High-temperature oxidation and mutual interactions of materials during severe accidents in LWRs

Martin Steinbrück

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Karlsruhe Institute of Technology

Founded in 2009

= FZK research center (1956) + University Karlsruhe (1825)

= 9000 employees

= 24 000 students
Nuclear Safety Research at KIT

- Safety of Nuclear Reactors
- Nuclear Waste Disposal
- Radiation Protection
- Nuclear Decommissioning Technologies
Safety of Nuclear Reactors
Severe Accident Research Expertise at KIT

- Reflood of an overheated core (CORA, QUENCH)
- Core melting phenomena and in-vessel corium behavior (LIVE)
- Direct containment heating (DISCO-H)
- Fuel coolant interaction (DISCO-FCI, DISCO-JET)
- Molten corium concrete interaction and ex-vessel corium coolability (BETA, COMET, MOCKA)
- Hydrogen behavior in reactor systems (HYKA)
- Development and application of SA code systems (MELCOR, ASTEC, WECHSL, GASFLOW, COM3D...)

![Image of reactor components and damage]
QUENCH project at KIT (program NUSAFE)
Investigation of hydrogen source term and materials interactions during LOCA and early phase of severe accidents including reflood

Separate-effects tests

Bundle experiments

PWR fuel element
QUENCH Facility

- Unique out-of-pile bundle facility to investigate reflood of an overheated reactor core
- 21-31 electrically heated fuel rod simulators
- Extensive instrumentation for T, p, flow rates, level, etc.
- So far, 17 experiments on SA performed (1996-today)
  - Influence of pre-oxidation, initial temperature, flooding rate
  - B4C, Ag-In-Cd control rods
  - Air ingress
  - Advanced cladding alloys
  - Debris formation and coolability

M. Steinbrück et al., Synopsis and outcome of the Quench experimental program, NED 240 (2010), 1714-1727.
QUENCH Separate-effects tests: Main setups

INRRO

TG

QUENCH-SR

BOX
Outline

- Phenomenology of severe accidents in light water reactors (LWR)
- High-temperature oxidation of zirconium alloys in various atmospheres
- Behavior of boron oxide control rods during severe accidents
- Silver-indium-cadmium control rod failure during severe accidents
LWR severe accident scenario

- Loss of coolant causes steady heatup of the core due to residual decay heat
- From ca. 1000°C oxidation of zirconium alloy cladding becomes significant
- From ca. 1250°C chemical interactions between the different core materials (stainless steel, Zr alloys, boron carbide ...) lead to the local formation of melts significantly below the melting temperatures of the materials
- From ca. 1800°C formation of melt pool in the core and relocation of melt/debris to the lower plenum (in-vessel, see TMI-2).
- Subsequently, failure of the RPV and release of corium melt into the containment (ex-vessel, see Fukushima)
Core materials in Light Water Reactors

- UO2(/PuO2) fuel: 100-200 t
- Zry cladding + grid spacers: 20-40 t
- Zry canister (BWR): 40 t
- Various steels, Inconel: >500 t (incl. RPV)
- B4C absorber (BWR, VVER, ...): 0.3-2 t
- AgInCd absorber (PWR): 3-5 t

Environment

- Water, steam
- Air
- Nitrogen

After failure of RPV/primary circuit
High-temperature oxidation of zirconium alloys

- Most cladding alloys consist of 98-99 wt% zirconium plus some alloying elements (Sn, Nb, Fe, Cr, ...)

<table>
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<tr>
<th>Element</th>
<th>Zircaloy-4</th>
<th>D4</th>
<th>M5</th>
<th>E110</th>
<th>ZIRLO</th>
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<tr>
<td>Nb</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<tr>
<td>Sn</td>
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<td>0.5</td>
<td>0.01</td>
<td>-</td>
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<tr>
<td>Fe</td>
<td>0.2</td>
<td>0.5</td>
<td>0.05</td>
<td>0.008</td>
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<tr>
<td>Cr</td>
<td>0.1</td>
<td>0.2</td>
<td>0.015</td>
<td>0.002</td>
<td>&lt; 0.01</td>
</tr>
</tbody>
</table>

