison between modelling and neutron tomography results of the maximal hydrogen concentrations of the QUENCH-L0 and -L2 tests related to the reference test QUENCH-L1

5. Conclusions

In the QUENCH-LOCA tests, different cladding alloys were studied with temperature-time scenarios prototypical for German PWRs. The results show that the residual strength and/or ductility of the claddings after burst are sufficiently high to ensure thermo-shock resistance during quench.

From the neutron imaging investigations the following conclusions can be derived:

- Neutron imaging is the only method to determine quantitatively the hydrogen distribution and concentration at the length scale of interest for cladding tubes after LOCA.
- A threshold temperature seems to exist below which no hydrogen enrichments are formed under the LOCA scenario applied. This threshold temperature may be connected with the monoclinic to tetragonal transition temperature of the zirconium oxide. The change of the crystalline structure results in changing the hydrogen diffusivity through the oxide layer. Above the transition temperature, band-shaped hydrogen enrichments are formed where the ballooning zone and with it the oxidation of the inner tube surface ends.

- The comparison between modelling and results of the neutron tomography investigations shows that cladding material parameters influence the secondary hydrogenation during LOCA. The model has to be improved by including these parameters in the computer codes.
- The QUENCH-LOCA program will be continued by performing tests using fresh and prehydrided optimized ZIRLO™ to extend the data basis of the materials behavior during LOCA.

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