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Corrosion and corrosion mitigation in pressurized water reactors

M. Helie

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DE LA RECHERCHE À L'INDUSTRIE



CORROSION AND CORROSION MITIGATION IN PRESSURIZED WATER REACTORS

M. HÉLIE



- **Safety**

- **Diversity**

❑ **Absolute necessity** to confine radioactive or contaminated products and materials



- Integrity of confinement barriers
- Decontamination and treatment of effluents
- Precautions during handling and storage

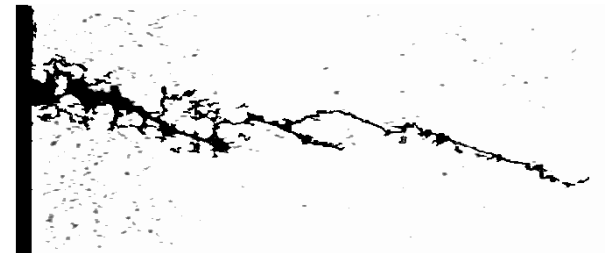


Containers for compacted ILW

- **Materials**
From unalloyed steel to passive alloys
(Fe, Ni, Ti base alloys)
- **Environments**
Aqueous, from deionized to sea water
From ambient to high temperature
- **Solicitations**
Chemical, mechanical, thermal,
radiolytic, bio-chemical ...



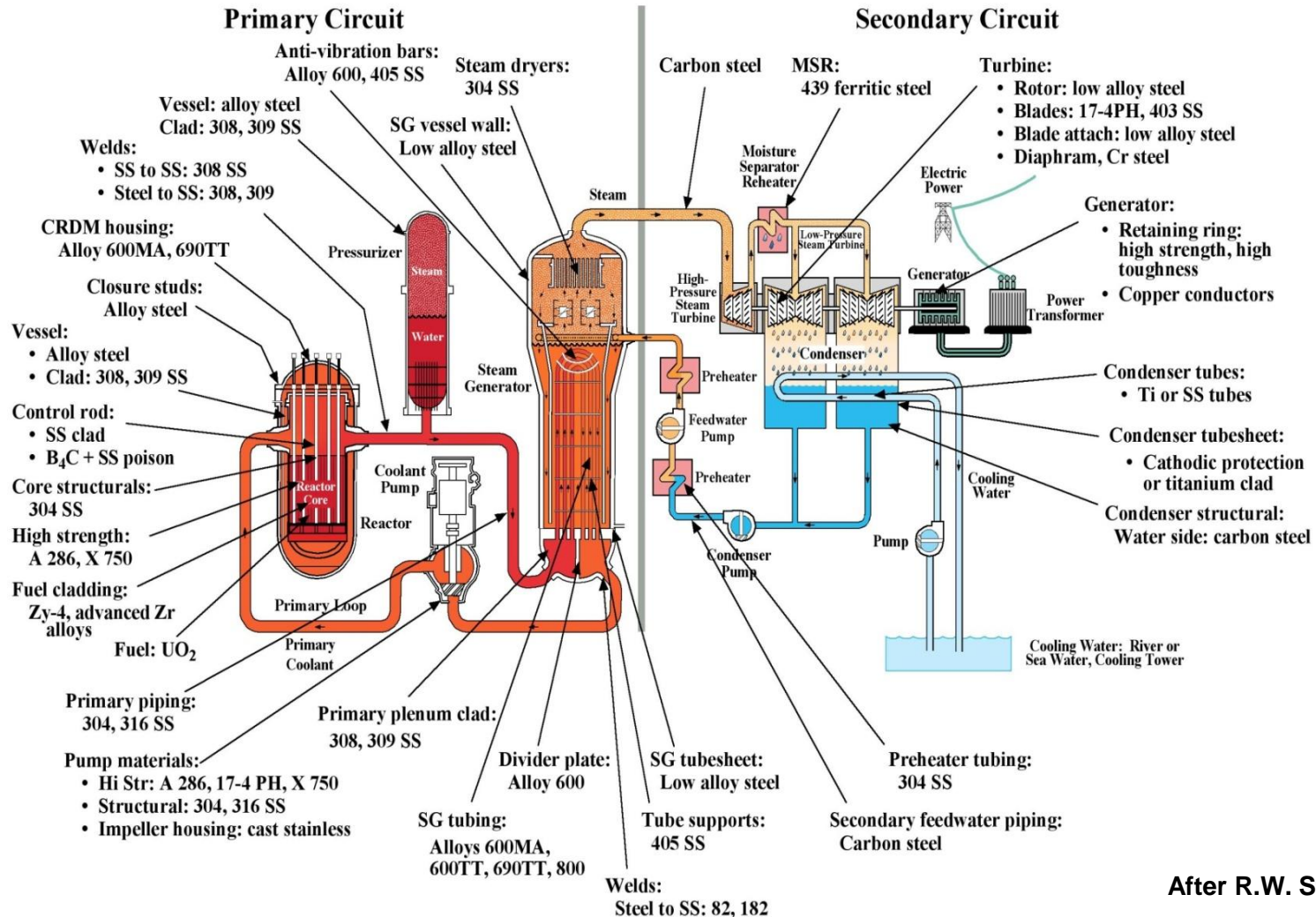
Corroded steel rebars in concrete structure



Crack in steam generator tubing

DIVERSITY OF METALLIC MATERIALS IN A PWR

PWR Materials



After R.W. Staehle

DIVERSITY OF ENVIRONMENTS IN A PWR

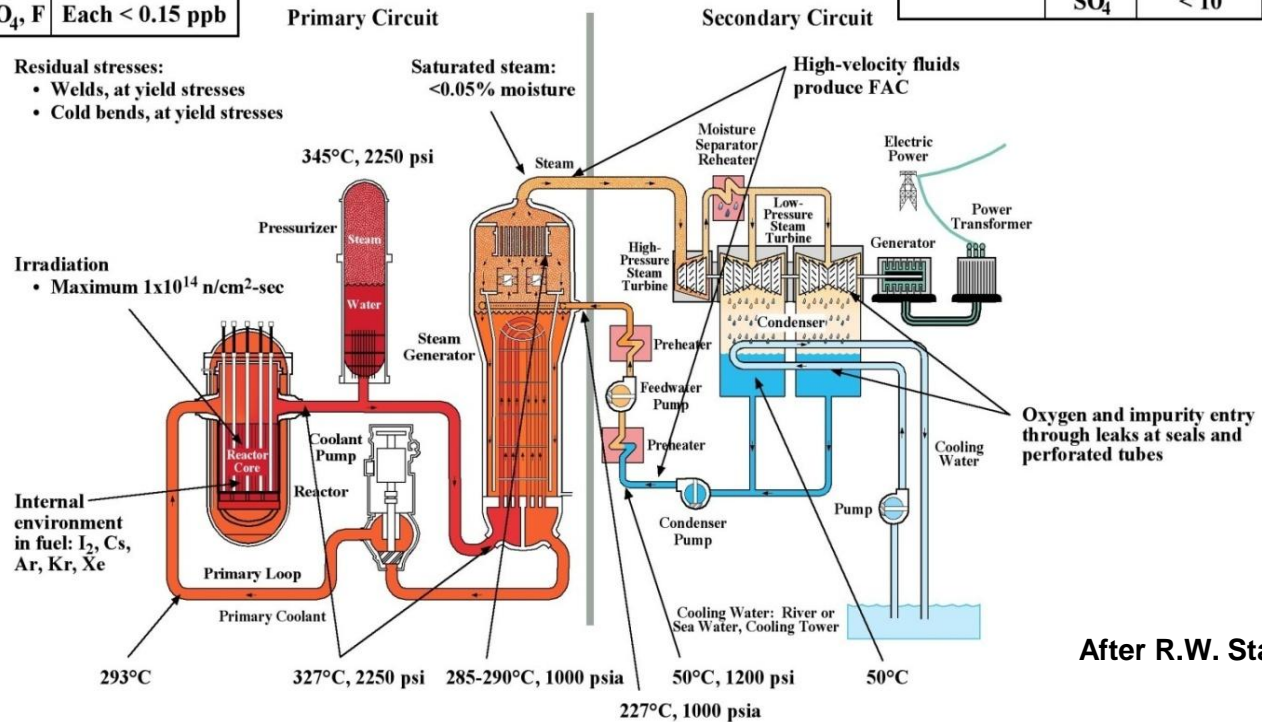
Primary Water Chemistry

Role	Species	Concentration
Burnable poison	H_3BO_3	1500 ppm to zero
pH adjust	LiOH	Adjust to meet 7.1-7.4 pH_T
Minimize radiolytic oxygen	H_2	25-50 STP cc/kg
Oxygen	O_2	< 5 ppb
Corrosion product	Fe	No spec.
	Ni, Co	
Contaminant	Cl, SO_4 , F	Each < 0.15 ppb