- In steam, oxygen, nitrogen, air, and various mixtures
- Temperature: 600-1600°C
Oxidation of zirconium alloys – chemical reactions

\[ Zr + 2H_2O \rightarrow ZrO_2 + 2H_2 \]  
\[ \Delta H_f \text{ at } 1500 \text{ K} \]  
\[ -585 \text{ kJ/mol} \]

\[ Zr + O_2 \rightarrow ZrO_2 \]  
\[ -1083 \text{ kJ/mol} \]

\[ Zr + 0.5N_2 \rightarrow ZrN \]  
\[ -361 \text{ kJ/mol} \]

- Release of hydrogen and heat
- Hydrogen either released to the environment or absorbed by Zr metal
Hydrogen detonation in Fukushima Dai-ichi NPPs ...

... main hydrogen source: zirconium - steam reaction
Oxidation in steam (oxygen)

Most LOCA and SFD codes use parabolic oxidation correlations (determined by the diffusion of oxygen through growing oxide scale).

\[ d_{\text{ZrO}_2} = \text{f}(T) \cdot t^{0.5} \]

Oxide thickness during oxidation of Zry at 1200°C in steam

20 min at 1200°C in steam
Breakaway oxidation

- Loss of protective properties of oxide scale due to its mechanical failure.
- Breakaway is caused by phase transformation from pseudo-stable tetragonal to monoclinic oxide and corresponding change in density up to ca. 1050°C.
- Critical times and oxide thicknesses for breakaway strongly depend on type of alloy and boundary conditions (ca. 30 min at 1000°C and 8 h at 600°C).
- During breakaway significant amounts of hydrogen can be absorbed (>40 at.%, 7000 wppm) due to local enrichment of H2 in pores and cracks near the metal/oxide boundary (“hydrogen pump”).
In-situ investigation of hydrogen uptake during oxidation of Zry in steam by neutron radiography

Zry-4, 1000°C
30 g/h steam, 30 l/h argon

- Rapid initial hydrogen uptake
- Further strong hydrogen absorption after transition to breakaway
**Oxidation in atmospheres containing nitrogen**

- Air ingress into reactor core, spent fuel pond, or transportation cask
- Nitrogen in BWR containments (inertization) and ECCS pressurizers
- Prototypically following steam oxidation and mixed with steam

**Consequences:**

- **Significant heat release** causing temperature runaway from lower temperatures than in steam
- **Strong degradation of cladding** causing early loss of barrier effect
- **High oxygen activity** influencing FP chemistry and transport
Oxidation of Zr alloys in N2, O2 and air

1200 °C

Air

Oxygen

Nitrogen

\( \Delta m, \% \)

Time, s

0 200 400 600 800 1000

\(~ \) Linear oxidation kinetics

Parabolic oxidation kinetics

Parabolic reaction kinetics

Oxidation rate in air is much higher than in oxygen or steam
Oxidation of Zr alloys in N2, O2 and air

1200 °C

\[ \Delta m, \% \]

\[ \text{Time, s} \]

- Air
- Oxygen
- Nitrogen

1 h
1.5 h
3 h

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Consequences of air ingress for cladding

1 hour at 1200°C in steam

1 hour at 1200°C in air

Loss of barrier effect of cladding
Mechanism of air oxidation

- Diffusion of air through imperfections in the oxide scale to the metal/oxide interface
- Consumption of oxygen
- Remaining nitrogen reacts with zirconium and forms ZrN
- ZrN is re-oxidized by fresh air with proceeding reaction associated with a volume increase by 48%
- Formation of porous and non-protective oxide scales

1 – initially formed dense oxide ZrO₂
2 – porous oxide after oxidation of ZrN
3 – ZrO₂ / ZrN mixture
4 – α-Zr(O)
Experiments on mechanism of nitrogen attack

Specimens:
- Pre-oxidized in O2 at 1200 °C (↑)
- Homogenized 3h at 1400 °C in Ar
- Reaction in N2 1h at 1200 °C
Reaction of ZrOx with nitrogen

1200°C

Time, s

Δm, %

Oxygen load:
- 0% (β -Zr)
- 0.7% (β -Zr(O))
- 5.7% (α -Zr(O))
- 33.1% (substoich. ox.)
- 35% (stoichiometr. ox.)

