

LWR Fuel Behaviour Under Severe Core Damage Conditions (1000 to 2000 °C)

A. Fiege

*Kernforschungszentrum Karlsruhe GmbH, Projekt Nukleare Sicherheit,
Postfach 3640, D-7500 Karlsruhe 1, Germany*

Abstract

The paper describes the LWR fuel rod behavior under severe core damage conditions (between 1000 and 2000°C) which is dominated by the competing effects of the high temperature oxidation of Zircaloy (Zry) cladding in steam and the chemical interactions between Zry cladding and UO_2 fuel.

1.) Introduction

LWR safety studies have shown that small break loss-of-coolant accidents and anticipated transients, in combination with the failure of one of the required safety systems, can lead to overheating of the fuel rods beyond the present design basis accident limits of 1200°C and result in severe fuel damage and fission product release. The TMI-2 accident, on the other hand, has demonstrated that a severe fuel damage transient will not necessarily escalate to an uncontrolled core meltdown accident, as was assumed in earlier risk studies.

Therefore, comprehensive research programs have been initiated in various countries to investigate the relevant damage mechanisms acting with increasing temperature on an uncovered core and to develop models for estimating the damage in the core, when the design limit temperature is exceeded, but the transient can be stopped before core meltdown/1/,/2/.

The principal phenomena of interest are:

- the high temperature oxidation and embrittlement of Zry cladding material in steam, the influence of hydrogen and steam starvation on the oxidation kinetics, and the resultant hydrogen production,
- the chemical interaction between UO_2 and Zry cladding, below and above the melting point of Zry, especially the formation of liquid phases between Zry cladding and UO_2 , which can destroy the fuel structure far below the melting point of the UO_2 fuel,
- the integral behavior of fuel rods and bundles, especially the influence of spacer grids, absorber material, and control rod guide tubes on the UO_2 /Zry interaction, and the fragmentation of severely embrittled or partly molten fuel rods during quenching.

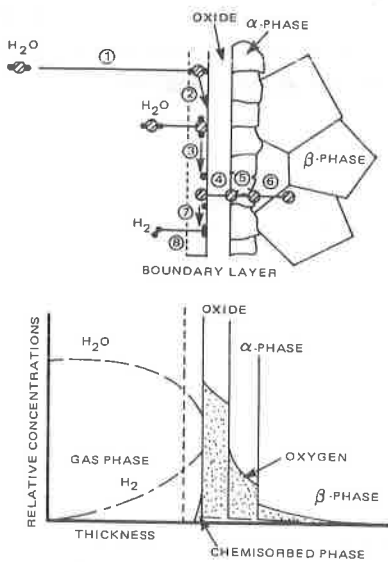


Fig. 1: Physical Processes during Zircaloy-Steam Oxidation and the Corresponding Concentration Gradients, /3/.

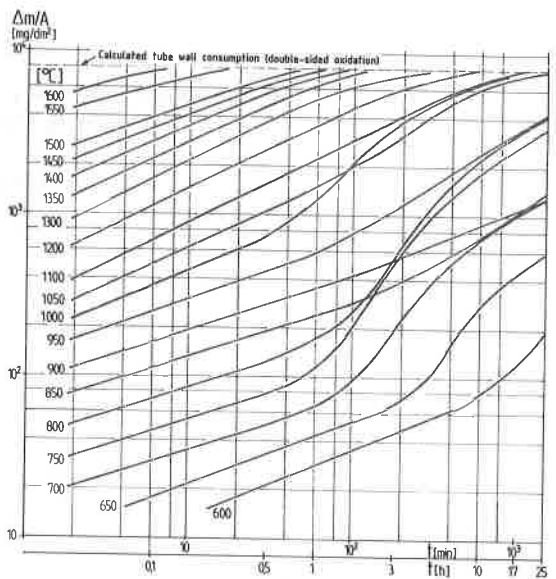


Fig. 2: Mass Increase of Zircaloy-4 Cladding in Steam versus Time, /4/.

2.) High Temperature Oxidation of Zircaloy in Steam

The oxidation of Zircaloy in steam is a complex process which is, in a simplified way, shown in Fig. 1/3/. The elementary steps are: gaseous diffusion of steam through a thin hydrogen rich layer on the cladding surface (1), chemisorption onto the surface (2), dissociation of the water molecule into oxygen and hydrogen (3), diffusion of oxygen into the zirconium dioxide layer (4), into the oxygen stabilised α -phase (5) and the β -phase, respectively (6). Steps (7) and (8) are the recombination of hydrogen and the desorption of gaseous hydrogen.