Secondary Water Chemistry

Role	Species	Conc., ppb
pH control	NH_3	$\approx X$
O_2 decrease	N_2H_4	$\leq 8xO_2$
Leaks	O_2	< 10
Boil off remnant	H_2	≈ 1
Corrosion product	Cu	< 1
	Fe	< 5
Contaminant	Na	< 5
	Cl_2	< 10
	SO_4	< 10

Bulk PWR Environments: Water Chemistry, Stress, Thermal, Radiation

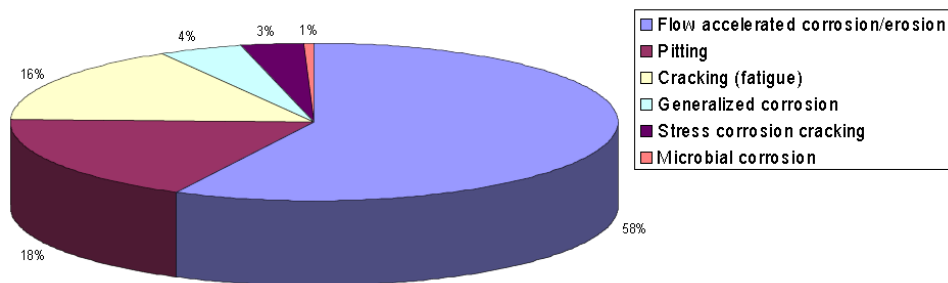


After R.W. Staehle

DIVERSITY OF CORROSION PHENOMENA IN A PWR

Events linked to corrosion and safety (IRSN survey, 2010, French PWRs)

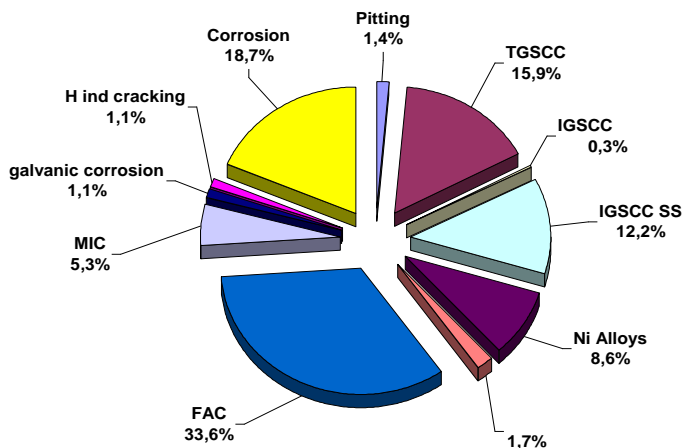
Origin of degradations



Predominant mechanisms

Flow Accelerated Corrosion (FAC)
Stress Corrosion Cracking (SCC)

Corrosion phenomena leading to reactor shutdown (R. Killian, 1995-2005 – worldwide survey)



Predominant mechanisms

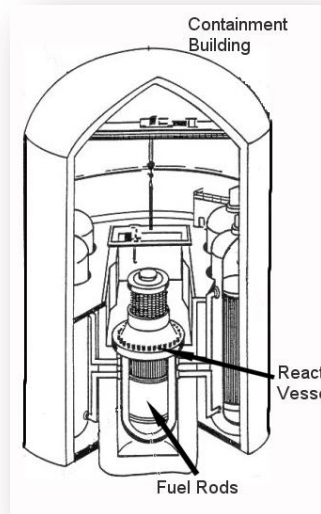
Flow Accelerated Corrosion (FAC)
Stress Corrosion Cracking (SCC)



- ❑ **Fuel elements:** the corrosion of zircaloy cladding is the limiting factor for residence time

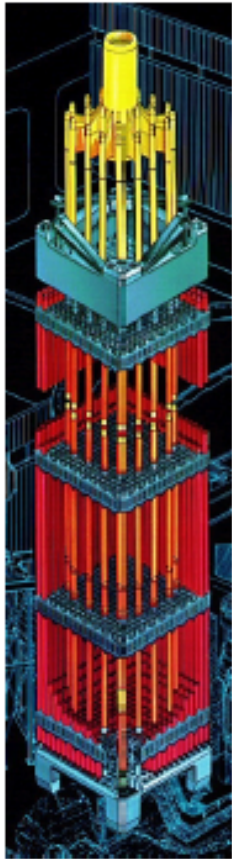


- ❑ **Primary circuit:** vessel resistance is linked to irradiation damage whereas SCC affects steam generator tubing



- ❑ **Reactor building:** evolution of concrete and corrosion of rebars

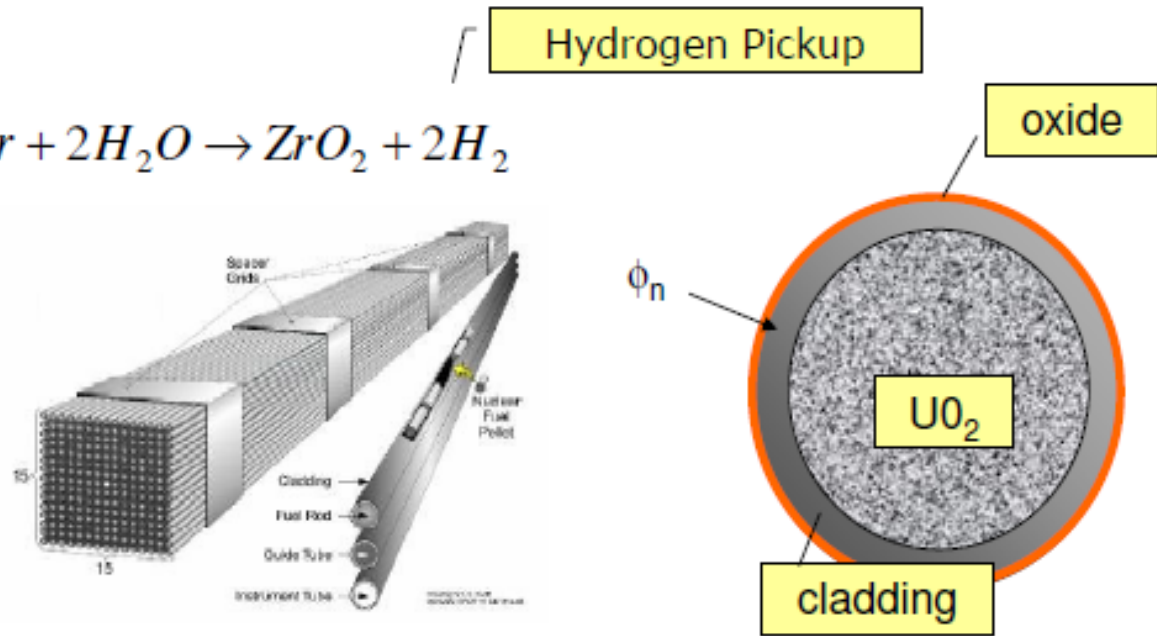
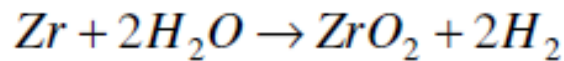




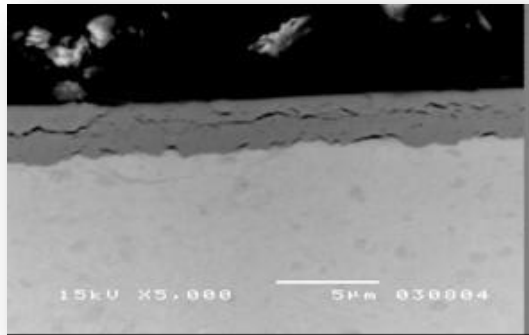
After A. Motta

Light Water Reactor Nuclear Fuel

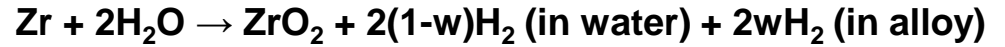
Immersed in water in reactor core, Zr alloy cladding undergoes hydriding and uniform corrosion on its outer diameter, and iodine SCC on its inner diameter