0% (β -Zr)
0.7% (β -Zr(O))
5.7% (α -Zr(O))
33.1% (substoich. ox.)
35% (stoichiometr. ox.)
Oxidation in mixed steam-air atmospheres

Zry-4, 1 hour at 1200°C

H₂O
0.7 H₂O
0.3 air
0.3 H₂O
0.7 air
0.7 H₂O
0.3 air
0.1 H₂O
0.9 air

Increasing degradation with raising content of air in the mixture
Oxidation in mixed atmospheres

1 hour at 1000 °C in steam

1 hour at 1000 °C in 50/50 steam/N2

- Strong effect of nitrogen on oxidation and degradation
- Nitrogen acts like a catalyst (NOT like an inert gas)
- Enhanced hydrogen source term by oxidation in mixtures containing nitrogen
QUENCH-16 bundle test with air ingress

Off-gas composition during the air ingress phase (after pre-oxidation in steam)

ZrN formation at the end of air ingress phase

ZrN re-oxidation during quench phase

Hydrogen and nitrogen release during quench phase

Nitrogen consumption

Oxygen starvation

Gas flow rate, mg/s

H₂

N₂

O₂

Temp.

Temperature, K

9000 9500 10000 10500 11000 11500

0 50 100 150 200

9500 10000 10500 11000 11500

0 50 100 150 200

9000 9500 10000 10500 11000 11500

0 50 100 150 200

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Absorber materials in LWRs

**Boron carbide**
- Used in boiling water reactors (BWR), VVERs, some pressurized water reactors (PWR)
- Control rods (PWR) or cross-shaped blades (BWR)
- Surrounded by stainless steel (cladding, blades) and Zry (guide tubes, canisters)

**AgInCd alloy**
- Used in PWRs
- Surrounded by stainless steel cladding and Zry guide tubes
- Rods in Zry guide tubes combined in control rod assemblies

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**BWR control rod**
- Zry guide tube: Tmelt=1900°C
- SS cladding: Tmelt=1450°C
- B4C: Tmelt=2450°C

**PWR control rod**
- Zry guide tube: Tmelt=1900°C
- SS cladding: Tmelt=1450°C
- AglnCd: Tmelt=800°C
Degradation of B4C control rods (1-pellet)

Post-test appearance and axial cross section of B4C/SS/Zry specimens after 1 hour isothermal tests at temperatures between 1000 and 1600 °C
Eutectic interaction of stainless steel with B4C

1 h at approx. 1250 °C

4 wt.% B4C

1 wt.% B4C

0.3 wt.% B4C

Complete liquefaction of stainless steel

1/3 of SS liquefied
Eutectic interaction of stainless steel with B4C

Rapid and complete melting of SS at 1250°C starting at B4C/SS boundary
Oxidation of boron carbide; main chemical reactions

\[ B_4C + 8H_2O(g) \rightarrow 2B_2O_3(l) + CO_2(g) + 8H_2(g) \quad -760 \text{ kJ/mol} \]

\[ B_4C + 6H_2O(g) \rightarrow 2B_2O_3(l) + CH_4(g) + 4H_2(g) \quad -987 \text{ kJ/mol} \]

\[ B_2O_3 + H_2O(g) \rightarrow 2HBO_2(g) \quad +341 \text{ kJ/mol} \]

- Release of hydrogen, various carbon-containing gases and heat
- Formation of a superficial boron oxide layer and its vaporization
Oxidation kinetics of B4C in steam

Strongly dependent on B4C structure and thermohydraulic boundary conditions like pressure and flow rate
Oxidation of B4C absorber melts

Transient oxidation of B4C/SS/Zry-4 absorber melts in steam between 800 and 1550 °C

Oxidation rate during reaction of absorber melts and pure CR components in steam
Degradation of B4C control blade (BWR bundle test)  
CORA-16