The reaction rate between Zircaloy and steam is strongly temperature dependent. Fig. 2 shows the mass increase due to the oxygen uptake versus reaction time, determined by isothermal tests in an unlimited steam supply/4/. On a log-log scale the slopes of the curves indicate cubic kinetics below 1000°C and parabolic behavior from 1000°C to 1600°C, for hold times $\leq 0,5$ h. The oxide layer is adherent and protective. The long term oxidation between 600 and 800°C and at 1000°C is characterized by a transition to linear kinetics resulting from oxide scale cracking, the so-called breakaway effect. From 850 to 950°C, that is in the two phase ($\alpha + \beta$)-Zr region, a change from cubic to parabolic oxidation is caused by a moderate breakaway effect. At and above 1050°C, no change in rate law towards accelerated oxidation can be detected.

The data indicate that most of the correlations which are in use for LOCA conditions (i.e. $T \leq 1200^\circ\text{C}$, $t \leq 15$ min) are accurate up to temperatures of 1500°C (e.g. Cathcart, Leistikow, Kawasaki, see/5/).

In general it can be stated that in the temperature region between 1000 and 1500 °C the available data are consistent and of high quality. Most of these data yield parabolic rate constants between 40 and 80% of the well

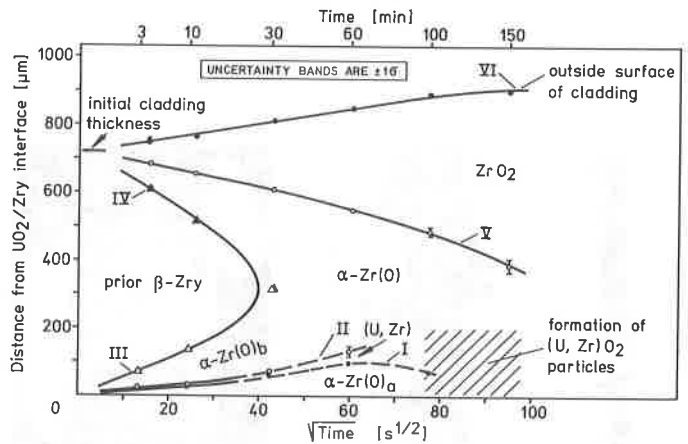
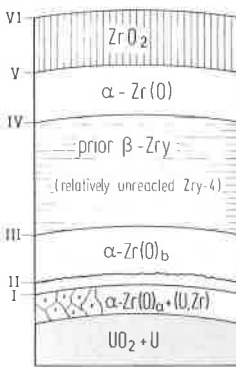
known Baker-Just equation/6/. Above 1500°C only two complete data sets are available, that of Baker-Just and that of Urbanic and Heydrick /7/. The latter data give lower rates of reaction than Baker-Just, but show a sharp increase in the ZrO_2 growth rate above 1600°C which is due to the change in ZrO_2 crystal structure from tetragonal to cubic. The oxidations kinetics of liquid Zry are not well known at present.

In the case of limited steam supply and/or in the presence of steam/hydrogen mixtures, the oxidation kinetics can be different. In tests at 1200 - 1700 °C Chung and Thomas /3/ found that the ratio of the parabolic rate for hydrogen/steam mixtures to that for pure steam decreased with increasing temperature and decreasing steam supply rate. For very small steam supply rates (but still larger than the "steam starvation" limit), significantly smaller linear oxidation rates were observed in hydrogen/steam mixtures, which indicate that the oxidation rate was limited either by the gaseous transport of the steam molecules or as the result of chemical reactions between the chemisorbed oxygen on the ZrO_2 surface and the gaseous hydrogen molecules in the boundary layer (hydrogen blanketing). The effects of steam starvation and possibly also of hydrogen blanketing are very important. The zirconium-steam oxidation in an uncovered core is an exothermal reaction. It produces large amounts of heat which add to the nuclear decay heat and result in a temperature excursion in the core. The moderating effects of limited steam supply and of hydrogen would result in lower core heatup rates during core uncover and lead to lower peak fuel rod temperatures. At KfK and BNWL additional experiments are being performed to quantify these effects and to provide the data base for the mechanistic modeling of the reaction behavior of Zircaloy under limited steam supply and in a hydrogen containing atmosphere/8,/1/.

3.) Interaction between Zircaloy Cladding and Oxide Fuel

UO_2 and Zircaloy are thermodynamically unstable with respect to each other. In addition to the outside corrosion of Zircaloy in steam chemical interactions are therefore expected at high temperatures on the inner surface of the cladding. These interactions can influence the integrity of the fuel rods and the fission product release.

reaction layer
interface

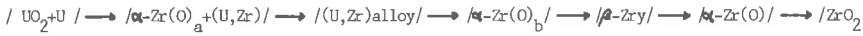


$T = 1200\text{ }^\circ\text{C}$; $p_{ext} = 40\text{ bar}$; atmosphere = Ar + 25 vol.% O_2

Fig. 3: Isothermal Zircaloy-4 Reaction in Oxidizing Atmosphere below the Melting Point of Zry, Sequence of Reaction Layers and their Thickness versus Time./9/.