ZIRCALOY: UNIFORM CORROSION IN PRIMARY MEDIUM



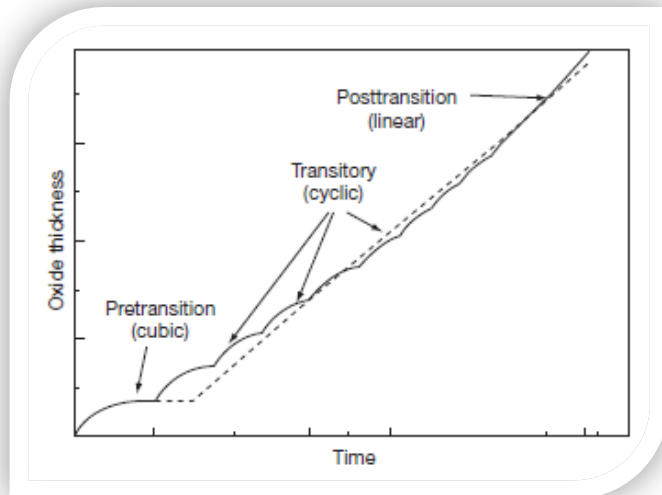
In primary conditions, the corrosion reaction is as follows:



w = fraction of H_2 absorbed by the alloy



- Progressive buildup of oxide layer
- Hydriding of the alloy



Schematic of zircaloy corrosion showing pre-transition, transition, and post transition in the cyclic oxidation process

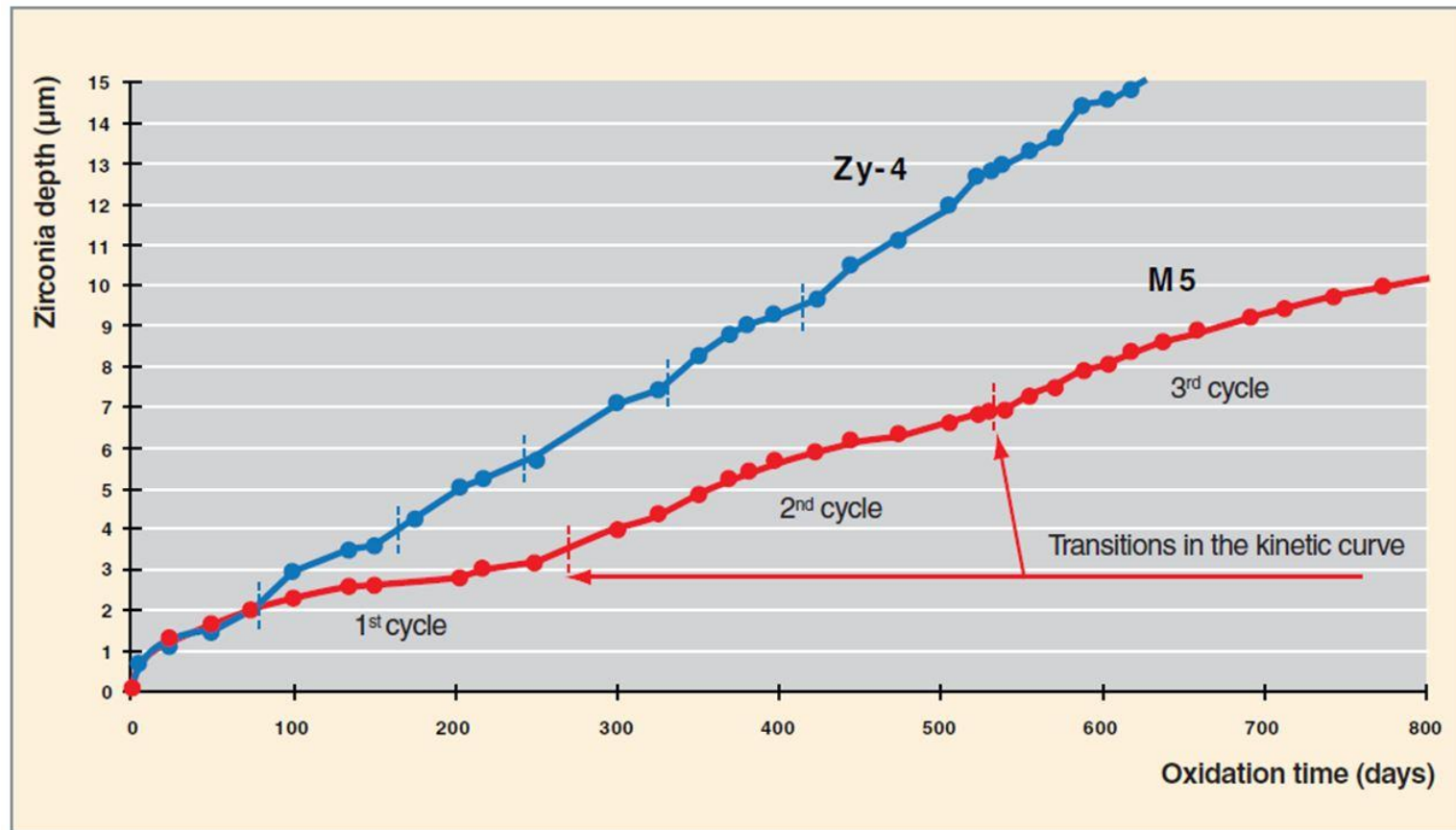


Hydrides

PWR – CWSR Zy4 - $\text{ZrO}_2 > 50 \mu\text{m}$

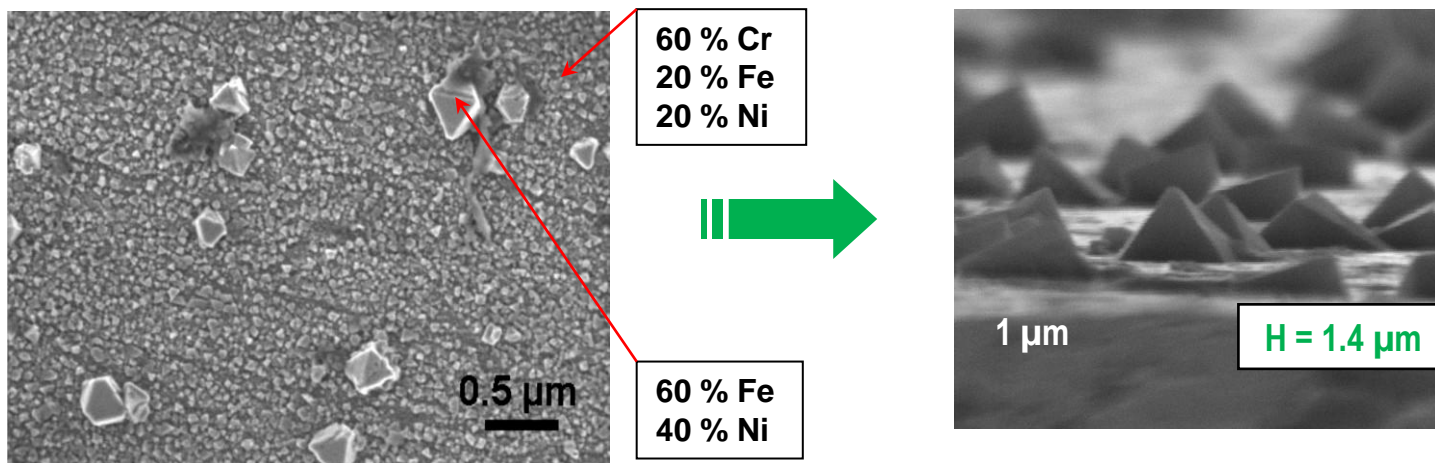
After P. Bouffioux & B. Cheng

Replacement of Zircaloy-4 alloy with M5™ alloy



Zircaloy-4 and M5™ oxidation kinetics. Autoclave tests in water with 10 ppm Li and 650 ppm B at 360°C. The kinetics appear as cyclic. M5™ oxidation rate, the slowest on the average, displays the highest transition thickness

- **Internal layer** made of chromium oxide and small grains of chromium enriched spinel $(\text{Fe, Ni})(\text{Cr, Fe})_2\text{O}_4$
- **External layer** of nickel ferrite crystallites $(\text{NiFe}_2\text{O}_4)$



□ Consequences

- Oxide dissolution. Activation Ni \Rightarrow ^{58}Co \Rightarrow ^{60}Co in the core : **Dose rate increase**
- Intergranular oxidation – selective chromium oxidation

□ Mitigation

- pH adjustment to minimize oxide solubility. Zn addition to replace Ni in oxide ?