- Complete loss of absorber blade
- Dissolution of cladding and fuel
- Massive melt relocation (B4C, SS, Zry, UO2)
Gas release due to oxidation of B4C (melts)

- **Hydrogen**
  - Up to 290 g H2 per kg B4C
  - Up to 500 kg additional H2 production for BWRs

- **Carbon monoxide/dioxide**
  - Ratio depending on temperature and oxygen activity
  - Non-condensable gases affecting THs and pressure
  - CO combustible and poisonous

- **Methane**
  - Would have strong effect on fission products
  - Bundle experiments and SETs reveal only insignificant release of CH4

- **Boric acids**
  - Volatile and soluble in water
  - Deposition at colder locations in the circuit
Energetic effects of B4C oxidation

- Oxidation of B4C in steam: 13 MJ/kgB4C
- Oxidation of B4C in oxygen: 50 MJ/kgB4C
- Significant contribution to energy release in the core

For comparison:

- Oxidation Zr in steam: 6 MJ/kgZr
- Fuel value of mineral oil: 12 MJ/kgoil
- Fuel value of black coal: 30 MJ/kgcoal
Possible consequences for Fukushima accidents

- Boiling water reactors with cruciform-shaped blades
- 1 control blade = 7 kg B4C + 93 kg SS
- Complete liquefaction of the blade at T>1200°C

Fukushima Daiichi NPPs:
- Unit 1: 97 control blades
- Unit 2-4: 137 control blades

- Complete oxidation of B4C inventory by steam:
  - 195/275 kg H2
  - 2700/3800 kWh (10/14 GJ)
Failure of AgInCd absorber rod

- Ag-In-Cd control rods fail at temperatures above 1200°C due to the eutectic interaction between SS and Zry-4
- Failure is very stochastic (from local to explosive) with the tendency to higher temperatures for symmetric samples and specimens with inner oxidation
- No ballooning of the SS cladding tube was observed before rupture
- Burst release of cadmium vapour is followed by continuous release of indium and silver aerosols and absorber melt

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Zry guide tube
\( T_{\text{melt}} = 1900°C \)

SS cladding
\( T_{\text{melt}} = 1450°C \)

AgInCd
\( T_{\text{melt}} = 800°C \)
Different failure types of AgInCd absorber rod

- **SIC-02** (asym. rod)
  - Local failure at 1230°C

- **SIC-05** (symmetric rod)
  - Global failure at 1350°C
Explosive failure of SIC-11 w/o Zry guide tube

No balloning before explosive failure!
QUENCH-13 control rod appearance

- No direct interaction between AIC and steel
- Increasing interactions between relocated AIC and Zry in gap with temp.
- Increasing interaction between melt and steel with increasing Zr content
QUENCH-13 bundle test: aerosol release

- First burst release of cadmium vapor, then aerosols mainly consisting of silver and indium.

![Graph showing temperature and power over time with different aerosol concentrations.](image-url)

- **PSI Bi2**: no relevant species
- **AEKI I3**: Cd
- **PSI Bi1**: Cd, In, Ag, W
- **AEKI I8**: Cd, In, Ag, W, Zr, Sn, Fe
Summary

- Chemical interactions may strongly affect the early phase of a severe nuclear accident.
- The main hydrogen source term is produced by metal-steam reactions.
- Exothermal chemical reactions can cause heat release larger than the decay heat and hence strongly contribute to the power generation in the core.
- Nitrogen does not behave like an inert gas during the conditions of a severe accident.
- Eutectic interactions between the various materials in the core (i.e. B4C-SS, SS-Zry) cause liquefaction of materials significantly below their melting temperatures.
- Boron carbide may (at least locally) significantly contribute to release of heat, hydrogen and other gases.
THANKS to ...

- The QUENCH team at KIT
- Bożena Sartowska and Wojtek Starosta for inviting me and hospitality
- YOU ... for your attention
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Phase diagram Zr - O

Liquid

L+β
L+α
L+α
α +cub. ZrO_{2-x}
α +tetr. ZrO_{2-x}
α +mon. ZrO_{2-x}

β + α
β
α

ZrO_{2}
modif.:
c=fcc
t=fct
m=mon.

