Corrosion issues in LWR : Other phenomena

D. Feron

FROM RESEARCH TO INDUSTRY

CORROSION ISSUES IN LWR

« OTHER PHENOMENA »

Nuclear corrosion sumer school | NuCoSS-15, Bled, Slovenia | July 5-10, 2015

Damien Féron, CEA/DEN/DPC/SCCME

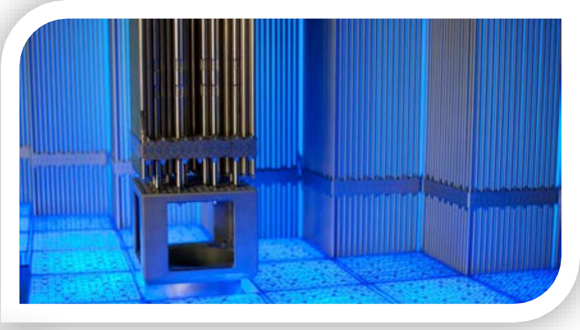
JULY 2015

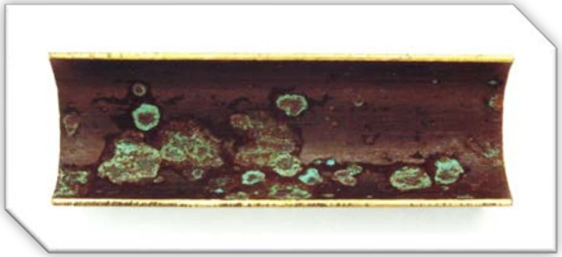
Content: EAC, FAC, MIC in LWrs have been discussed already. Are there some other phenomena of importance in these reactors?

Background

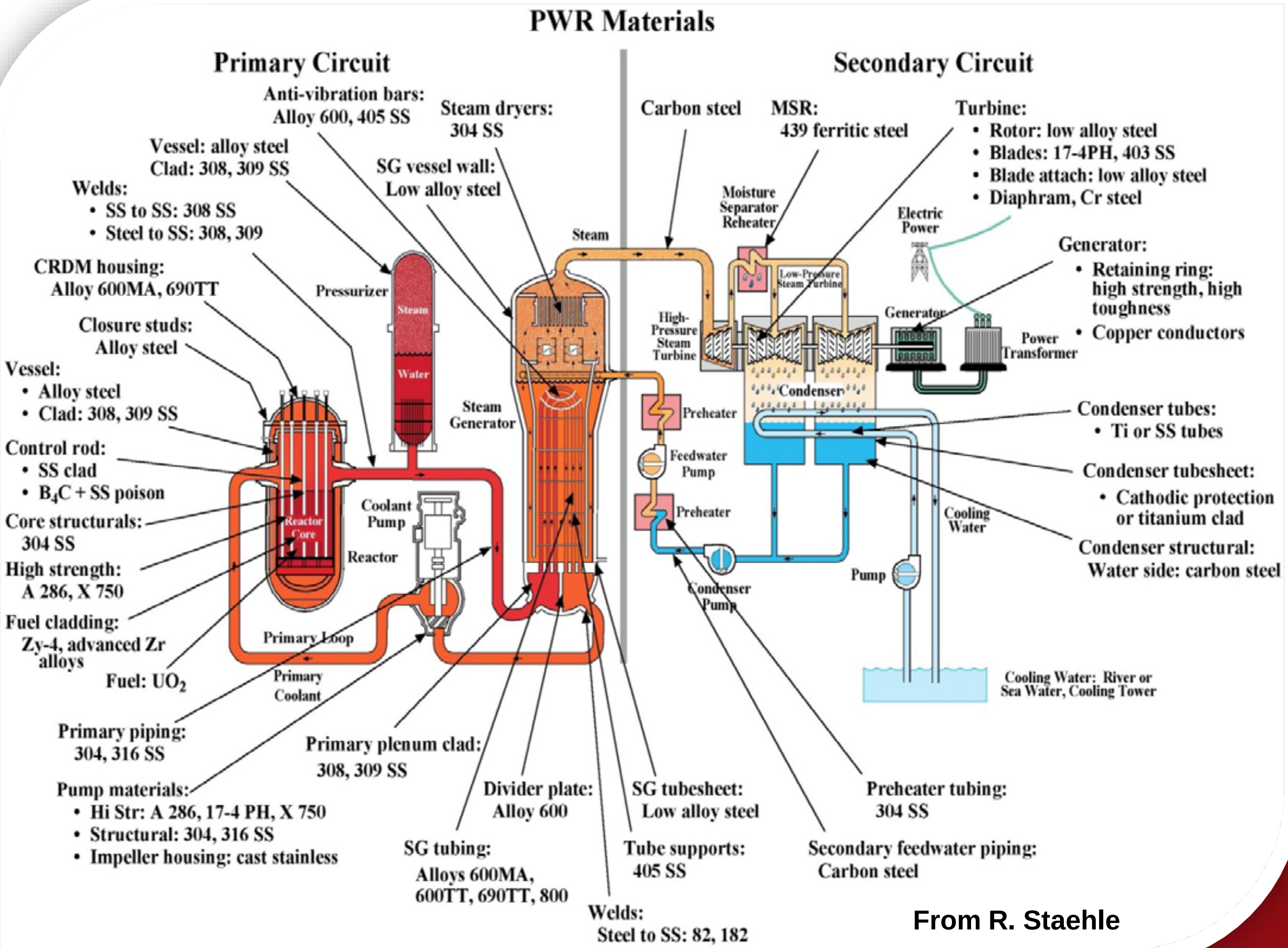
Cladding behavior

Concrete behaviour



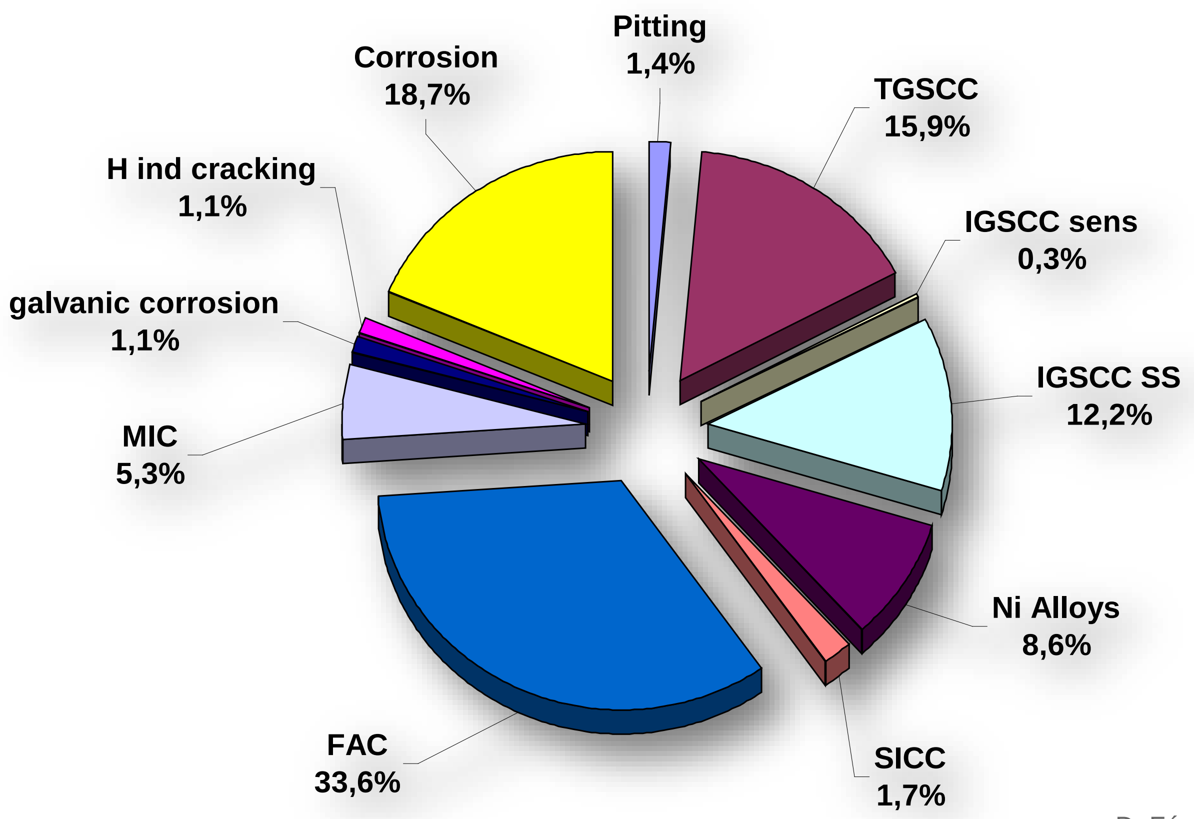


BACKGROUND

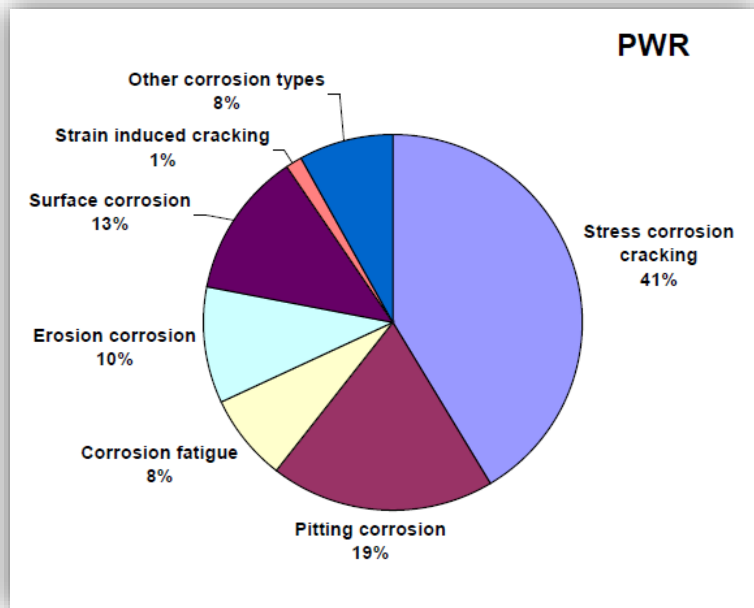


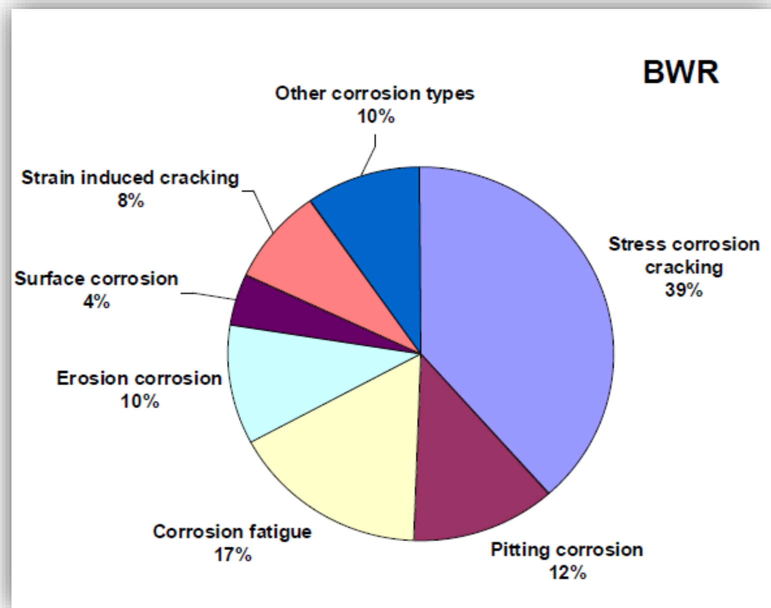
From R. Staehle

Evaluation of Worldwide Corrosion Events
Distribution of Corrosion Types
PWRs & BWRs (1995 – 2004)



From Renate Killian, Areva NP

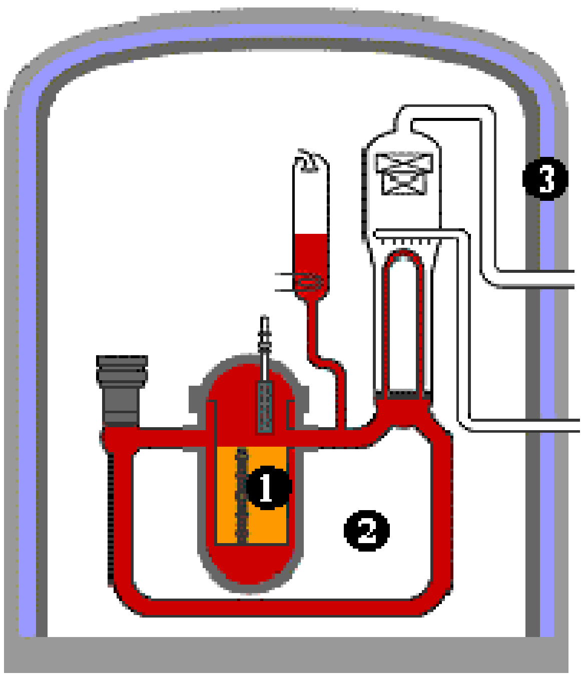




From H.-P. Berg, R&RATA #4, Vol. 2, 2009, December

Distribution of corrosion types in PWR and BWR plants in Germany (1968-2001)

SAFETY BARRIERS IN PWRS



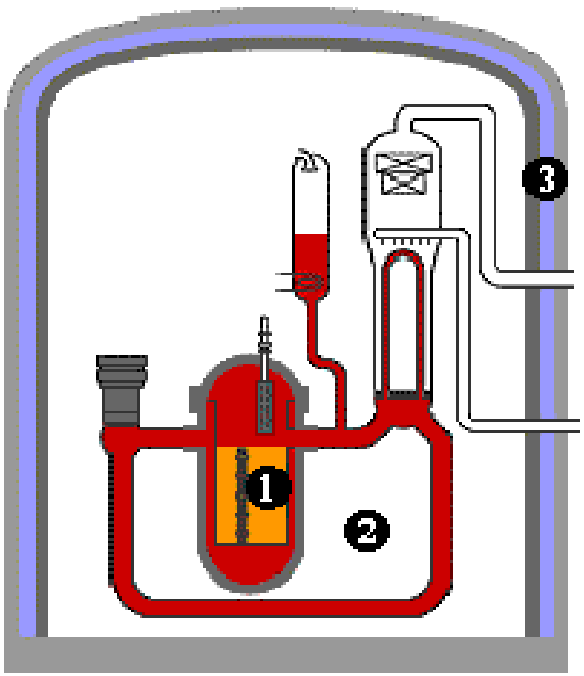
❶- **first barrier - fuel cladding** : the fuel, inside which most of the radioactive products are already trapped, is enclosed within a metal cladding;

❷- **second barrier – reactor coolant boundaries** : the reactor coolant system is enclosed within a pressurized metal envelope that includes the reactor vessel which houses the core containing the fuel rods;

❸ - **third barrier – reactor containment**: the reactor coolant system is itself enclosed in a thickwalled concrete containment building (for the EPR™ reactor, the containment is a double shell resting on a thick basemat, the inner wall being covered with a leak-tight metallic liner).