Below the melting point of Zircaloy the extent of the reaction depends decisively on the fuel/cladding contact conditions /9/. If there is no solid/solid contact, oxygen is transported from the UO_2 to the Zircaloy only in the gas phase and the resulting reactions are negligible. If solid contact exists due to external overpressure or different thermal expansions of cladding and fuel at high temperatures, Zircaloy reduces the UO_2 to form oxygen-stabilized α -zirconium and metallic uranium. The uranium reacts with Zircaloy to form a (U,Zr) alloy rich in uranium which is liquid above $\sim 1150^\circ\text{C}$.

In an oxidizing atmosphere the reaction layers form in a particular sequence at all reaction temperatures and times (Fig. 3, left-hand side)



The right-hand side of Fig.3 shows the thickness of the different reaction zones versus \sqrt{t} . After a certain time, which is strongly temperature dependent, the β -phase of the Zry cladding is totally consumed and converted to α -Zr(O). The growth of the reaction layers initially obeys a parabolic rate law, and the diffusion of oxygen into the cladding is the rate-determining step. After some time, the growth rate of the various phases decreases due to the finite cladding wall thickness.

The UO_2 /Zircaloy reaction on the inner surface of the cladding occurs as rapidly as the outside corrosion in steam. Oxygen uptake by the Zircaloy causes the cladding to become embrittled. Due to the combined external and internal cladding oxidation the embrittlement of Zircaloy tubing occurs about four times faster than oxidation from either surface alone.

The UO_2 /Zry interaction can only continue until oxygen saturation is reached in all the α -Zr(O) phases (about 6 wt %). The UO_2 /Zry interaction can not proceed beyond oxygen saturation of the α -Zr(O) due to insufficient oxygen potential of the stoichiometric fuel. Therefore, ZrO_2 will not form on the cladding inside surface. However, the high oxygen potential of the outside environment results in the formation of a ZrO_2 layer on the cladding outside surface. When oxygen saturation in the combined α -Zr(O) layer is reached, the initially formed metallic (U,Zr) layer is converted to a (U,Zr) O_2 mixed oxide solid solution. The final stable reaction products of the combined cladding interactions are ZrO_2 and (U,Zr) O_2 .

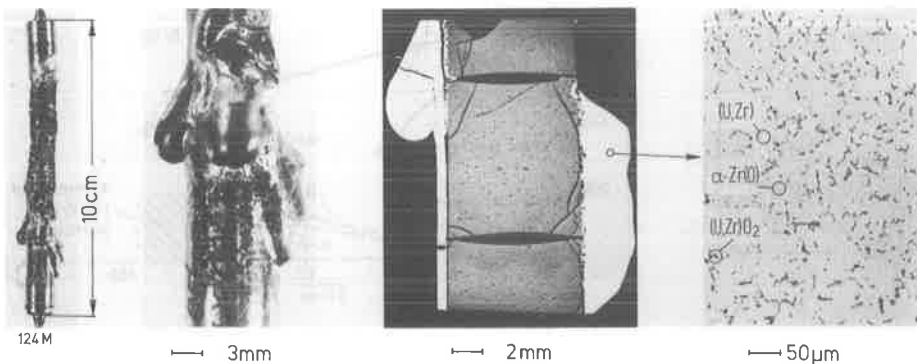


Fig. 4: Transient UO_2 /Zry-4 Interaction Experiment ($T_{max} = 2000^\circ\text{C}$, $dT/dt = \pm 10 \text{ K/S}$, $P_{ext} = 1 \text{ bar}$), /10/.

Above the melting temperature of the Zircaloy cladding, which depends upon the oxygen content, the molten Zircaloy reduces the UO_2 fuel by forming, initially, a homogeneous (U,Zr,O) melt./10/. Once a certain oxygen content in the (U,Zr,O) melt is exceeded, solid (U,Zr) O_{2-x} particles precipitate at high temperatures to form a liquid-solid phase mixture. The final stable reaction product between UO_2 and Zr(O) is, at high temperatures, a (U,Zr) O_{2-x} solid solution.

During cooling the (U,Zr,O) melt decomposes into α -Zr(O) and a (U,Zr) alloy rich in uranium. The (U,Zr) O_{2-x} decomposes into (U,Zr) O_2 and (U,Zr) (See Fig.4). These phases observed in the solidified melt are consistent with the U-Zr-O ternary and the α -Zr(O)/ UO_2 pseudo-binary phase diagrams.