ZrO_{2} at.%O wt.%O

Zirconium-Oxygen Phase Diagram*

T e m p e r a t u r e in °C

T e m p e r a t u r e in °C

Zr Zr

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26


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Phase diagram Zr - H

Sieverts’ law:

$$\frac{H}{Zr} = k_s \sqrt{p_{H_2}}$$

with

$$k_s = A e^{\frac{-B}{RT}}$$
Phase diagram iron - boron

Decrease of melting temperatures due to eutectic interactions

Temperature in °C

Fe

B in wt.%

B in at.%

Fe

FeB

Fe2B

δ-Fe

γ-Fe

α-Fe

7.2

~17

912 °C

1538 °C

1394 °C

1174 °C

1500 °C

1650 °C

1700 °C

2092 °C

1538 °C

912 °C

1174 °C

1394 °C

1500 °C

1650 °C

1700 °C

2092 °C
Basics – kinetics

\[ \frac{\Delta m}{S} = k_m(T) \cdot t^n \]

- For \( n=0.5 \): protective, parabolic
- For \( n=0.33 \): protective, cubic
- For \( n=1 \): non-protective, linear
- \( n=0.5 \rightarrow 1 \): breakaway
Oxidation of Zr alloys in various atmospheres

1200°C

Δm, %

Time, s

Air

H₂O

O₂

PO + Air

α-Zr + N₂

PO + N₂

N₂

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Nitride formation under local and global oxygen starvation conditions

**Local oxygen starvation:**
Formation and re-oxidation of nitride phase at metal-oxide phase boundary

**Global oxygen starvation:**
Pre-oxidation in steam and subsequent reaction in pure nitrogen

Nitride formation only in the absence of oxygen in the gas phase and in the presence of oxygen in the solid phase!
Reaction of $\alpha$-Zr(O) with nitrogen

1200 °C, 6.5 wt% O
Investigation of hydrogen source term and materials interactions during LOCA and early phase of severe accidents including reflood

- Separate-effects tests
- Bundle experiments
- PWR fuel element
**QUENCH Separate-effects tests: Main setups**

**Thermobalance**
- 1600 °C
- 1250 °C (steam)
- Specimens: 0-2 cm
- MS coupling

**BOX Facility**
- 1700 °C
- Oxidising, reducing atmosphere (incl. steam)
- Specimens: 1-2 cm
- MS coupling

**INRRO Facility**
- 1500°C
- Specimens: 1-2 cm
- Transparent for neutrons

**QUENCH-SR Rig**
- 2000 °C
- Induction heating
- Oxidising, reducing atmosphere (incl. steam)
- Specimens: 15 cm
- MS coupling

**LAVA Furnace**
- 2300 °C
- Induction heating
- Inert, reducing atmosphere
- Specimens: 1-2 cm
- MS coupling

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**Water storage**
**Liquid flow controller**
**Controlled evaporator mixer**
**Air lock**
**Specimen**
**Control center**
**Gas flow controllers**
**Gas supply system**
**TC**
**Mass spectrometer**
**Computer system**

**Gas inlet**
**Ar/O₂, N₂, air**

**Vacuum system**
**Specimen**
**High-temperature furnace**
**Gas inlet Ar/O₂, N₂, air**
**Analytical balance**

**ZrO₂ crucible**
**W crucible**
**ZrO₂ tube**
**quartz tube**

**Zr-4 melt specimen**
**ZrO₂ crucible**
**W crucible (susceptor)**

**Neutron beam**
**H₂O-cooling**
**Air lock**
**Sample**
**Neutron camera system**

**In-situ NeutronenRadiographie ReaktionsOfen**

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Core degradation - summary

Melting temperatures [°C]

- UO₂: 2850°C
- B₄C: 2450°C
- Zry 4: 1760°C
- SS: 1450°C
- AgInCd: 800°C

Late phase

Complete core degradation

Melting of UO₂, ZrO and (U, Zr)O₂

Severe core degradation

Melting of metallic Zry and α-Zr(O) causes UO₂-liquefaction

Local core degradation

Liquefaction due to eutectic interactions

Early phase

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