If one of the barriers is leaking, the reactor is stopped

CORROSION & SAFETY BARRIERS



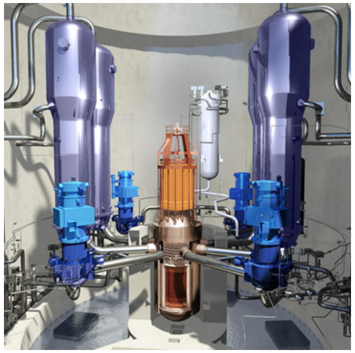
❶ - **fuel cladding** : zirconium alloys / limited residence time (3 years)
❷ - **reactor coolant boundaries** : pressure vessel (irradiation damages) but also pipes and steam generator tubes / life time of the plant (repairs except for the RPV)
❸ - **reactor containment**: concrete of the reactor building (life time duration and accidental situations)

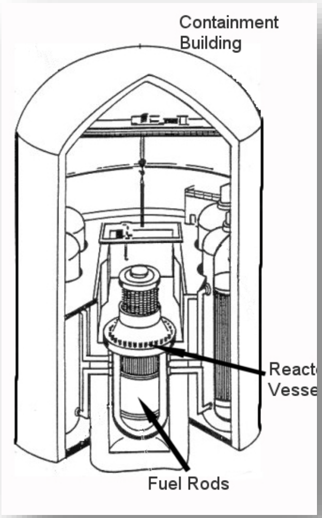
Maintaining the integrity and leak tightness of just one of these barriers is sufficient to contain radioactive fission products.

CORROSION PHENOMENA LINKED WITH SAFETY BARRIERS

Fuel cladding : **corrosion of zirconium alloys** limits the residence time of fuel materials

Reactor coolant boundaries : pressure vessel (irradiation damages) is limited by irradiation damages, while **stress corrosion cracking of the nickel base alloys tubes of the SG** limits the life time of steam generators





Reactor containment: concrete and reinforced concrete evolution (repairs possible)

FUEL CLADDING

CORROSION OF ZIRCONIUM ALLOYS

IN LWRS CONDITIONS

Few numbers

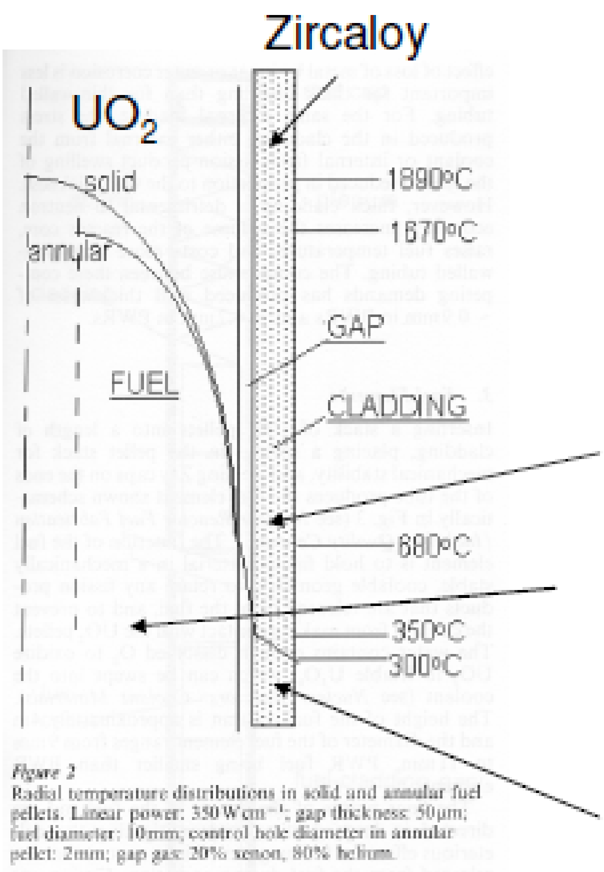


Figure 2
Radial temperature distributions in solid and annular fuel pellets. Linear power: 350 W cm^{-1}; gap thickness: 50μm; fuel diameter: 10mm; control hole diameter in annular pellet: 2mm; gap gas: 20% xenon, 80% helium.

Pressure vessel: 40-60 years operation, < 1 dpa

Fuel: 3-5 years in reactor

About 20-40 displacements per atom (dpa)

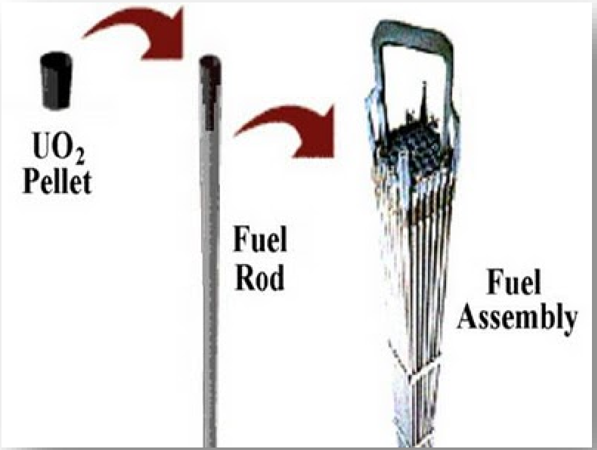
About 40,000 dpa, highly radioactive

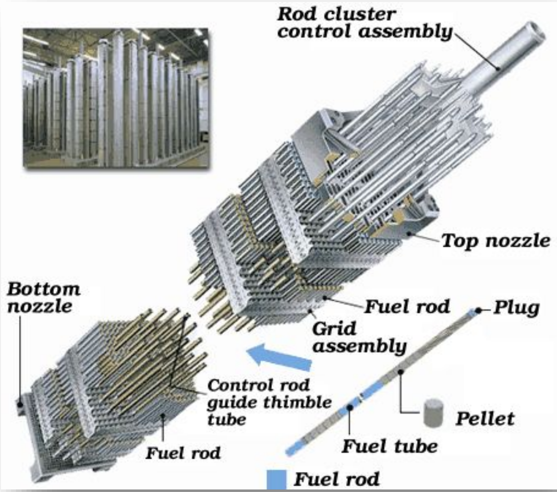
ZrO_2 oxide layer up to 120 micron and [H] content up to 700 wt ppm

From A. Motta

Operational conditions and challenges

- ❑ Chemistry: lithium /boron & hydrogen (Zn injection)
- ❑ Total residence time: 3 years increased to 5 years
- ❑ Burnup: from 30 GWd/t to 75-100 GWd/t
- ❑ Fuel cycles increased from 18 to 24 month cycle
- ❑ Evolution of the zircaloy alloy from Zircaloy4® to M5®





Bibliography IV

CLADDING MATERIALS & ENVIRONMENTS

Alloy	Zircaloy 2	Zircaloy 4	Zr- 1 Nb	Zr- 2.5 Nb
Sn %	1.2-1.7	1.2-1.7		
Nb %			1	2.4-2.8
Fe %	0.07-0.20	0.18-0.24		
Cr %	0.05-0.15	0.07-0.13		
Ni%	0.03-0.08			
O ppm	1200-1400	1200-1400	1200-1400	1200-1400
Co ppm	20	20	20	20
Hf ppm	100	100	100	100
U ppm	3.5	3.5	3.5	3.5
Application	LWR	LWR	LWR	LWR

Chemical composition of zirconium alloys used as cladding material

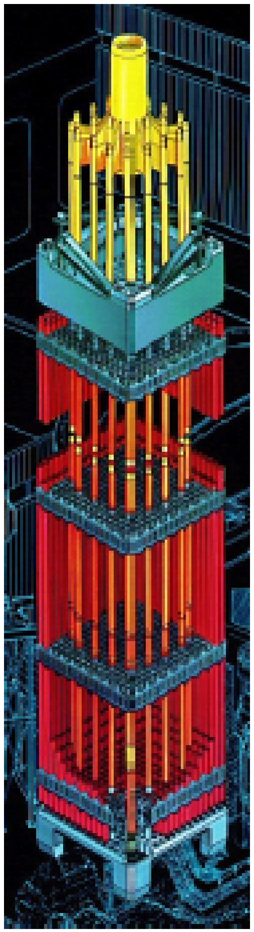
Bibliography I

Typical reactor environments to which zirconium alloys are exposed

	BWR	*PWR*	*VVER*	*CANDU*
Coolant	H_2O	H_2O	H_2O	D_2O
Inlet temperature (°C)	272–278	280–295	290	255
Outlet temperature (°C)	280–300	310–330	320	300
Pressure (MPa)	~7	~15	~15	~10
Neutron flux[a] ($n\,cm^{-2}\,s^{-1}$)	$4–7 \times 10^{13}$	$6–9 \times 10^{13}$	$5–7 \times 10^{13}$	2×10^{12}
Coolant chemistry				
$[O_2]$ (ppb)	~200	<0.05	< 0.1	<5
$[H_2]$ (ppm)	~0.03	2–5	–	0.5–1
pH	7	6.9–7.4		10.2–10.8
B (as H_3BO_3) (ppm)	–	0–2200	0–1400[16]	–
Li (as LiOH) (ppm)	–	0.5–5	0.05–0.6	1
Na (as NaOH) (ppm)	–	–	0.03–0.35	–
K (as KOH) (ppm)	–	–	5–20	–
NH_3 (ppm)	–	–	6–30	–

[a] $E > 1$ MeV.

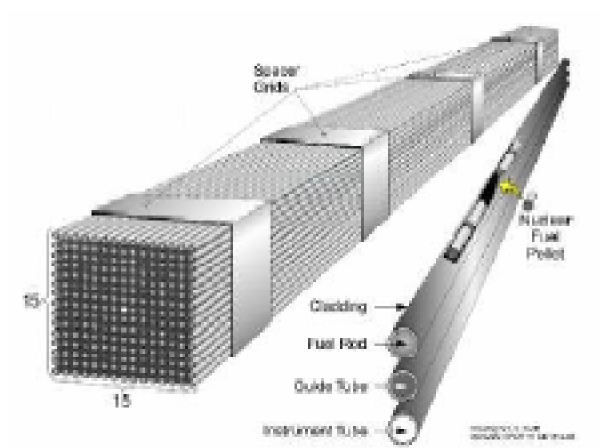
Ligth water reactor nuclear fuel cladding

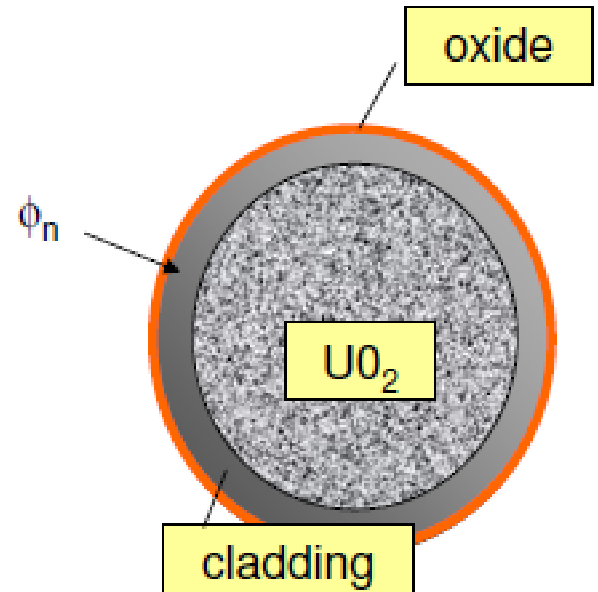


In reactor, Zr alloy cladding undergoes
- on the outersurface (water side)
  - General corrosion from primary water
  - Hydriding
- on the innersurface (oxide side)
  - Stress corrosion cracking (iodine)