Due to the chemical interaction between liquid Zircaloy and solid UO_2 , a macroscopic sudden disintegration of the UO_2 can occur after a specific reaction time at about 2000°C. The UO_2 is thus "liquefied" well below its melting point (2800°C), and enhanced fission gas and volatile fission product release must be expected. The amount of fuel which can be liquefied by molten Zircaloy depends on the initial oxygen concentration of the cladding. The higher the initial oxygen concentration of the melt, the smaller is the amount of fuel which can be dissolved.

An experimental program is underway to quantify the dissolution rate of UO_2 by liquid Zircaloy and the maximum solubility of UO_2 in liquid Zircaloy as a function of temperature, time and oxygen content.

4.) Integral Behavior of Fuel Rods and Bundles

The high temperature steam oxidation and the Zry/ UO_2 interactions described above are being investigated in separate effects tests which provide the data base for modeling. For the assessment of SFD codes a spectrum of out-of-pile and in-pile experiments is needed which includes the system interactive effects, e.g. the influence of realistic fuel rod geometry, spacer grids, absorber materials, control rod guide tubes and realistic thermal hydraulic boundary conditions/2/.

At present a series of single rod and small 3x3 bundle experiments are underway at KfK to investigate the phenomenon of temperature escalation due to the exothermal Zircaloy/steam reaction/11/. This temperature escalation is of extreme importance because it determines the time span between design basis conditions and the uncontrolled meltdown of the core.

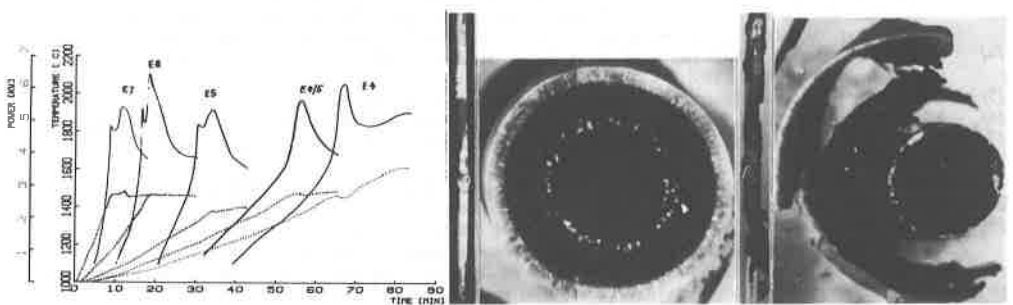


Fig. 5: Power and resultant Cladding Temperatures of ESSI 4,5,6,7 versus Time,/11/.

Fig. 6: Posttest Appearance of ESSI 4 and ESSI 7/11/.

Fig.5 shows the power and the resultant cladding temperature transients of tests ESSI 4,5,6,7. In each test, a temperature escalation due to the Zircaloy/steam reaction was observed. The temperature at which the escalation began increased with decreasing initial heatup rate. The maximum temperature rise rate was approximately the same in every test, about 6°C/s. The escalation began in the upper region of the rods and moved down the rods towards the lower end, opposite to the direction of steam flow. The maximum rod surface temperature, however, never exceeded 2200°C. For fast initial heatup rates the runoff of molten Zircaloy was a limiting process for the escalation. For slow heatup rates the formation of a protective oxide layer reduced the reaction energy.

The posttest appearance of the fuel rod simulators E4 and E7 (Fig.6) show that at slow heatup rates (E4) oxidation of the cladding was more or less complete, almost no UO_2 had been dissolved, and the fuel rod was relatively intact. Conversely, at fast heatup rates (E7), relatively little oxidation, almost complete dissolution of the UO_2 annular pellets, and runoff of molten cladding were observed. Cross sections of the rods were made at various elevations. Metallographic and microprobe analyses of the refrozen melt have shown that melt in contact with steam, and melt found between an oxide shell and remaining UO_2 formed a nearly stoichiometric uranium-zirconium mixed oxide (U,Zr) O_2 . These findings are in good agreement with the results of separate effects tests described above.

A large out-of-pile test facility, CORA, is under construction at KfK. It will be in operation by the end of 1985. The CORA facility will handle up to 7x7 electrically heated fuel rod simulators with a heated length of 1m. Also a certain number of solid pellet rods is feasible. Heatup rates of 0,5-4 K/s are possible to a maximum cladding temperature of about 2000°C. Ballooning and bursting of the cladding will be possible plus operation with cracked fuel pellets. The bundle is surrounded by a high temperature radiation shield to reduce radial heat losses. The atmosphere will normally be steam at atmospheric pressure. The maximum pressure is 12 bar, which is sufficient to cause close contact between fuel pellets and cladding. Two additional important features of the design are the quenching device and an excellent bundle inspection capability.

It is expected that these out-of-pile tests, together with the in-pile tests performed e.g. in PBF, ACRR, NRU and PHEBUS will provide the data base and the subsequent understanding of the physical and chemical processes which dominate the initiation, progression, termination and environmental consequences of severe core damage accidents.

5.) References

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