❑ Mechanism

Primary water leaks \Rightarrow boric acid concentration \Rightarrow local pH decrease

❑ Materials concerned

Low alloy steel bolts, primary pumps, steam generator and pressurizer manholes, valves, vessel head and vessel flanges, vessel itself in case of important spilling



Bolts corroded by boric acid

● **Use of austenitic stainless steels**

$T < 200^{\circ}\text{C}$ **⇒ Z5 CND 17-12**

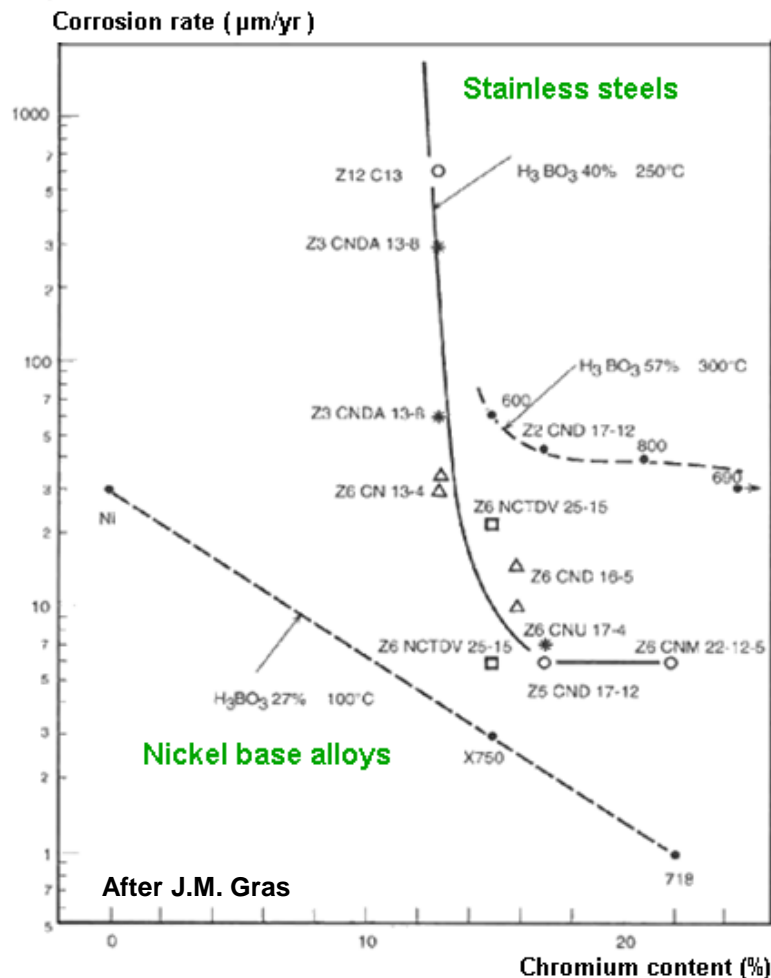
$200^{\circ}\text{C} < T < 250^{\circ}\text{C}$ **⇒ Z6 CNU 17-4**
⇒ Z6 NCTDV 25-15

$250^{\circ}\text{C} < T < 290^{\circ}\text{C}$ **⇒ Z6 CNM 22-12-5**

Beware of Stress Corrosion Cracking!

● **Primary pump studs**

Nickel coated low alloy steel



Uniform corrosion of stainless steels (H_3BO_3 40wt% at 250°C) and of nickel base alloys (H_3BO_3 27wt% at 100°C)

Boric acid deposit due to leaks



South Texas (USA)

Vessel bottom

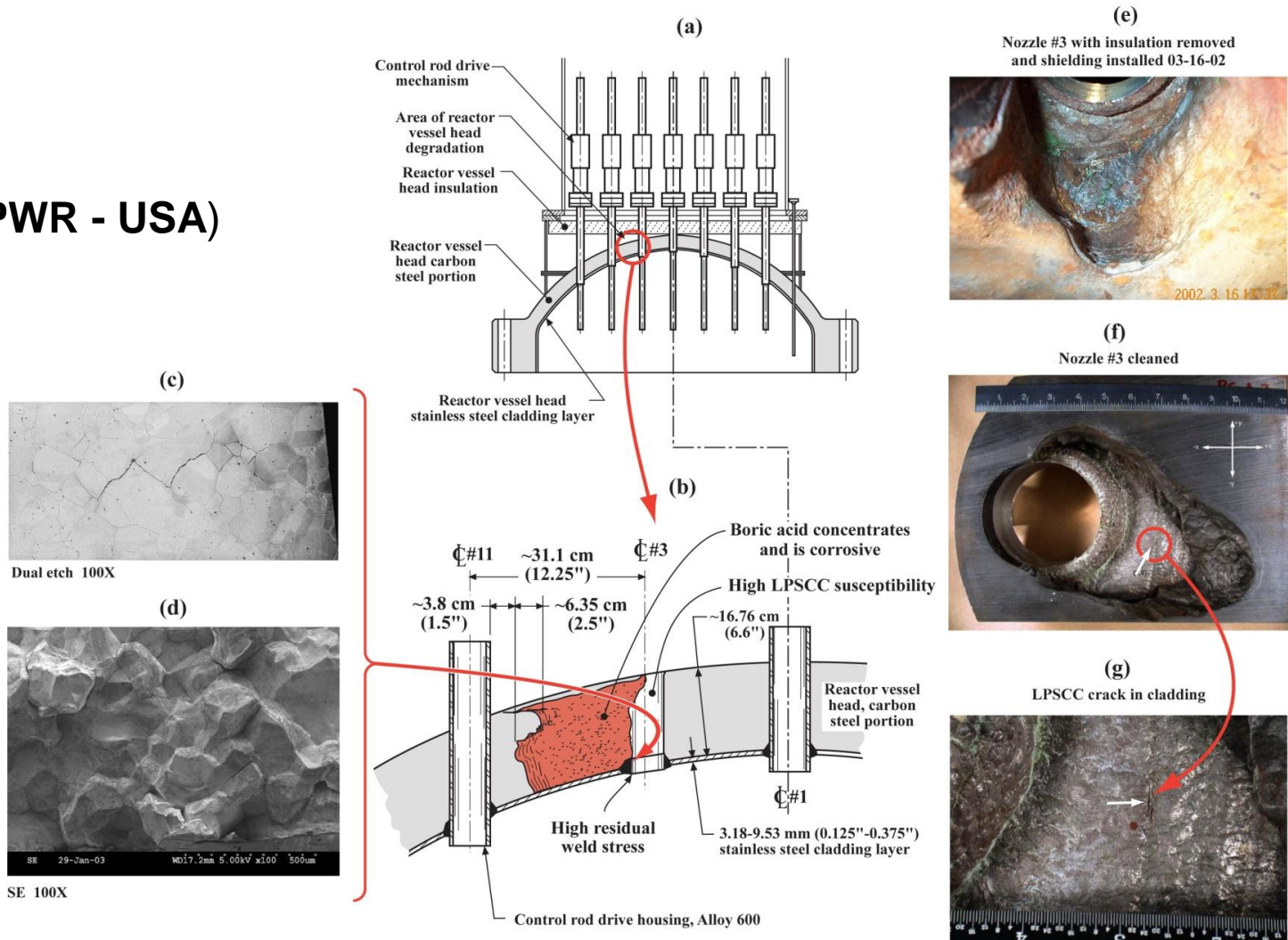


Nozzle 3 with insulation removed and shielding installed 03-16-02

David Besse (USA)

Vessel head

Davis Besse (PWR - USA)



❑ Nickel base alloys

- Primary side : Primary Water SCC (PWSCC - Coriou effect)
- Secondary side : InterGranular SCC (IGSCC)

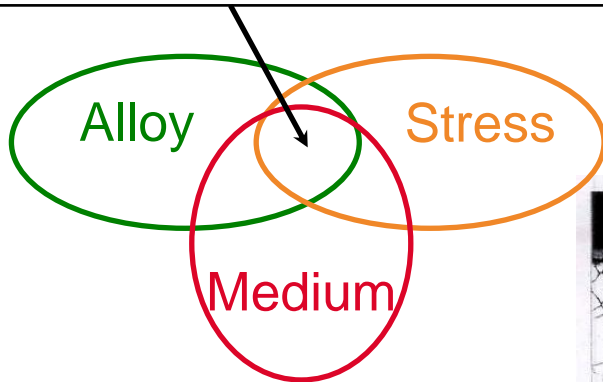
❑ Stainless steel

- Primary side (SCC)
- Irradiation Assisted SCC (IASCC)
- SCC under heat insulator (external surface)

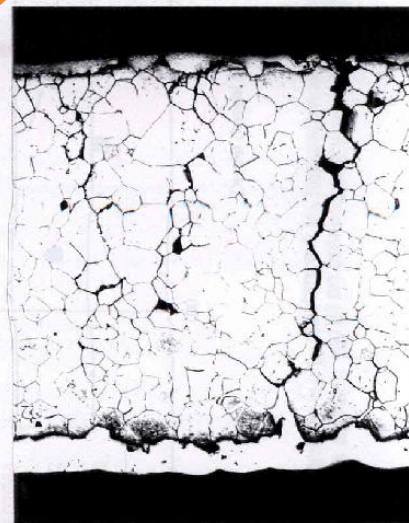
❑ Other alloys prone to SCC

- Brass (vapor or liquid polluted with NH_3 or sulfide) in condensers
- Low alloy or carbon steel for bolting and auxiliary circuits (sodium hydroxide, nitrates, chlorides, H_2S)
- Titanium in condensers (cathodic potential (H_2 embrittlement), hot medium with chloride)