Hydrogen Pickup

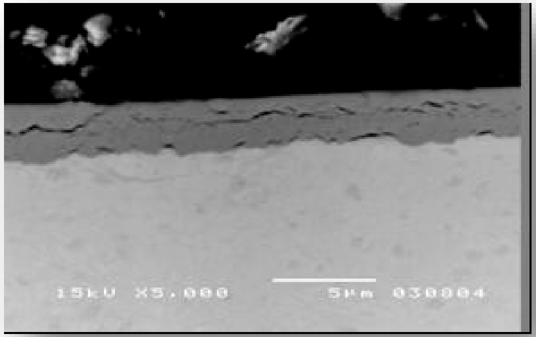
$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$$





From A. Motta

Generalised Corrosion of Zr alloys in LWR



Bibliography II

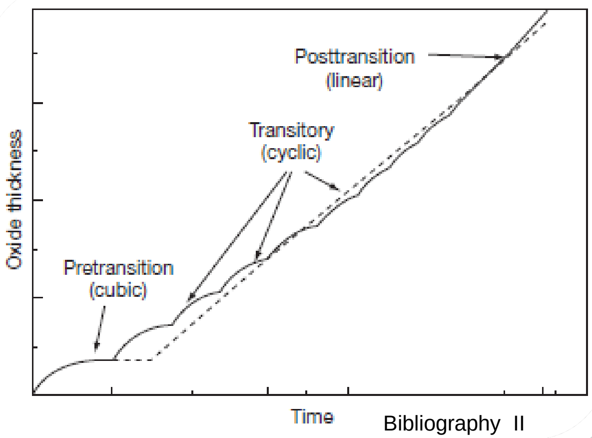
In primary water environments (water or steam), Zr alloy cladding undergoes corrosion according to:

$$Zr + 2H_2O \rightarrow ZrO_2 + 2(1\text{-}w)H_2 \text{ (coolant)} + 4wH_2\text{(metal)}$$

w= fraction of produced hydrogen absorbed by the metal

- **Progressive formation of a ZrO_2 layer**
- **Hydriding the cladding metal bulk**

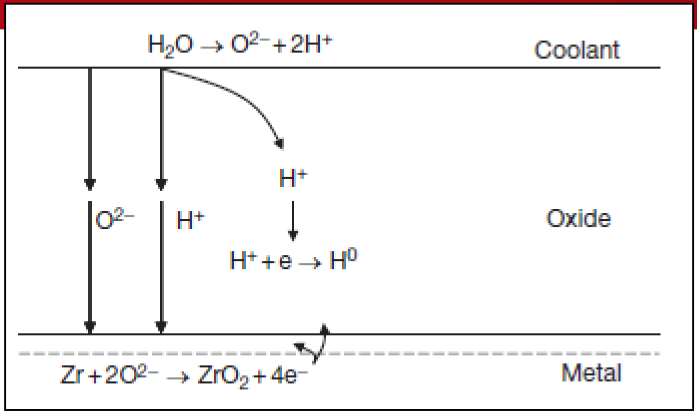
Uniform corrosion is the dominant mechanism observed in LWRs



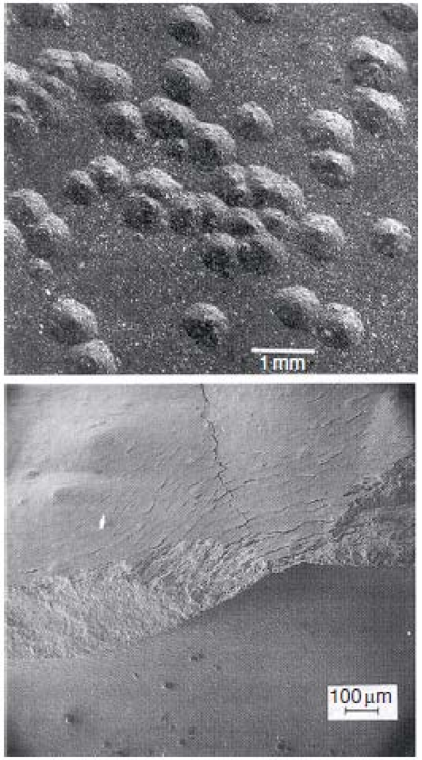
Bibliography II

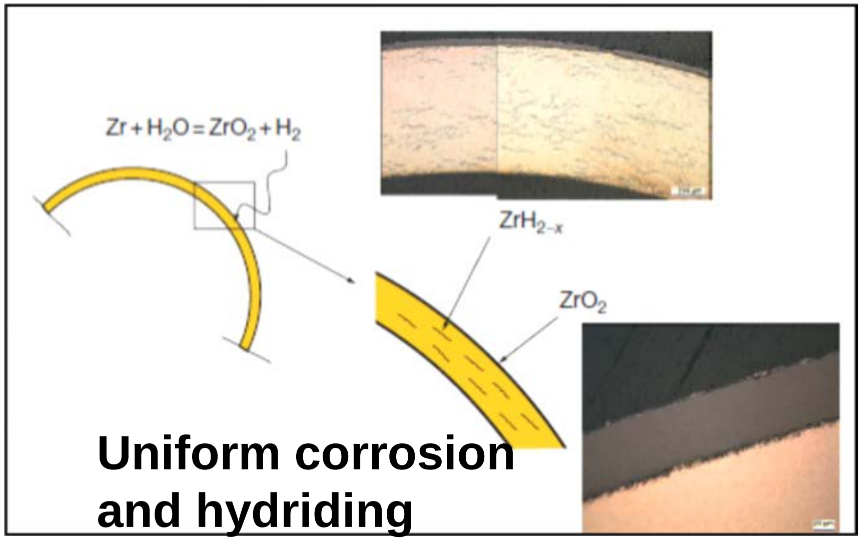
Schematic representation of the zirconium alloy corrosion showing the pretransition, the transitory and the postransitory regions

CORROSION OF ZR ALLOY CLADDING

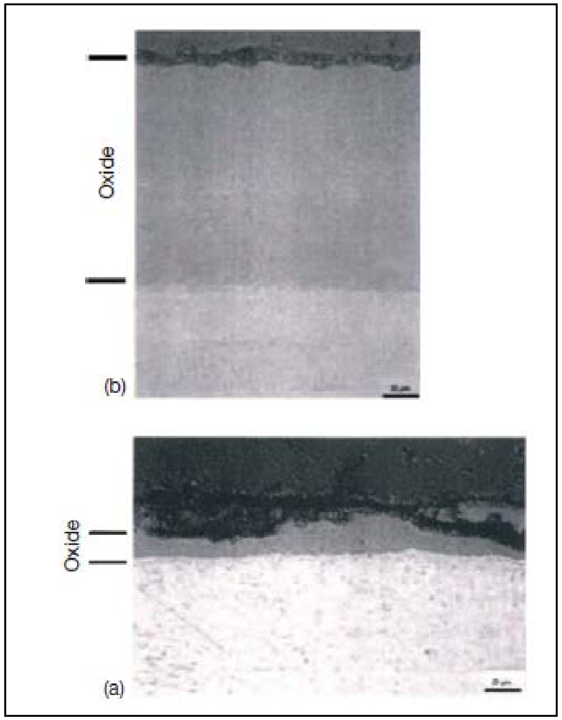


Schematic presentation of the general corrosion of zirconium alloys (uniform, nodular and shadow corrosions)





Uniform corrosion and hydriding

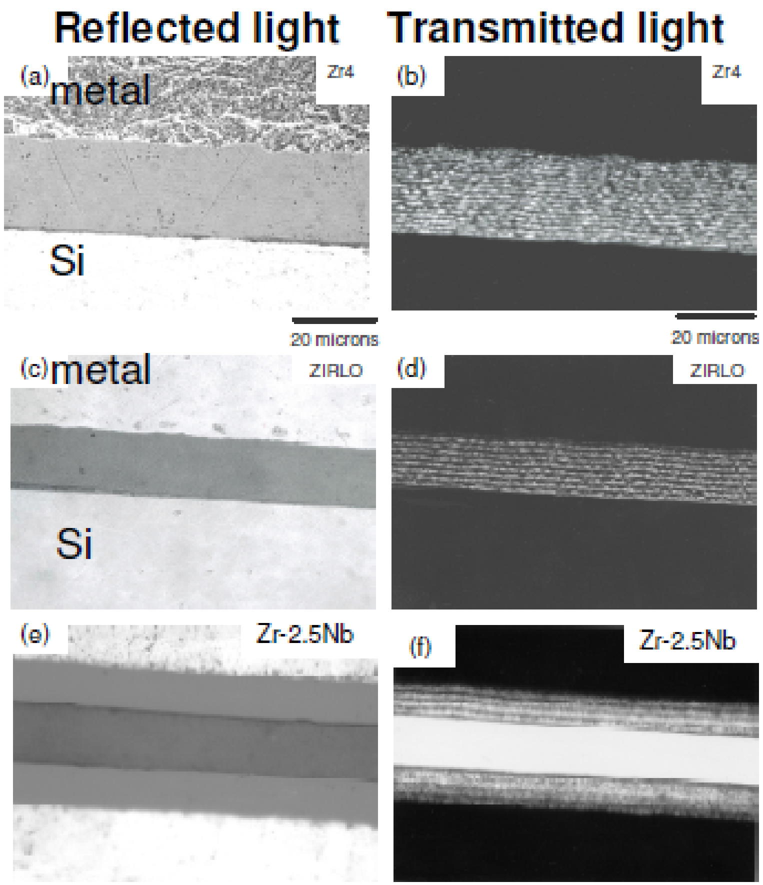


Bibliography II & bibliography IV

Shadow corrosion - BWRs
(b) Near stainless steel
(a) Away from SS

Nodular corrosion (oxygen, vapor – **BWRs**)

Transition thickness is characteristic of alloy, chemistry and very reproducible



From A. Motta

1.87 µm/period

2.13 µm/period

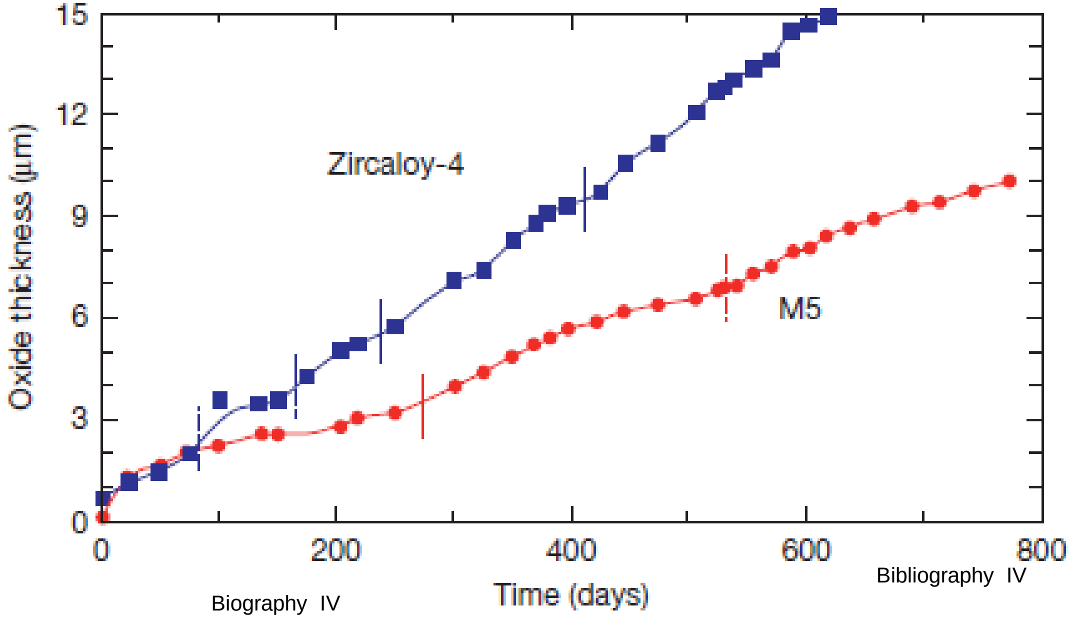
2.86 µm/period

Periodic structures observed

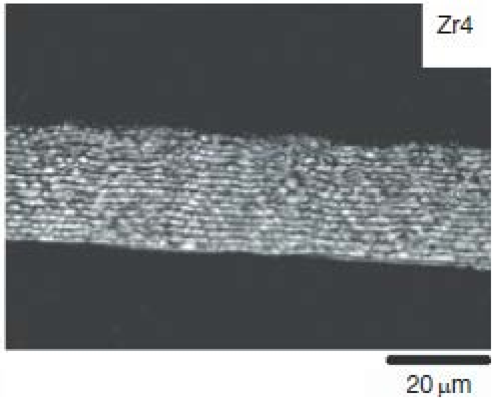
UNIFORM CORROSION OF ZIRCALOY

Oxidation rates of Zircaloy-4 and M5™

measured in primary water conditions by autoclave tests (at 360°C, with10 ppm of Li and 650 ppm of B in water). Cycles appear with transitions



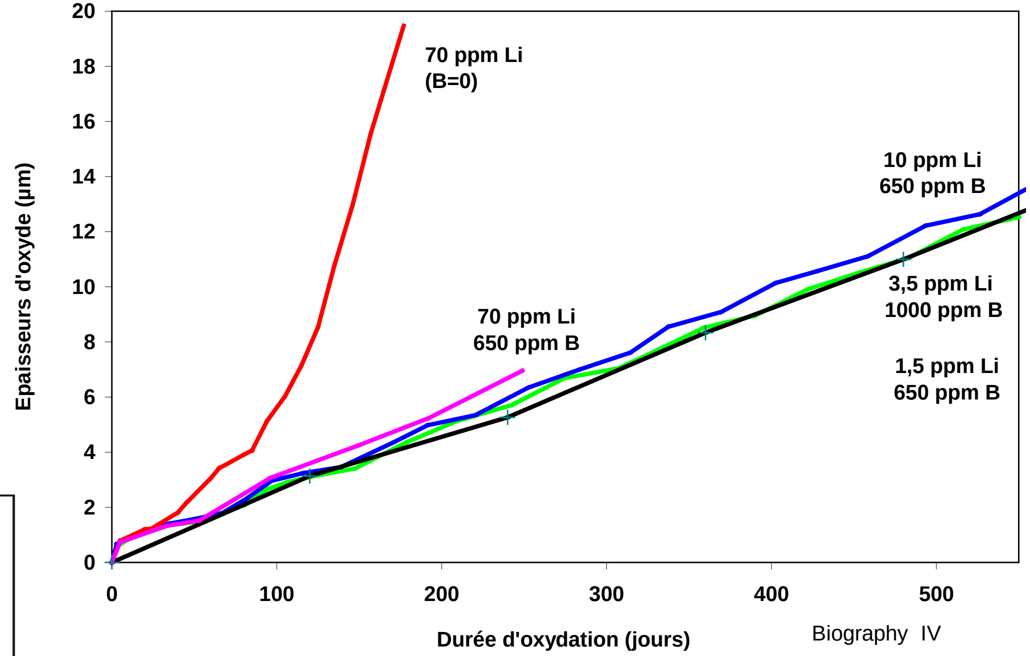
Biography IV

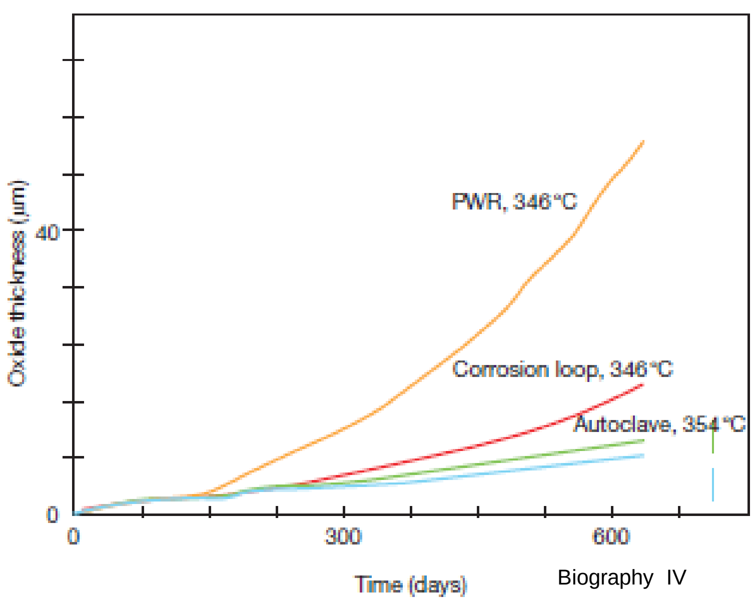


Bibliography IV

UNIFORM CORROSION OF ZIRCALOY

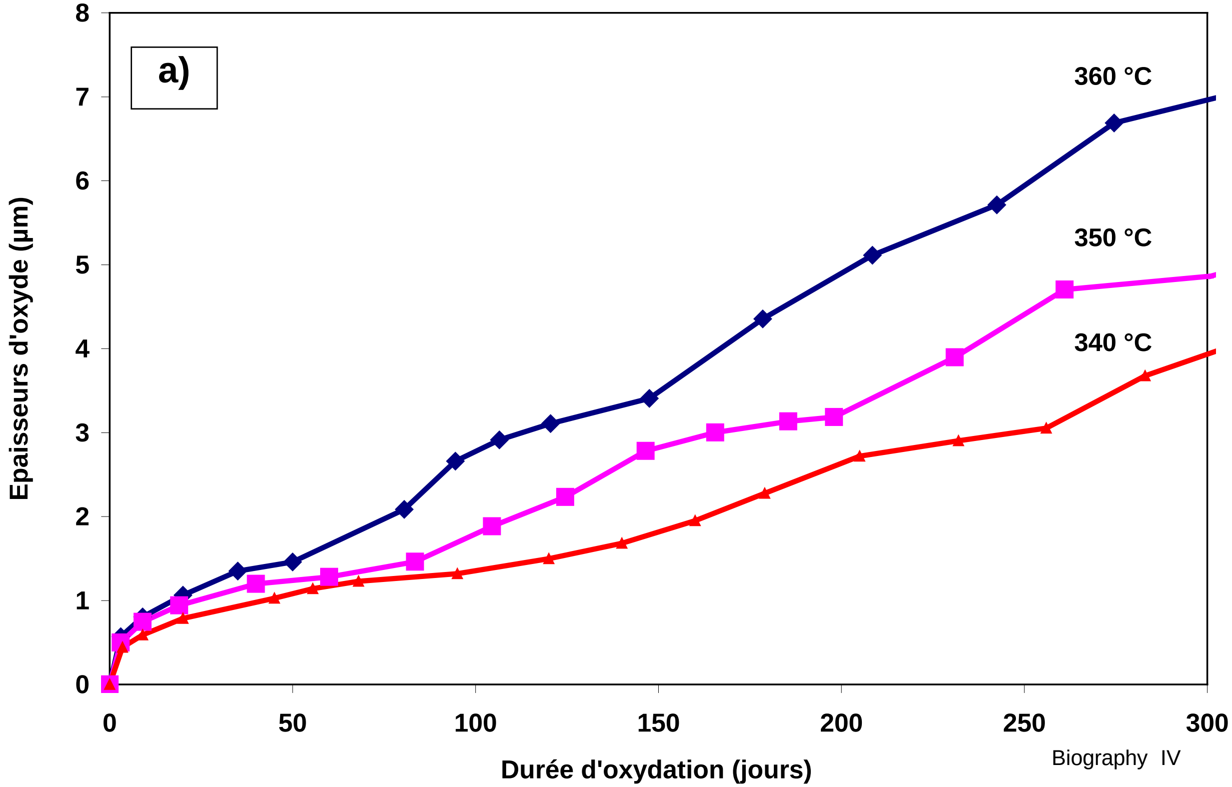
Influence of the chemistry (Lithium/boron) at 360°C
Influence of lithium - pH





Influence of the exposure conditions
(major influence of irradiation)

UNIFORM CORROSION OF ZIRCALOY

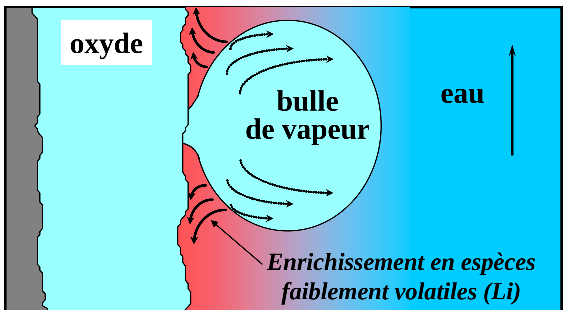


Temperature influence on the oxidation rate of Zyrcaloy-4 in primary water conditions

- Major influence of the temperature -

GENERAL CORROSION OF ZIRCALOY

Boiling on cladding
- Temperature increase
- Sequestration of non volatile species (Li)



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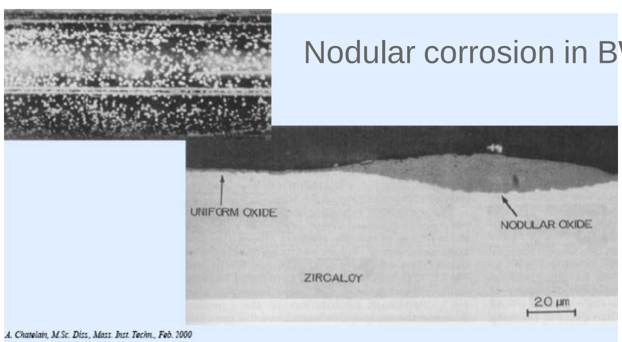
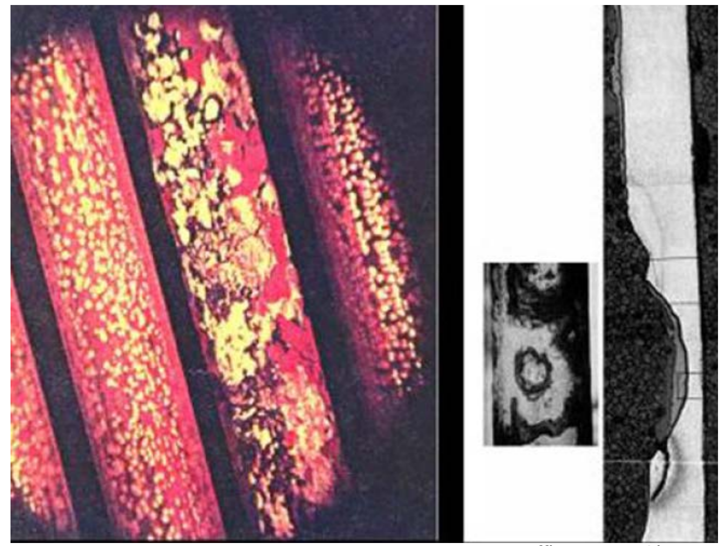


Nodular corrosion in BWR

Crud deposition on cladding
- Temperature increase
- Steam pockets


From P. Bouffioux & B. Cheng

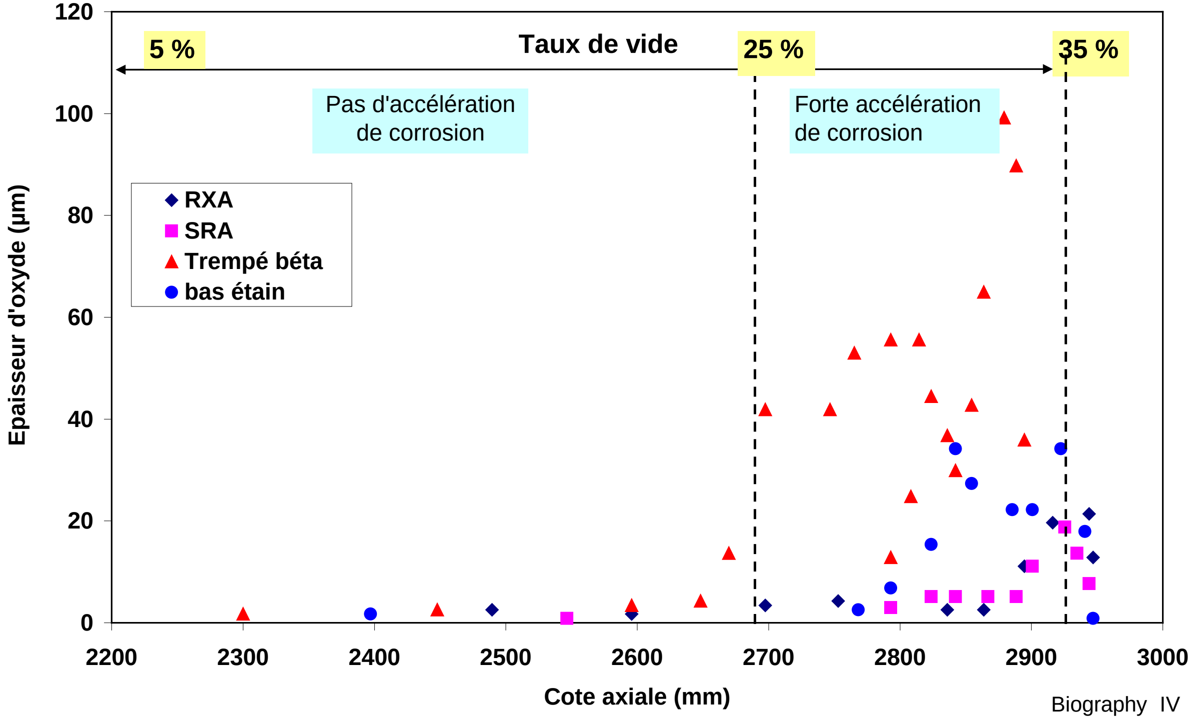
Cladding corrosion and crud deposits observed on BWR with brass condensers

Local increases of the temperature: one of the explanations of observed local degradations (nodular corrosion & Crud Induced Localized Corrosion – CILC)

GENERAL CORROSION OF ZIRCALOY

Axial profile of the oxide thickness measured along several claddings made of Zy4:

Important increase of the oxide thickness at the top of the fuel tubes where the temperature is the highest