Stress Corrosion Cracking

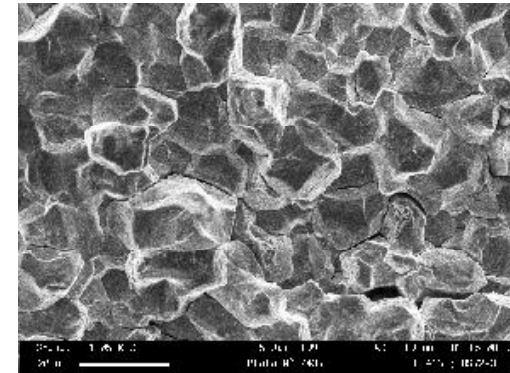


Lowering of R_m , A%
Rupture through
crack propagation



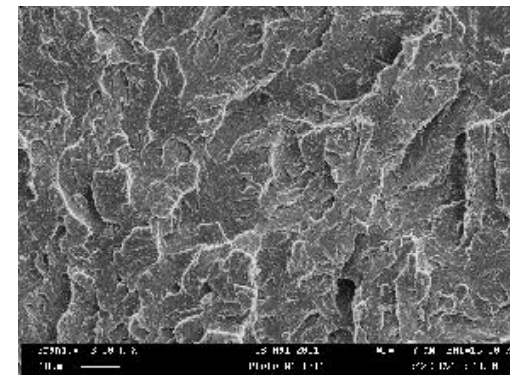
Welded alloy 600, SG tubing
Saint-Laurent-des-Eaux 1
(French PWR)

Intergranular Cracking



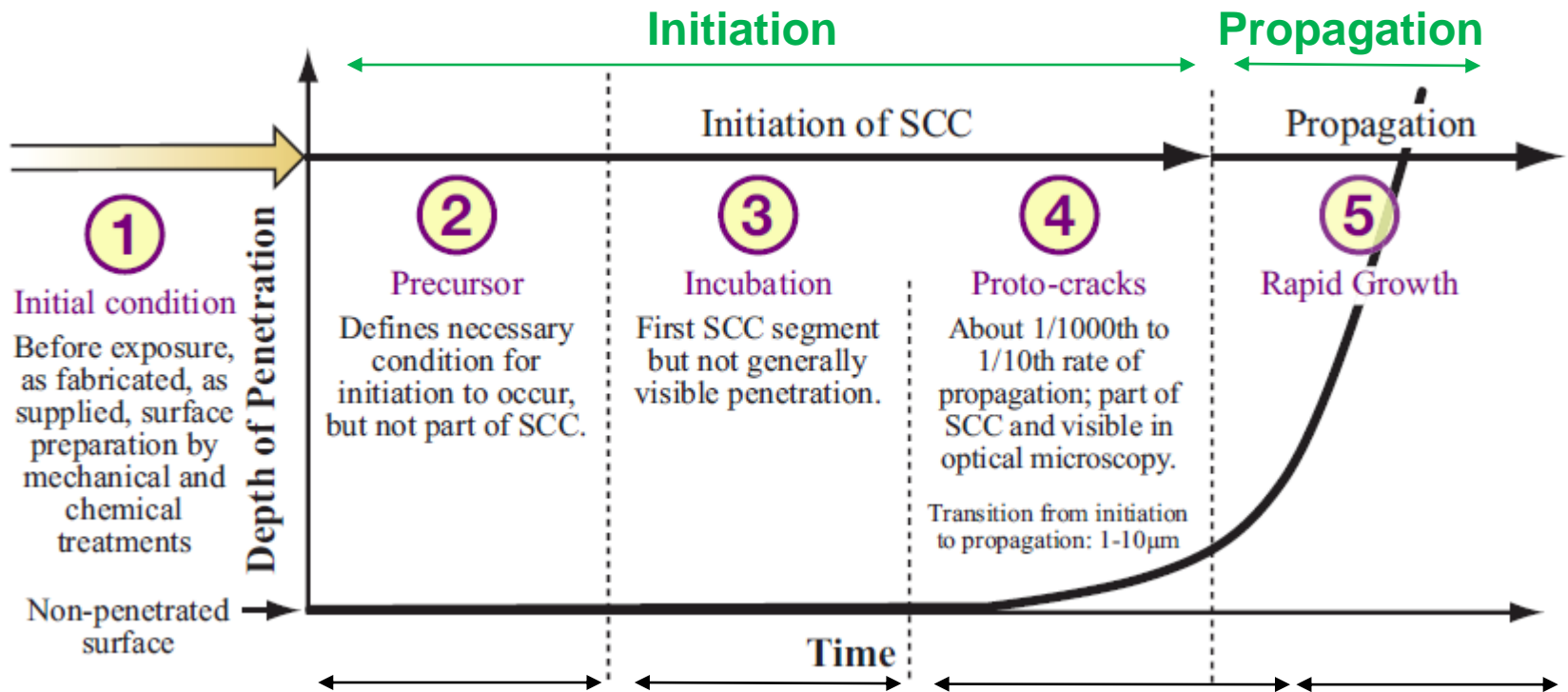
Alloy 600, SG tubing, primary water

Transgranular Cracking



17-4 PH steel, valve rod, high temp.

DIFFERENT STAGES OF STRESS CORROSION CRACKING

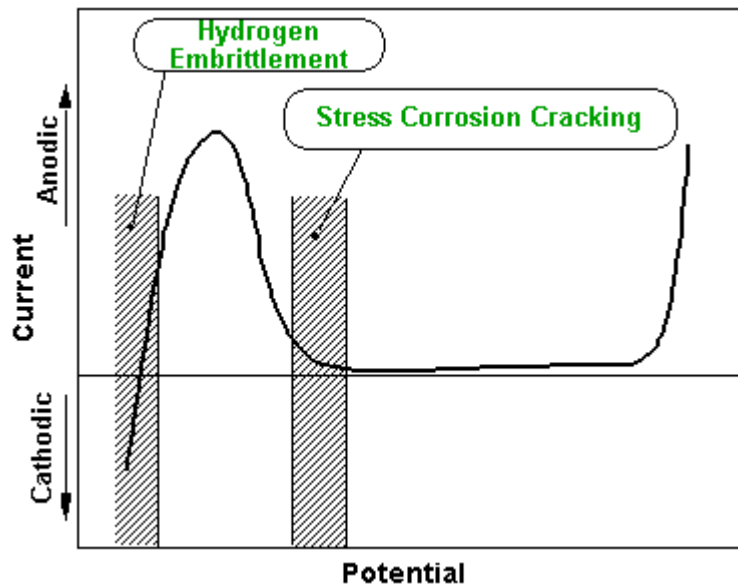


For Ni base alloys : Incubation Initiation Slow propagation Rapid propagation

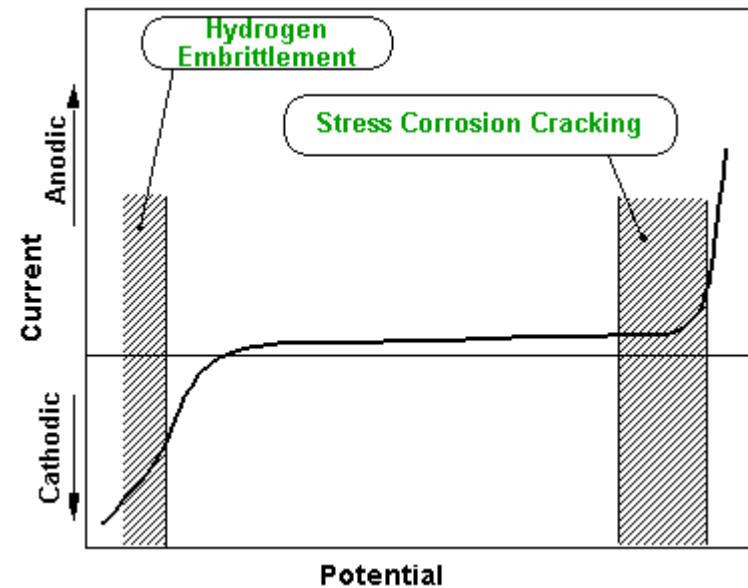
- (1) Importance of initial conditions
- (2) Preparatory phase (incubation)
- (3) Initiation phase followed by slow (4) and rapid propagation (5)

Zones of relative "instability" of protective layers

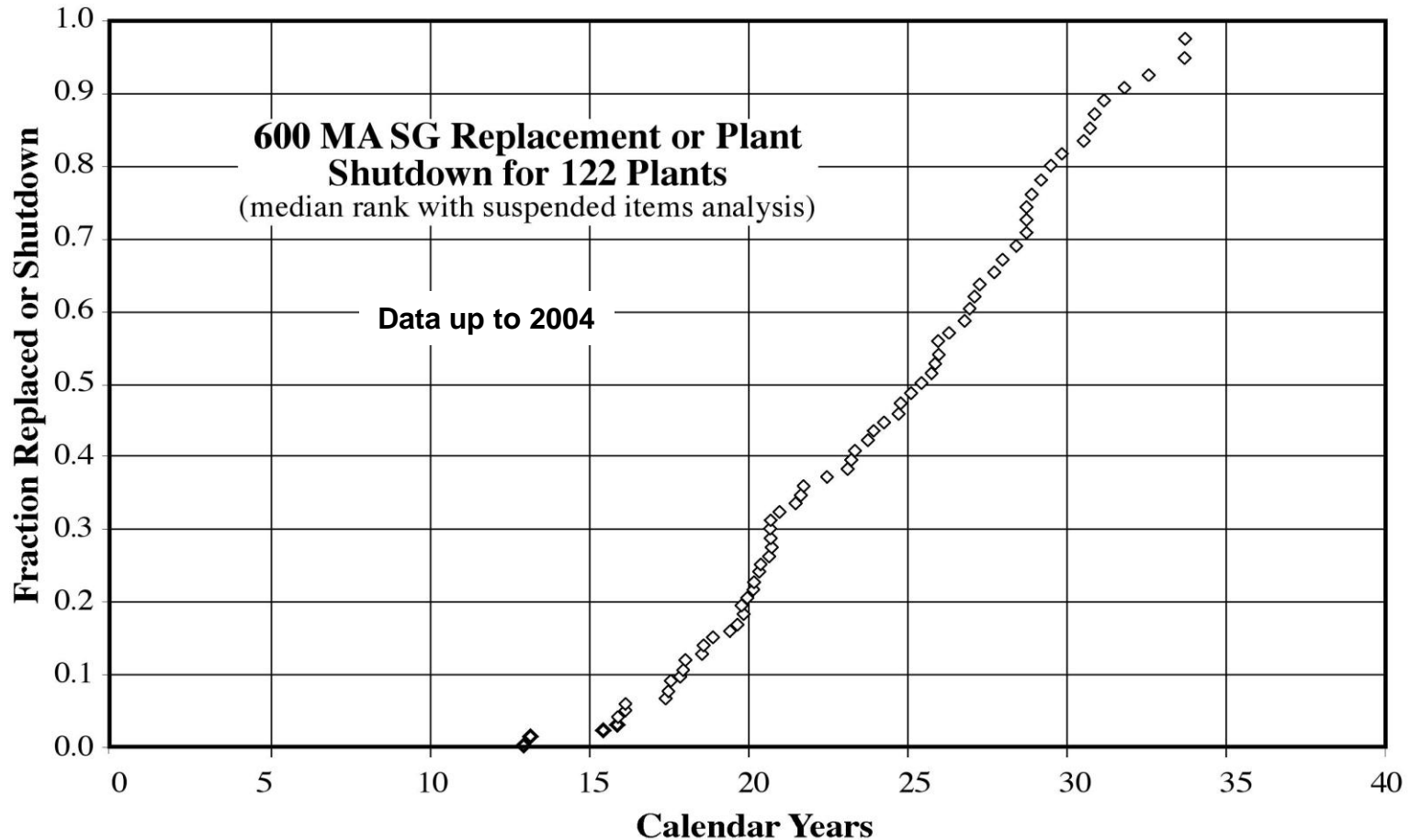
Systems with poor ability to passivate
cracking in the active/passive transition



Systems with strong ability to passivate
critical cracking potential



❑ Replacement of Steam Generators with Alloy 600 MA tubing by Steam Generators with Alloy 600 TT or Alloy 690 tubing