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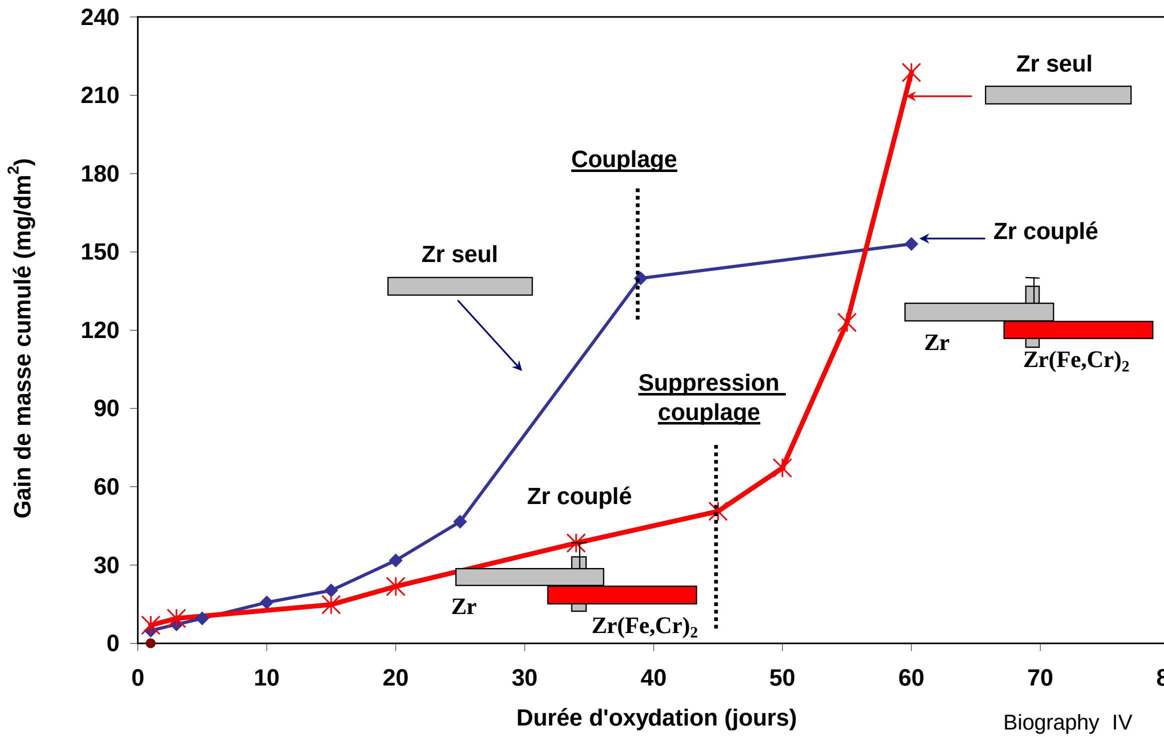
GALVANIC CORROSION OF ZIRCALOY

Galvanic corrosion / coupling effects
(at 360°C, with 10 ppm of Li and 650 ppm of B)

- *with no coupling, Zr oxidation rate is high*
- *Coupled to $Zr(Fe, Cr)_2$, Zr oxidation rates are lower*



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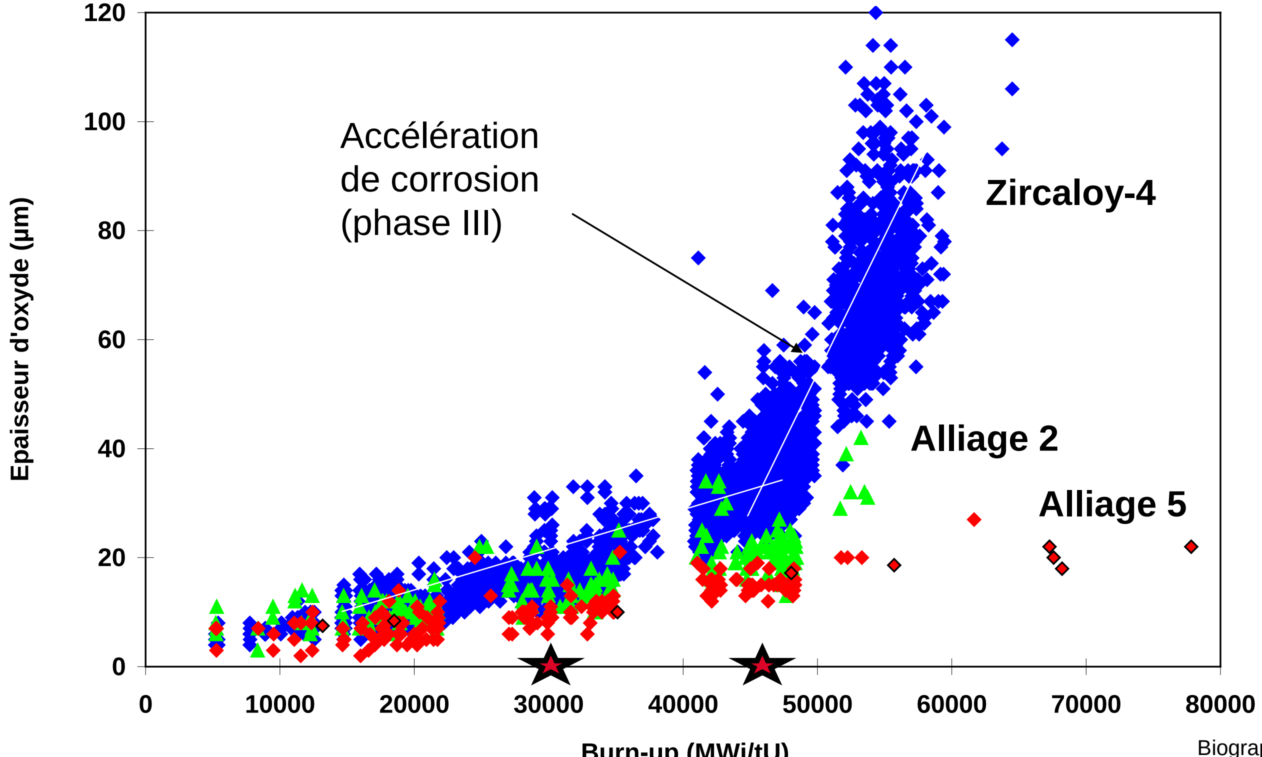
GENERAL CORROSION OF ZIRCALOY

Thickness of the oxide measured by Foucault currents, on site and in hot laboratories on claddings made of Zyrcaloy-4 (1.3 % Sn), M5^{TM} (alliage 5) and alliage 2 (0.5 % Sn)

Data obtained on French PWRs (Framatome and CEA data).



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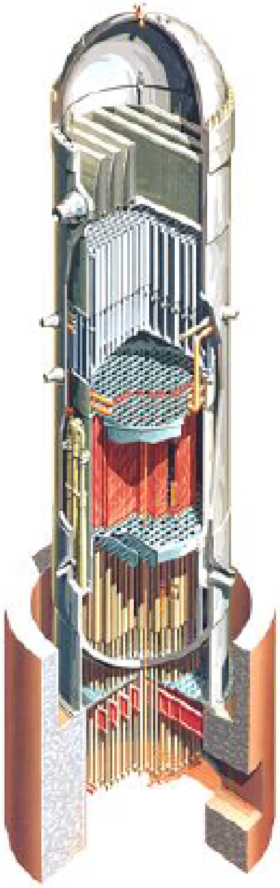
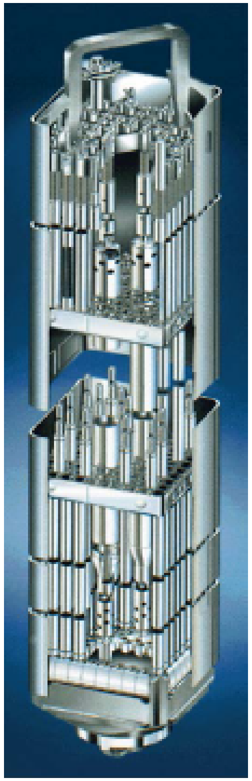
CORROSION OF ZR CLADDING

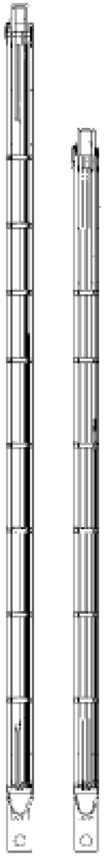
Shadow corrosion: specific to BWRs



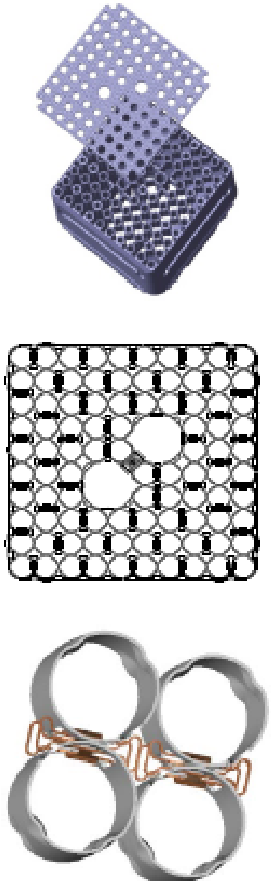
BWR 6



Fuel Bundle



Zircaloy fuel rods

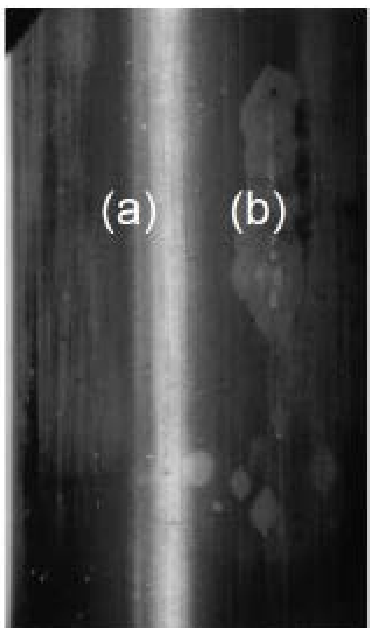


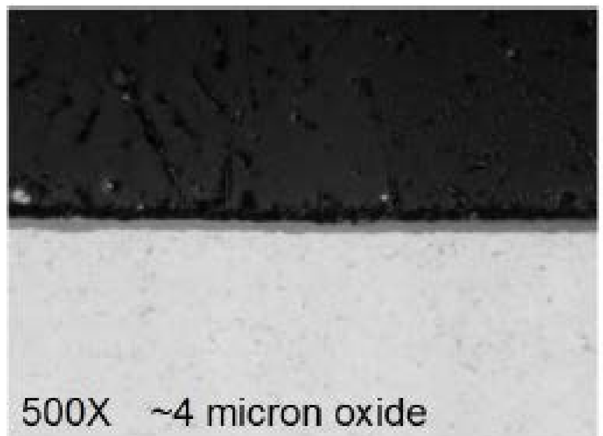
fuel rod spacers
(SS, Ni alloy)

(from Youg-Jim KIM & Ayljn Cukuc)

SHADOW CORROSION IN BWR

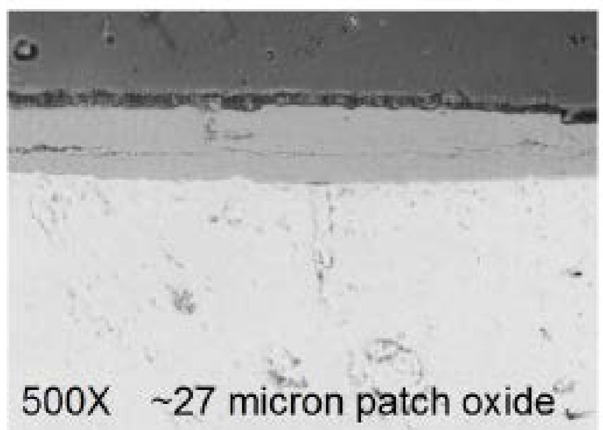
Shadow corrosion observed after in reactor service





Away from X-750 spacer

(a)



Beneath X-750 spacer

(b)

(from Youg-Jim KIM & Ayljn Cukuc)

BWR SHADOW CORROSION ON ZIRCALOY

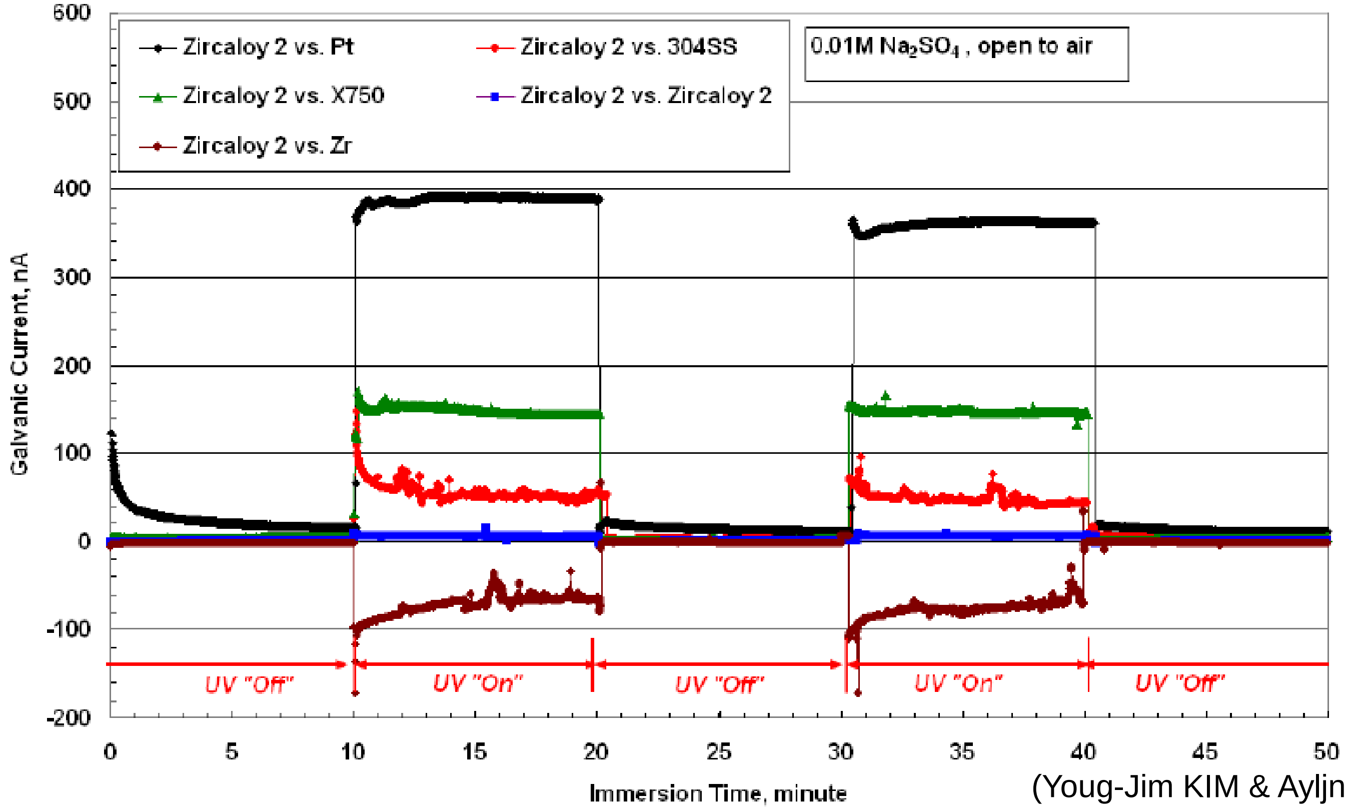
Main observations

- Ziracloy 2 surface adjacent to spacer (SS or Ni alloy)
- Thicker oxide in shadow
- No correlation with hydrogen pickup
- No shadow corrosion in PWR
- No shadow corrosion in lab.
- Radiation enhanced corrosion