CONSEQUENCES OF ALLOY 600 PWSCC

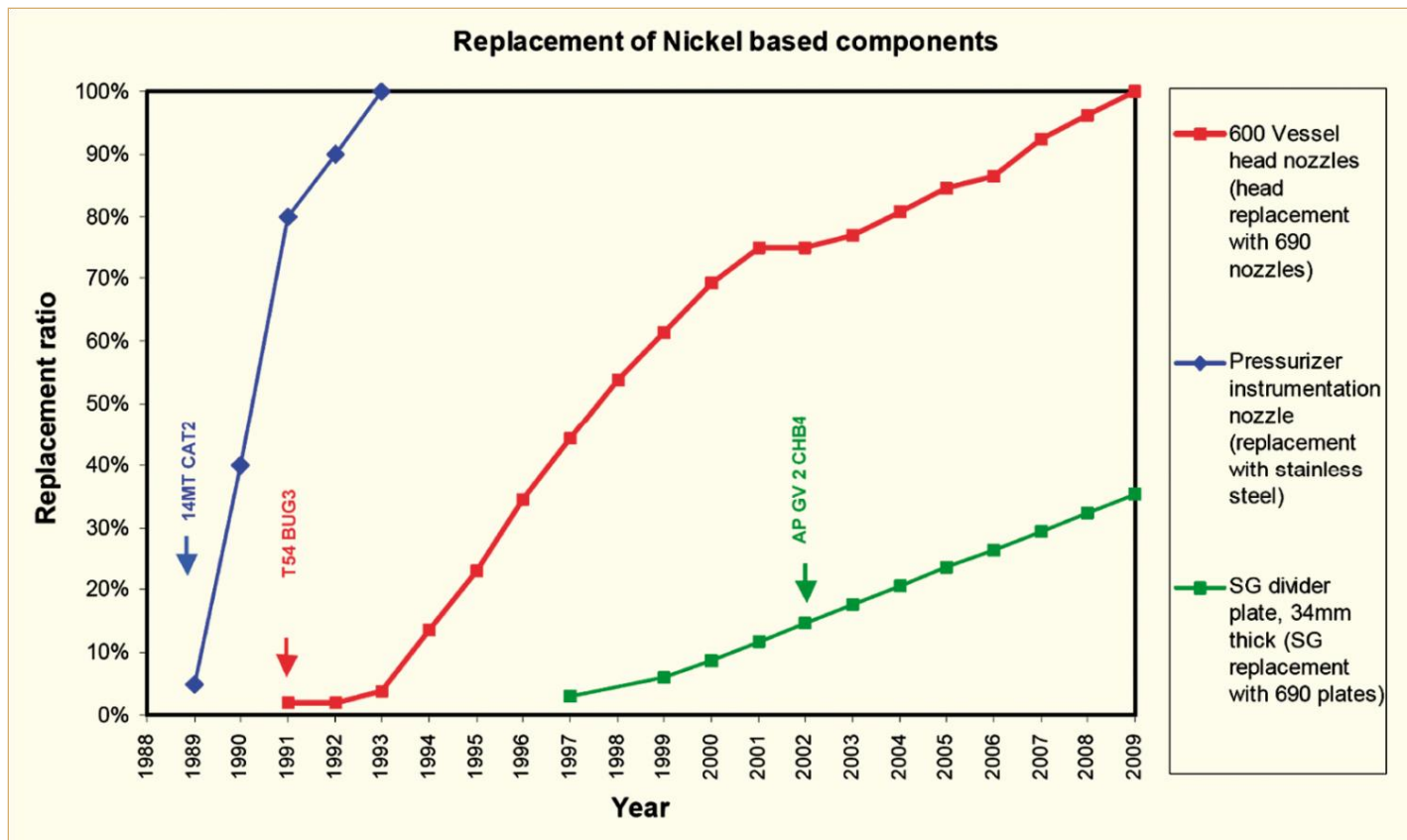


Replacement of a Steam Generator

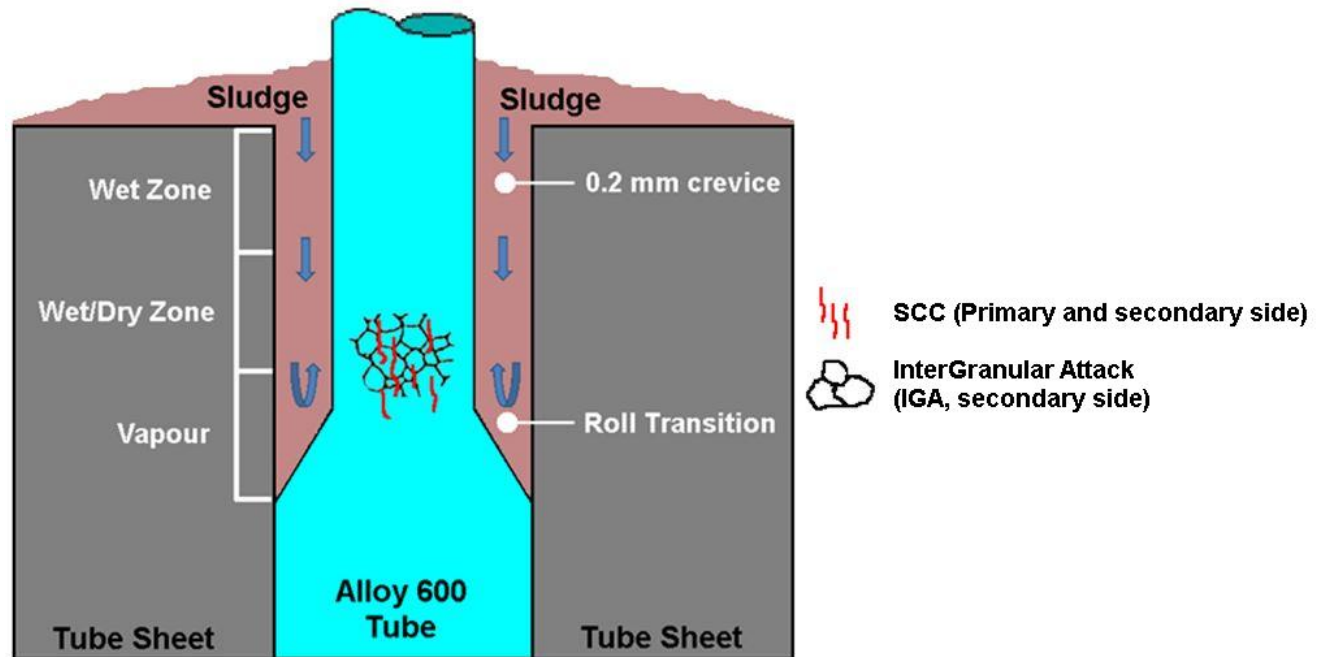
Since 1998, AREVA has carried out more than 80 steam generator replacements, covering half of the market in the United States

□ Replacement of Alloy 600 components with Alloy 690

- Pressurizer instrumentation nozzles
- Vessel head nozzles
- Steam Generator divider plates



- High stress level at the roll transition leading to SCC cracks in the tube-tube sheet crevice (in the USA mainly)



- Two-step rolling allowing a smoother transition
- Shot peening of the tubes
- Rolling all along the tube sheet to suppress the crevice and limit the sludge pile

SCC AND DENTING MITIGATION AT THE TUBE-TUBE SUPPORT PLATE INTERFACE



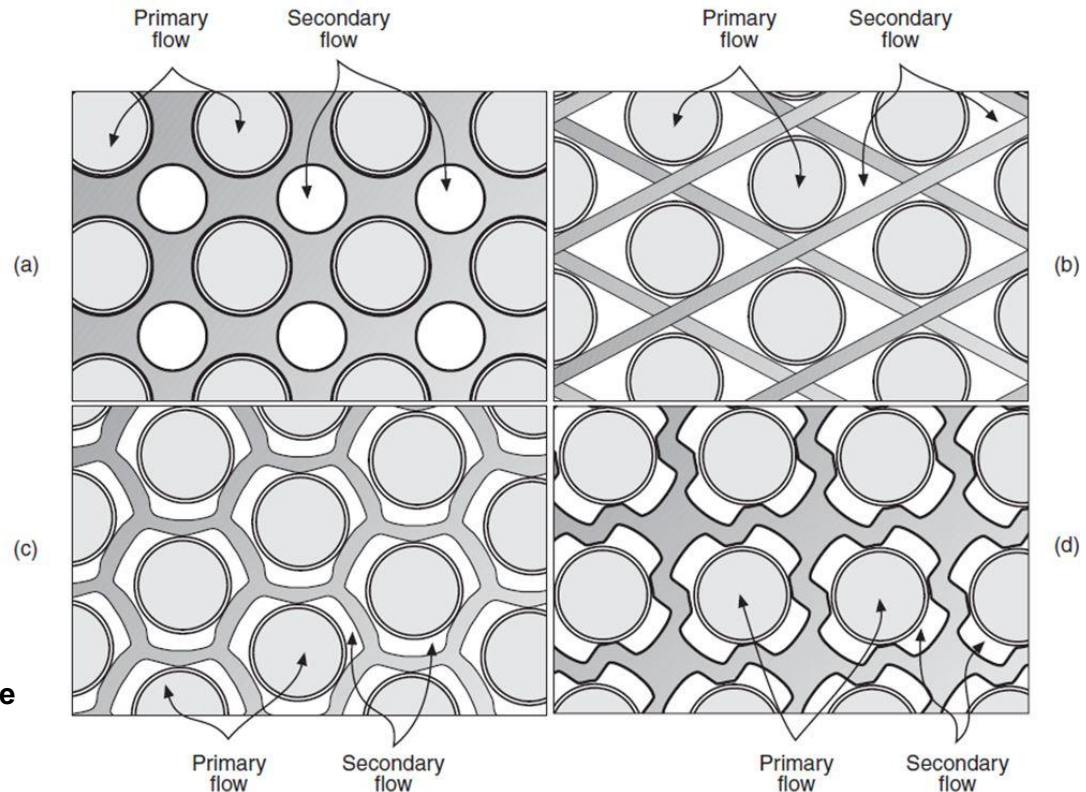
❑ Accumulation of corrosion products at the interface causing stresses

- Changing phosphate treatment (hideout problems) to AVT
- Evolution of tube support plate geometry

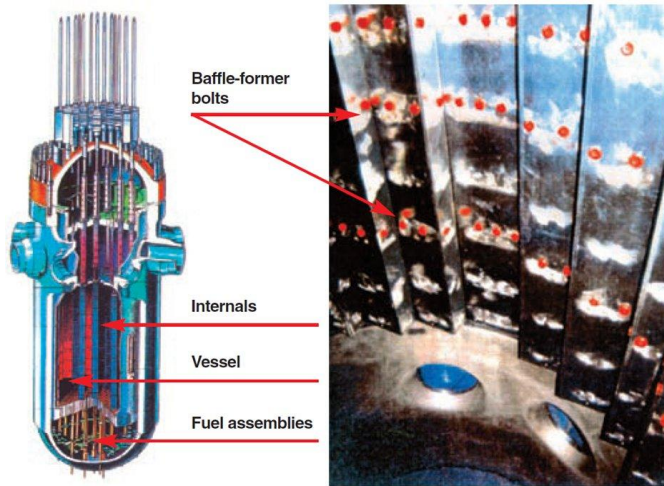
● Evolution of TSP geometry

- (a) Drilled hole
- (b) Egg crate
- (c) Broached trefoil
- (d) Broached quatrefoil

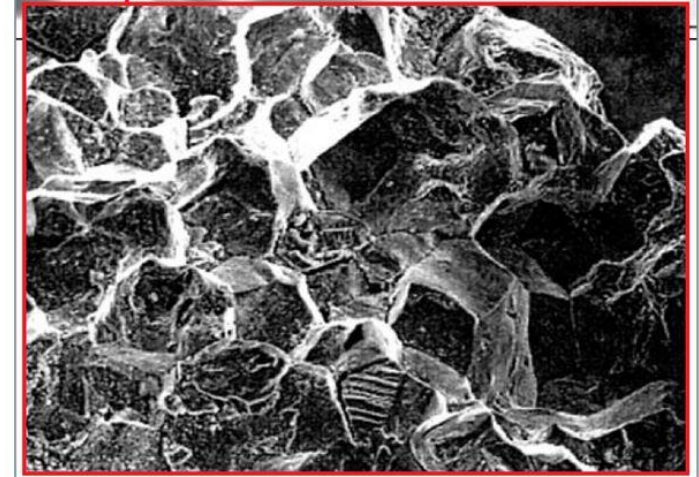
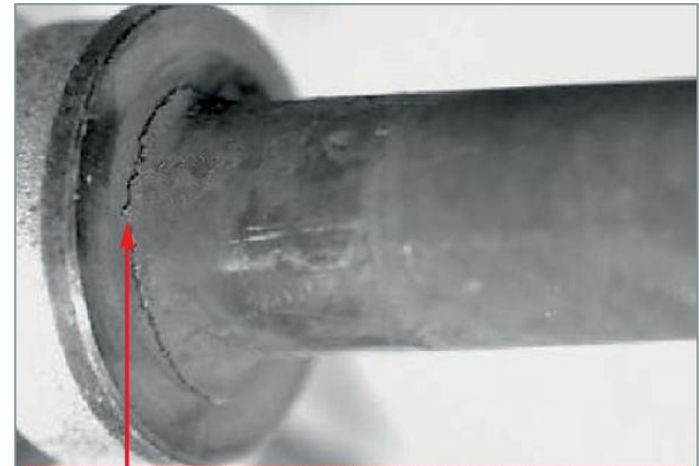
After R.W. Staehle