Root causes

- Dissimilar alloys
- Contact not necessary
- Distance between two alloys
- Water chemistry (oygen)
- Radiation

Galvanic corrosion tests



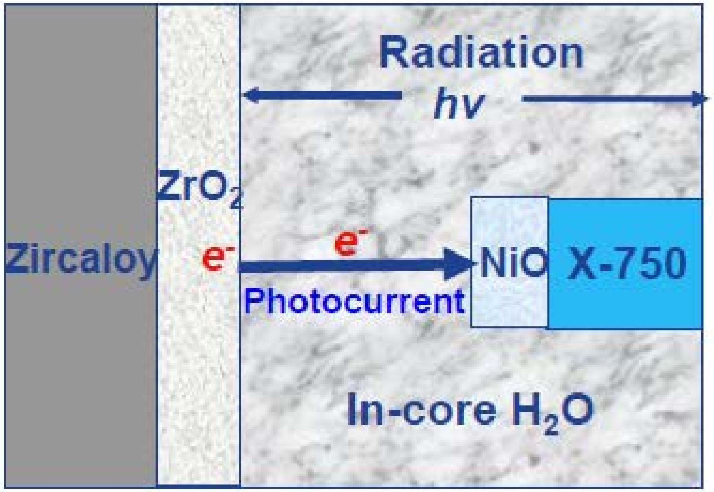
(Youg-Jim KIM & Ayljn Cukuc)

- UV « On »: positive current flow indicates the anodic dissolution of zircaloy 2
- UV is needed (radiation needed)

BWR SHADOW CORROSION ON ZIRCALOY

Mecanisms

- ***ZrO_2 (n-type film)***
  - The holes migrate to the surface, reacting with an donor state while the electron moves to the backside contact.
  - Anodic photocurrent
- ***NiO (p-type film)***
  - The electron migrates to the surface and reacts with oxidized chemical species in the electrolyte
  - Cathodic photocurrent



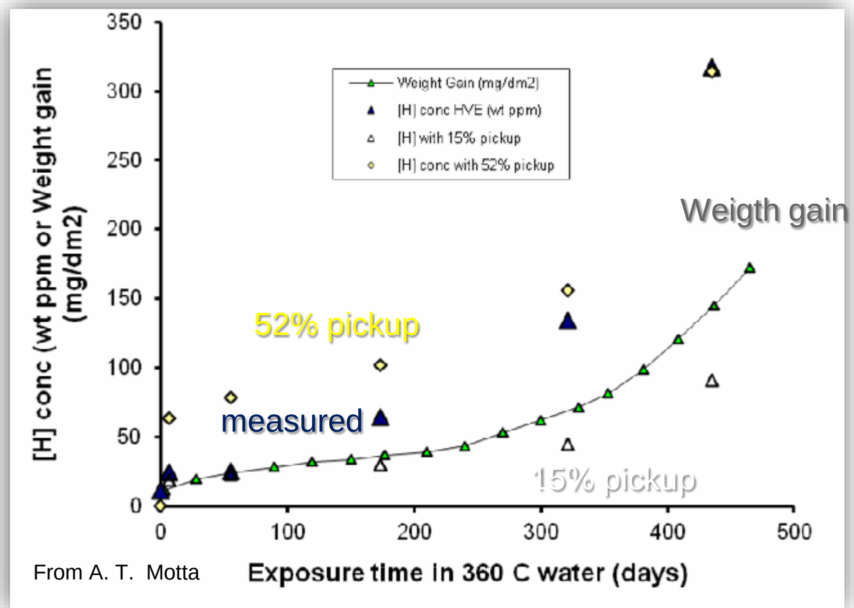
- **Zry2**: Low corrosion potential, anodic Dissolution, high corrosion rate
- **X-750**: High corrosion potential, cathodic reaction, low corrosion rate
- Electron transfer from Zry2 to X-750

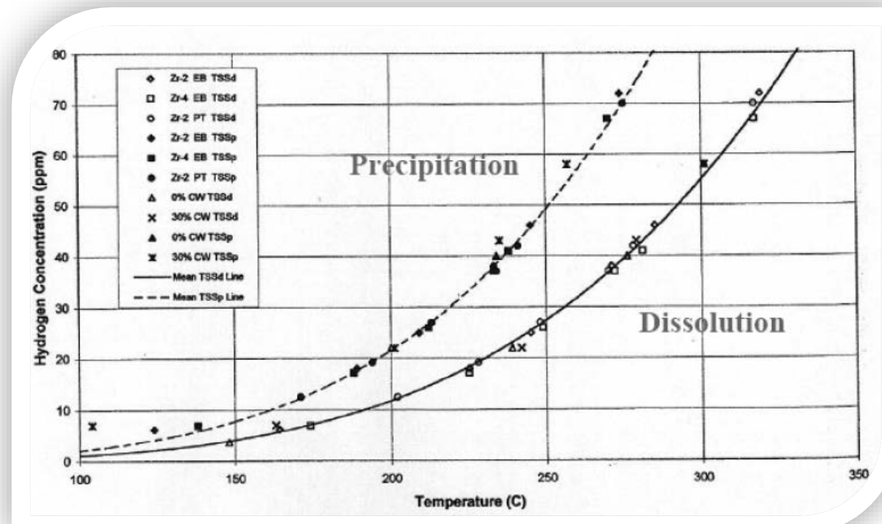
(Youg-Jim KIM & Ayljn Cukuc)

- **Galvanic corrosion**
- **Corrosion potential diffrence between the two alloys)**

HYDRIDING PHENOMENOLOGY

- The Zr alloy absorbs a fraction of hydrogen produced by the zirconium oxidation in primary environments (liquid water & steam
- The absorbed hydrogen precipitates as hydrides when the solubility limit is exceeded





From P. Bouffioux & B. Cheng

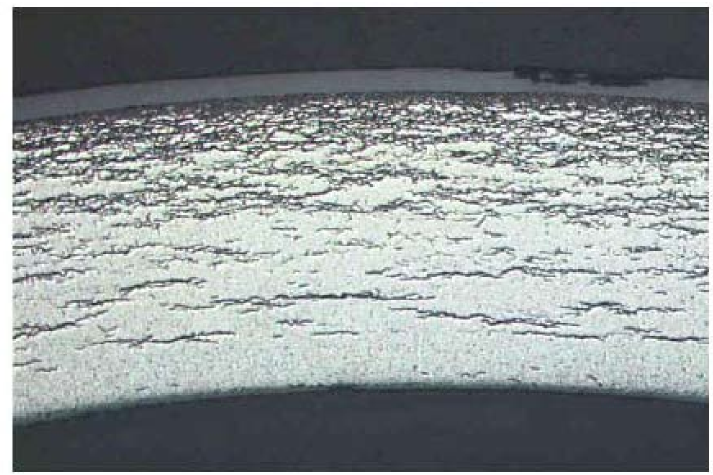
Hydrogen pickup fraction
(correlated to the oxide layer thickness)

Hydrogen precipitation and dissolution of Zr hydrites

HYDRIDE MORPHOLOGY

Zr hydride are formed over the whole cladding thickness

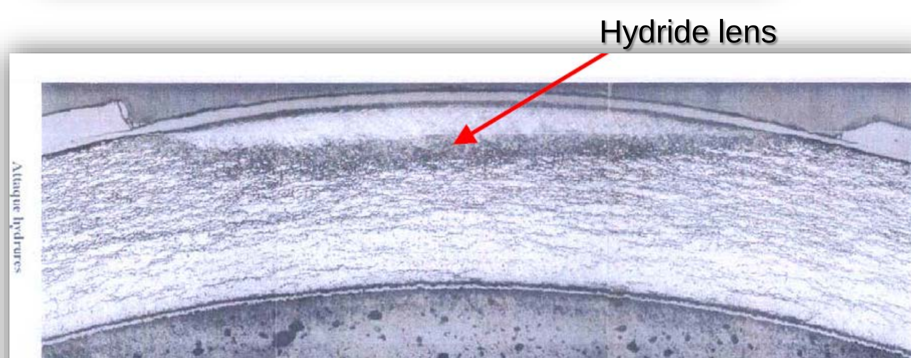
- In PWR with high burnup: a hydride rim (30-60 µm) is observed close to the colder outer surface (oxide thickness > 50µm)



From P. Bouffioux & B. Cheng

PWR – CWSR Zy4 - ZrO_2 > 50 μm

- If oxide layer delaminates, the outer surface will be colder (better cooling) and hydrogen precipitates to form hydride lens

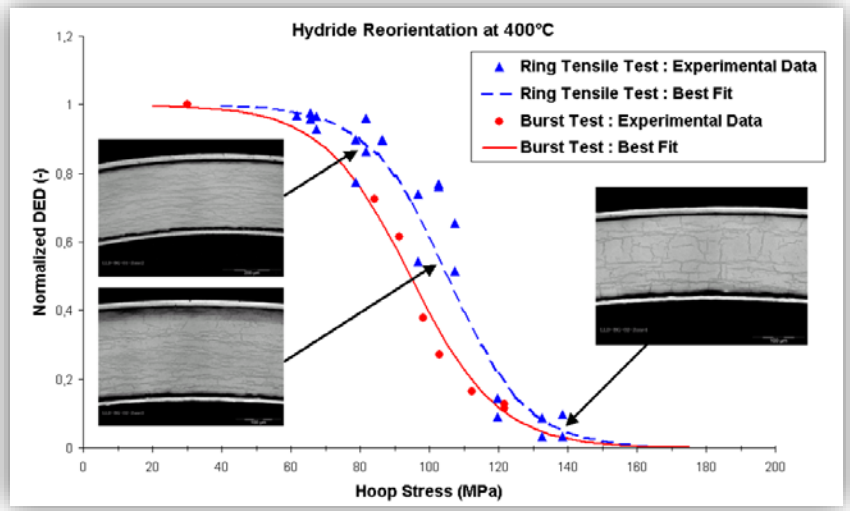


From P. Bouffioux & B. Cheng

HYDRIDE IMPACTS

- Crack initiates in the rim or lens and propagates (high burnups with Zircaly 4)
- Ductility is reduced
- Delayed hydride cracking (DHC - phenomenon occurs at lower temperatures, for instance during dry storage / crack initiation under reactor operation and crack propagation at lower temperatures)
- Hydride reorientation (HRO) occurs when tensile hoop stress are generated by internal pressure (during cooled down often) and results in a ductile cracking

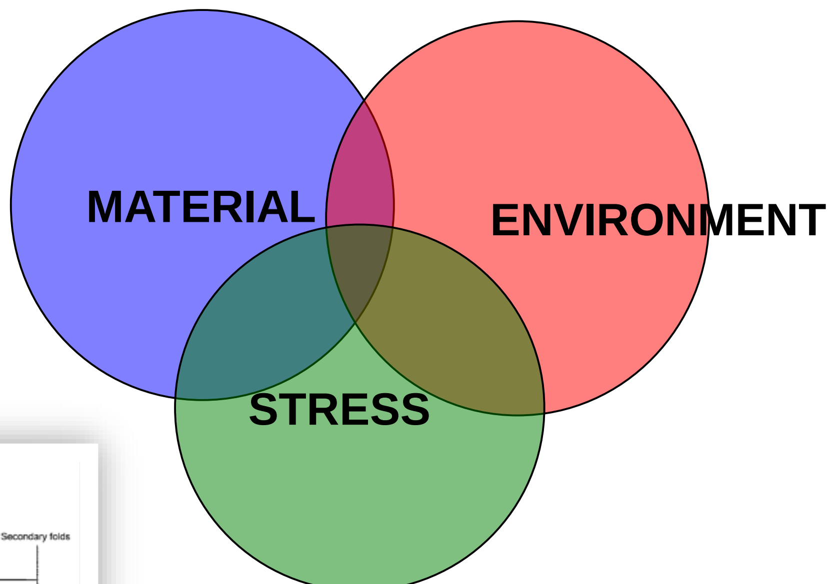
Ductile (1) to brittle (0) transition as function of the hoop tress

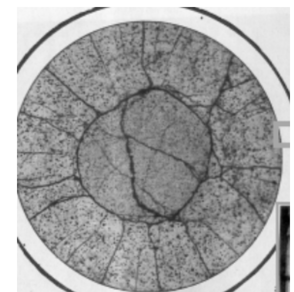


From P. Bouffioux & B. Cheng

Stress corrosion cracking of phenomena of zirconium cladding
Internal surface of the fuel tube

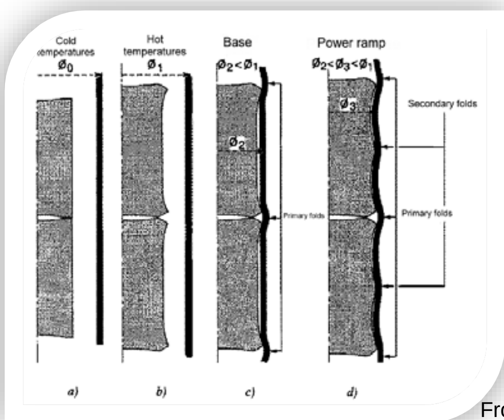
Sensitive materials:
Zr alloys (hydrides)





Bibliography IV

Chemical aggressive environment: release of fission products like Iodine (cracks in the pellets often due to rapid thermal transiants)

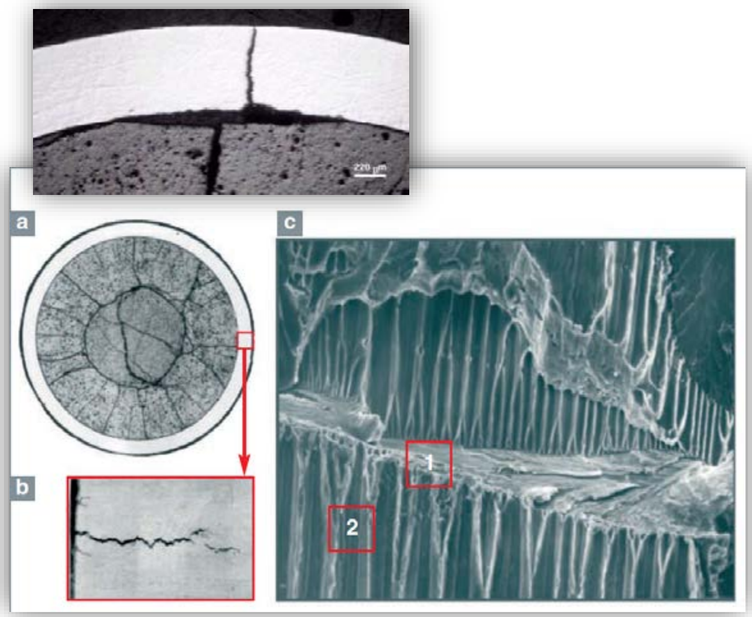


From P. Bouffioux & B. Cheng

Initially, compressive stress.
Tensile conditions due to the pellet swelling

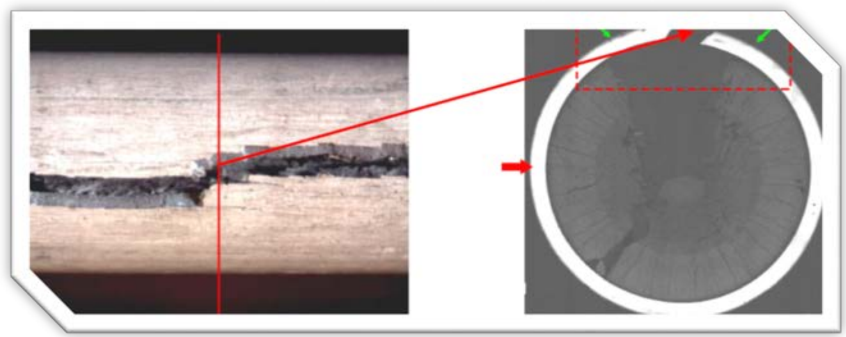
PELLET & CLAD INTERACTIONS MORPHOLOGY

Stress corrosion cracking of phenomena of zirconium cladding Internal surface of the fuel tube



Bibliography IV

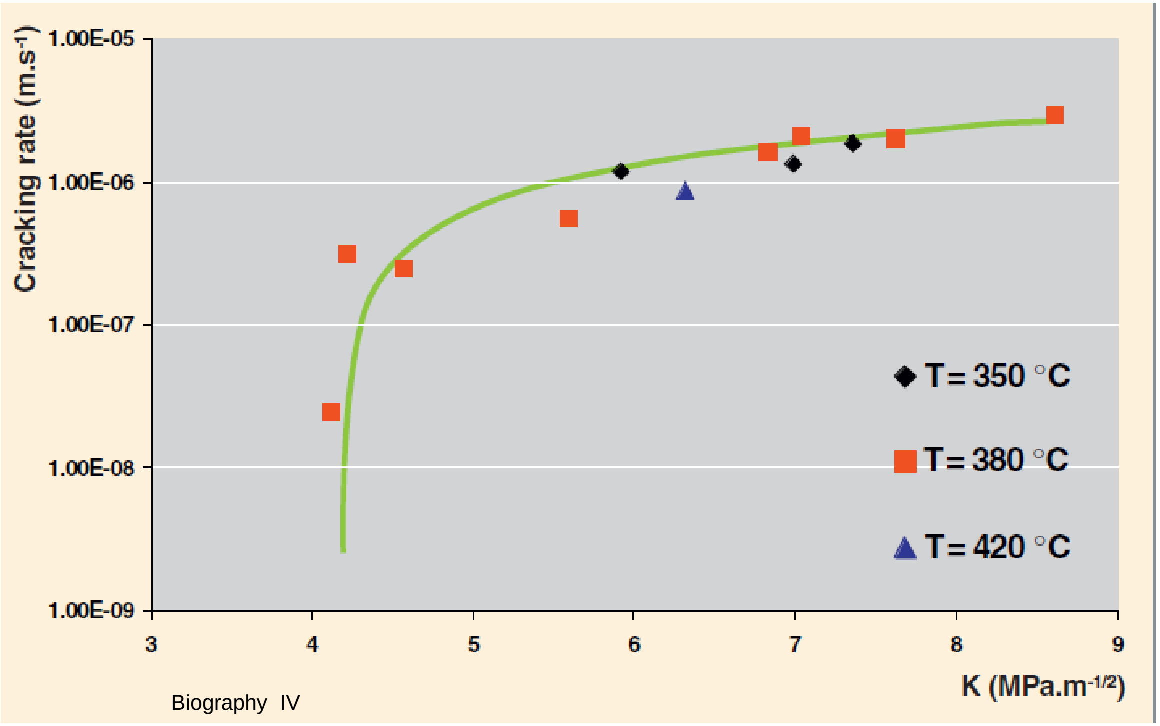
Stress corrosion cracking of clad during a power transient
a & b: during a power variation in test reactor
c: in presence of iodine during a laboratory test



From P. Bouffioux & B. Cheng

With hydrides, significant crack lengths may be observed

STRESS CORROSION CRACKING OF ZR
STRESS EFFECTS



Crack propagation rate as function of the initial stress intensity factor and for 3 temperatures
SCC-I / Zircaloy-4

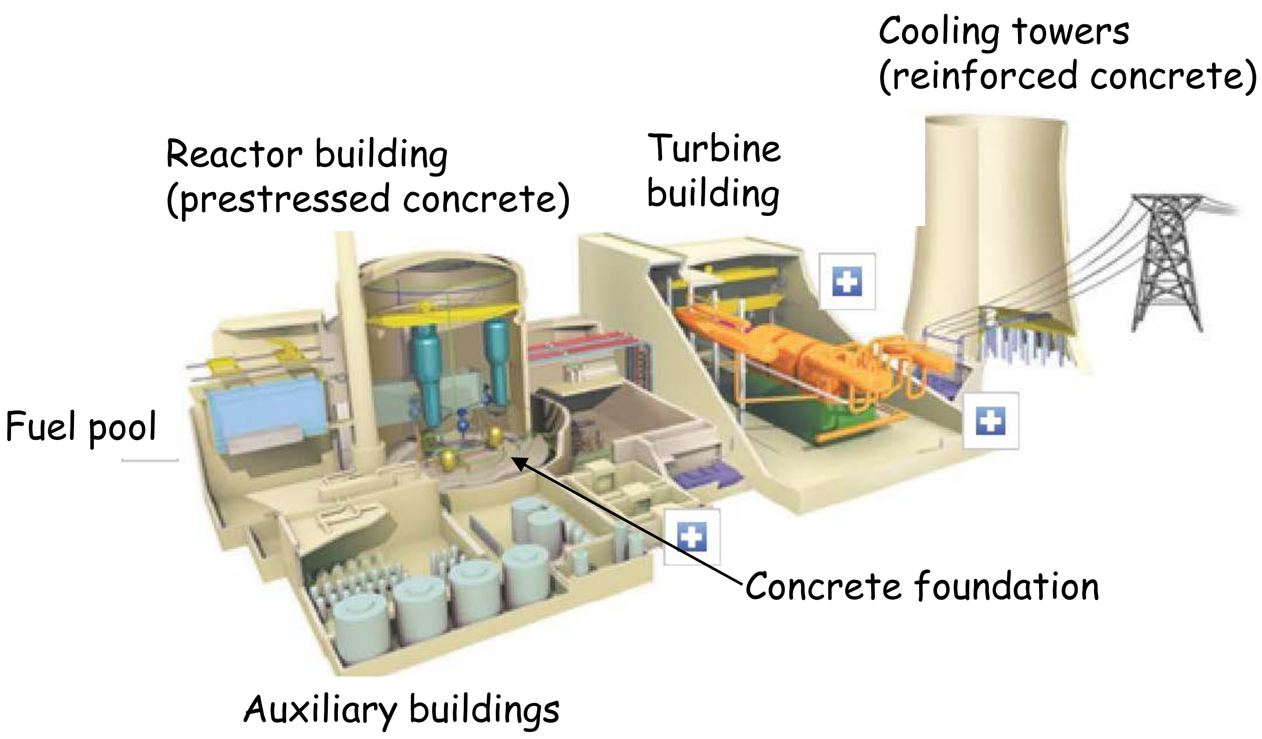
Summary

- Zr alloys are commonly used with success as material for cladding of fiuel rods in LWRs
- Internal and external surfaces are subject to corrosion phenomena
- In contact with primary water (liquid or vapor),
  - uniform corrosion occurs with the formation of an oxide ZrO2 layer with cycles and hydrogen pickup
  - Nodular and underdeposit corrosion is characteristic of BWRs
- Hydriding leads to cladding embrittlement
- Fretting and irradiation damages are also important degradation modes
- New products are developed to increase the burnup
- New investigations on accidental conditions (LOCA, ….)

CONCRETE DEGRADATION

CORROSION OF REBARS

CONCRETE & NPP



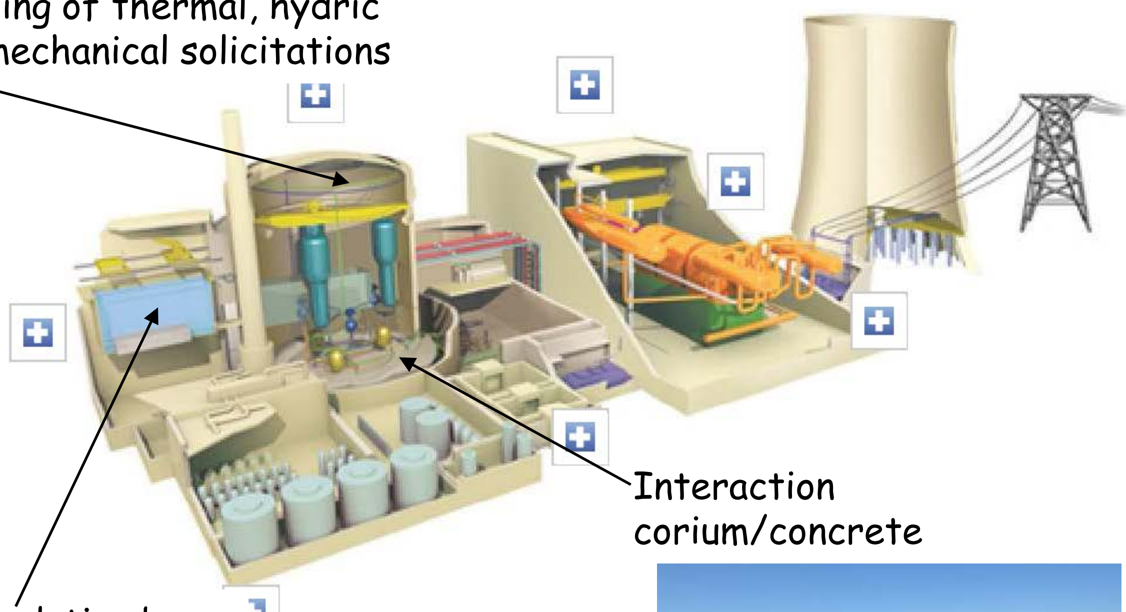
PWR 900 MWe

Dampierre NPPs

CONCRETE SOLICITATIONS IN NPP

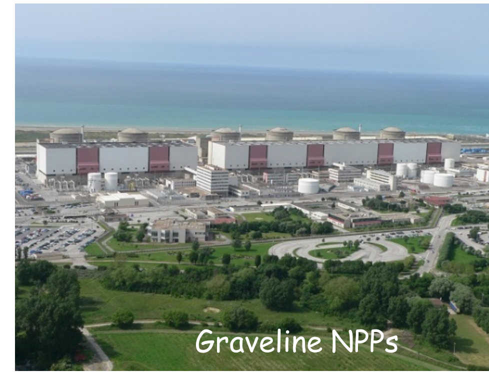
Concrete carbonation and corrosion of rebars

Coupling of thermal, hydric and mechanical solicitations



Interaction corium/concrete

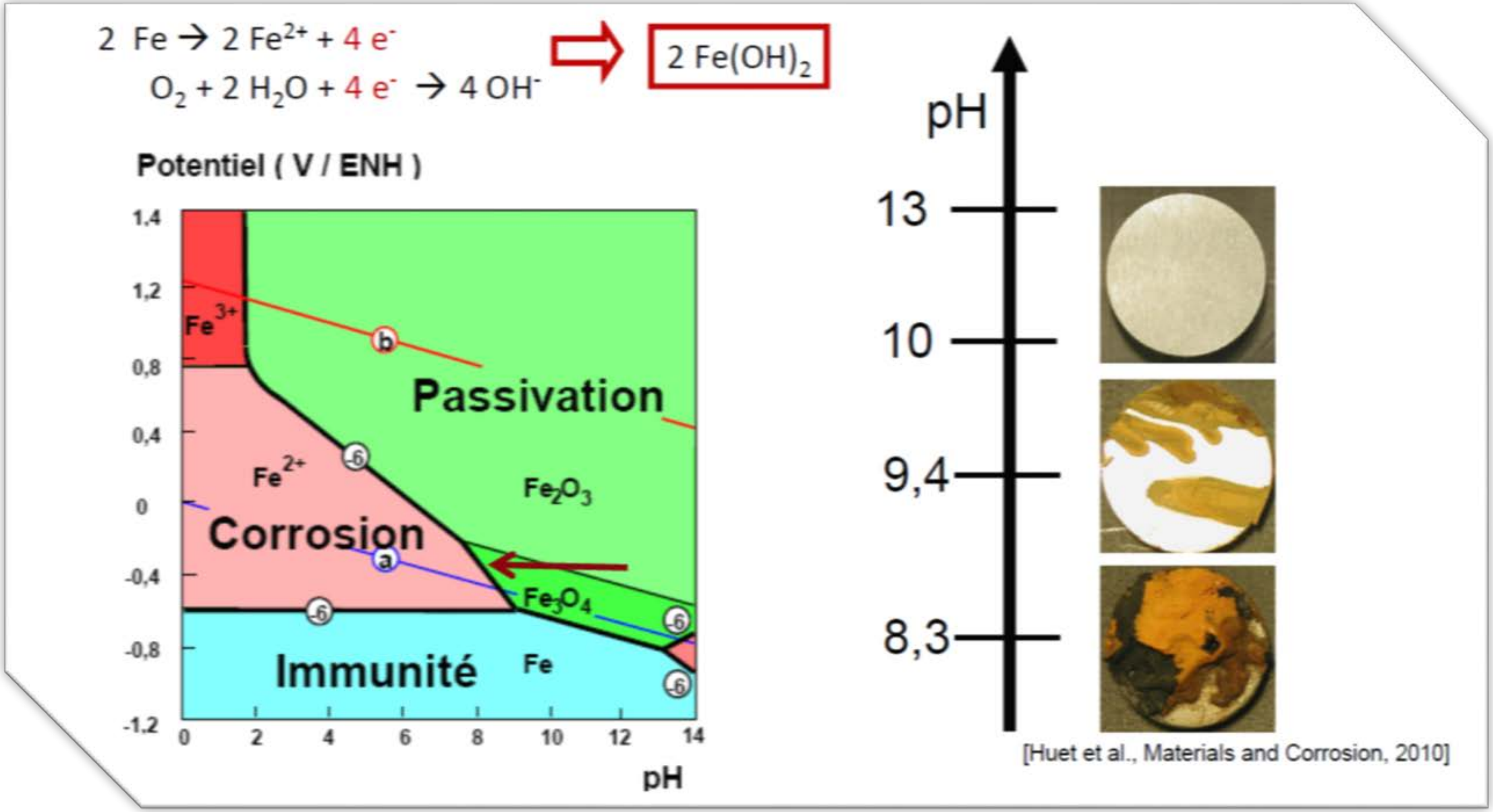
Degradation by boric acid



For seacoast NPPs: chloride corrosion

BEHAVIOR OF CARBON STEEL IN CONCRETE

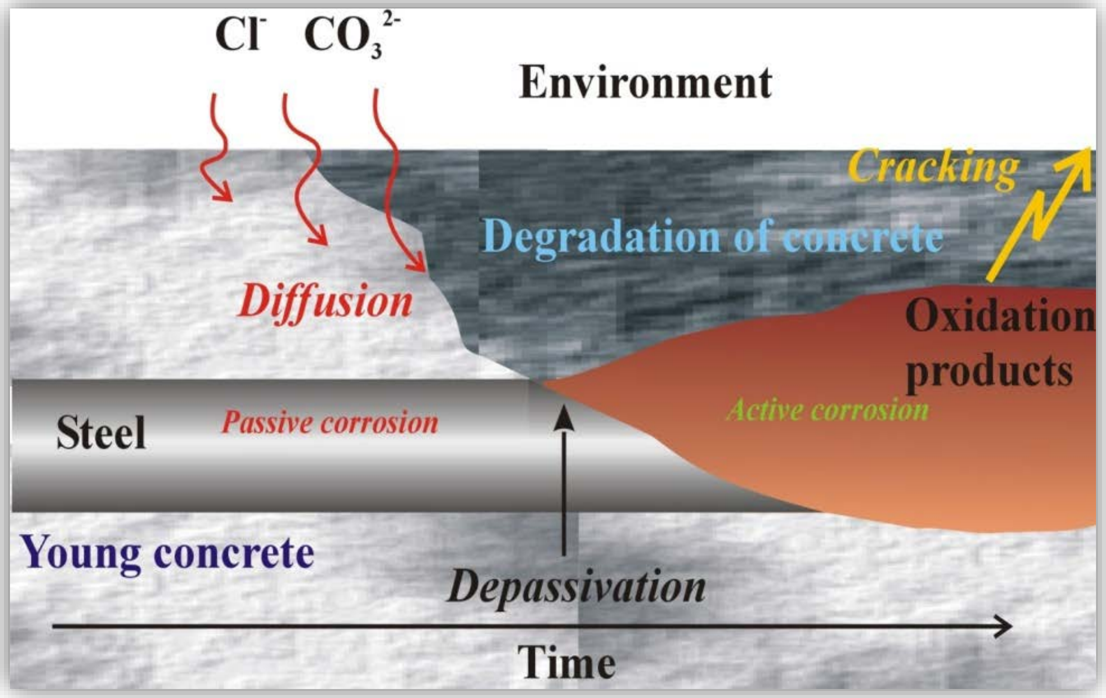
- In new concrete, pH is around 13 and the steel is passive
- With time, concrete minerals react with carbonic gas and pH decreases



[Huet et al., Materials and Corrosion, 2010]

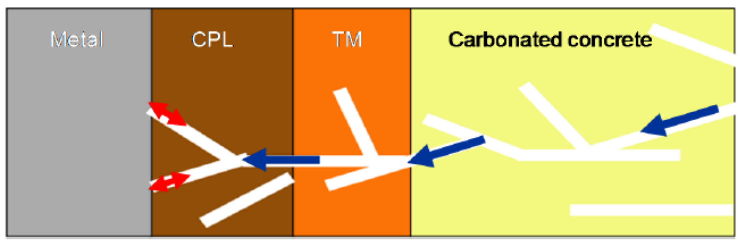
REBAR CORROSION

- Reaction with CO_2 leads to pH decreases
- Depassivation occurs as function of pH and pollutants like chlorides
- Expansive corrosion products
- Cracking of the concrete



From V. L'hostis & al.

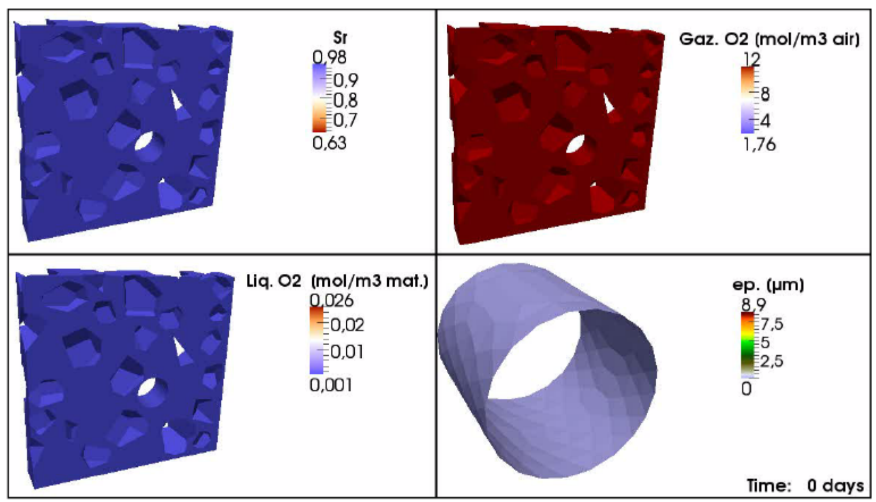
Mechanical modelling coupled with chemical evolution simulation (carbonatation), oxygen transport and corrosion



CPL : Corrosion Products Layer
TM : Transformed Medium

$$O_2\,\mathrm{Re}\,d(m,t)=\frac{4}{3}\,\frac{M(F_e)}{\rho(F_e)}\,k\;\varphi\,S_r(m,t)\,C_{O_2}(m,t)$$

$$\frac{\partial C_{O_2}}{\partial t}-D_{O_2}(S_r)\Delta C_{O_2}=\quad 0$$



T. de Larrard, B. Bary, E. Adam, F. Kloss, Microdurability, April 11-13, Amsterdam, Holland, 2012.

CORROSION OF THE COOLING TOWERS

First major consequence: loss of ductility needed under extreme conditions (storm)

Chinon

Belleville

From Dan J. Naus, AMP2010, Toronto, Canada

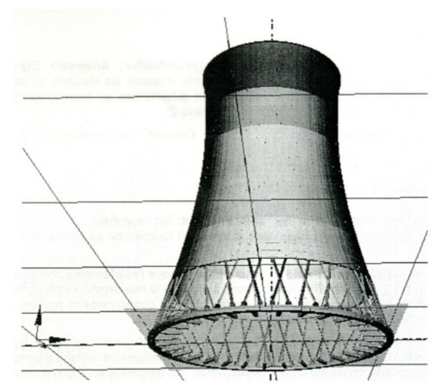


Fig 17. Vue 3D de la tour de Cattenom 2 (coque + supportage)

REBAR CORROSION

Pier(s) in the Mexico gulf (Progreso, Yucatan)

The two piers (1,2 km) have been built with reinforced concrete without maintenance up to around 2000….

Difference ?

THE MAIN TYPES OF DETERIORATION OF COMPONENTS

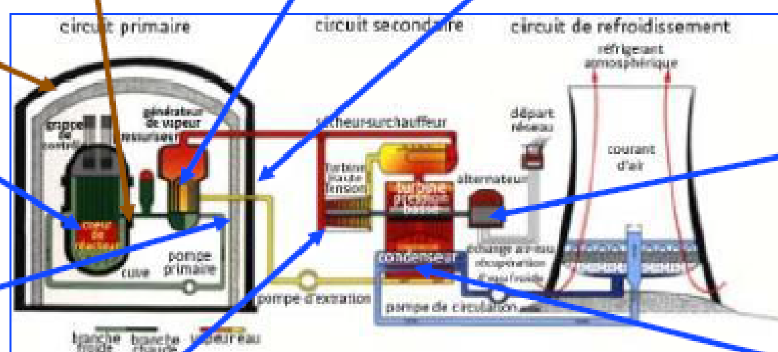
Vessel
- Irradiation ageing

Steam generators
-Stress corrosion cracking (CSC)
- Wear
- Clogging - Fouling
- Fatigue cracking

Secondary pipework and nuclear auxiliaries
- Stress corrosion Cracking
- Deposit corrosion
- Erosion-corrosion
- Fatigue

Containment
- Concrete aging

Vessel internals
- Wear
- Stress corrosion cracking
- Irradiation Assisted Stress corrosion cracking (IASCC)



Generator
- Fouling by corrosion of copper (GST system)
- Fatigue (rotor)
-Fatigue-corrosion (splice plates)
- CSC (Z50MC18-4 binding wires)

Primary pipework:
- Thermal ageing

Turbine
- Stress corrosion (discs, shafts, vane clamps)
- Fatigue (shafts, rotors, clamps and vane bases)
- Corrosion-erosion (internals)
- Erosion (vanes, diaphragms)

Condenser
Stress corrosion of brass
Hydridation of titanium
Erosion
Impacts

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Have a nice nuclear corrosion summer school

NuCoSS - 15

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