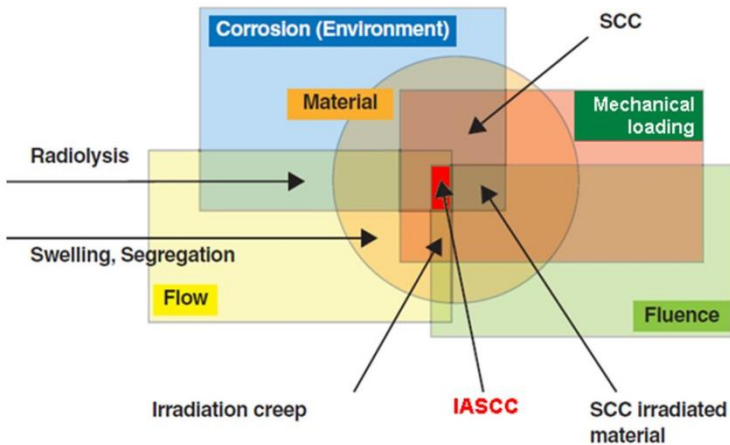
IASCC OF STAINLESS STEEL VESSEL INTERNALS



PWR vessel internals



IASCC on an internal bolt of the French CPO series

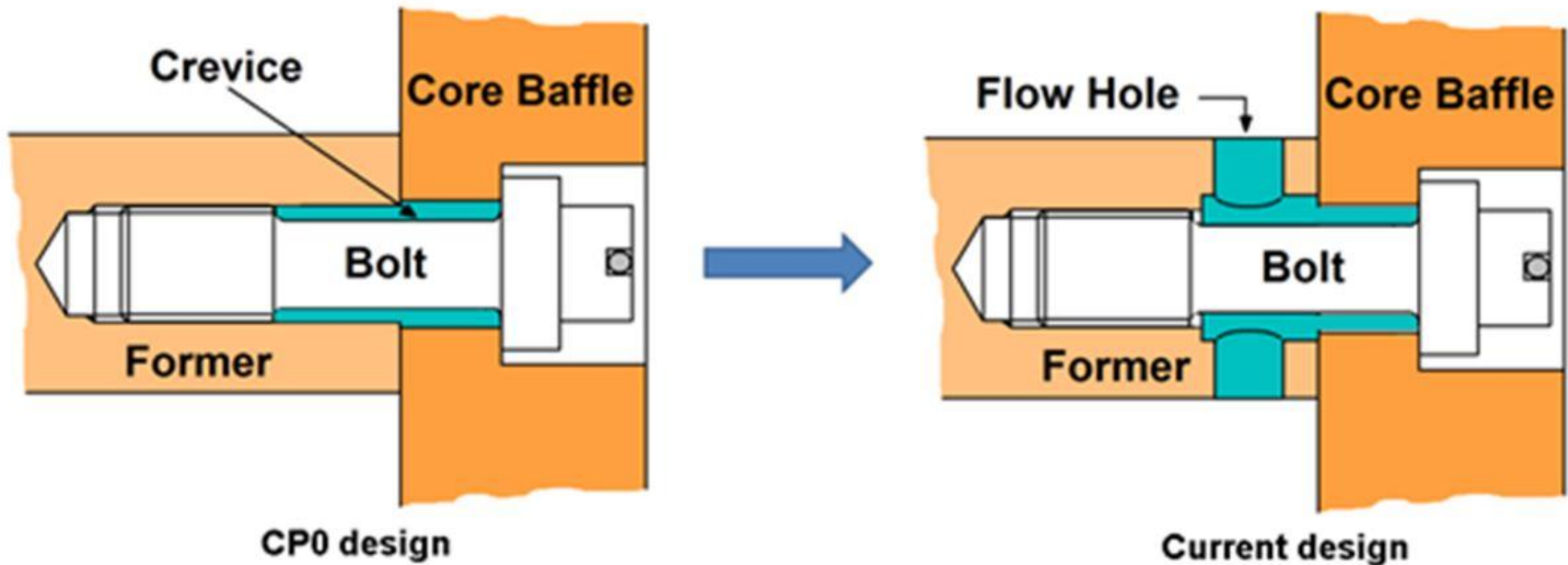


Sinergy factors involved in IASCC

❑ Crevice around the bolt shank

- Local boiling due to γ heating of the bolt
- LiOH, H_3BO_3 and oxidizing species concentration

Drilling of a flow hole to suppress local crevice conditions



FAC is a chemical and thermohydraulic degradation (not mechanical, not erosion)

□ Conditions of occurrence

- Unalloyed steels covered with a passive oxide layer (magnetite)
- In contact with high flow rate water or wet vapor
- No FAC in dry vapor

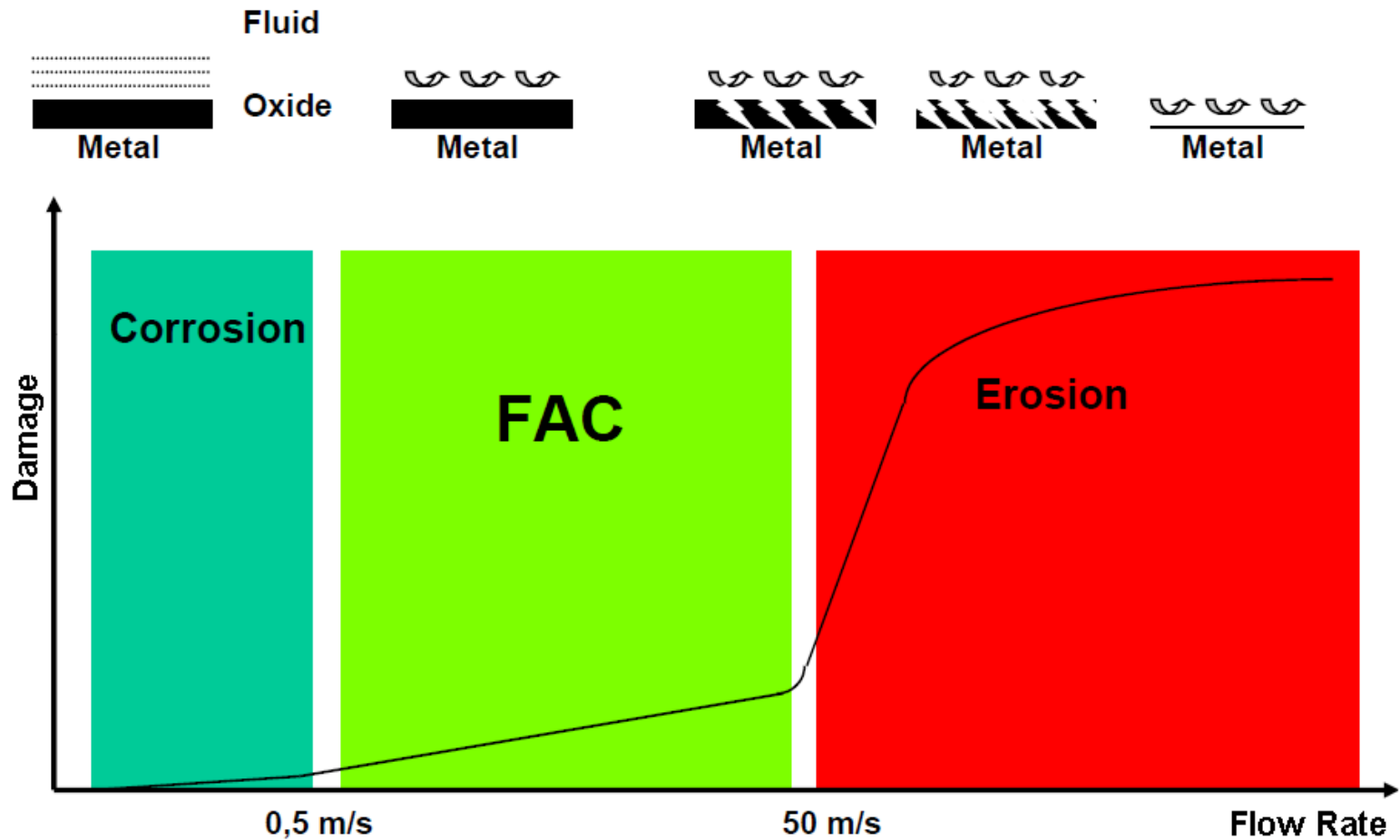
□ Chemical stationary conditions

- Corrosion rate = Rate of oxide layer dissolution
Rate of oxide layer dissolution **inversely proportional** to $[M^{z+}]$ at the interface metal - solution

● No water flow $\implies [M^{z+}] \approx \text{saturation} \implies \text{Low Corr. rate} \implies \text{NO FAC}$

● High water flow $\implies [M^{z+}] \approx 0 \implies \text{High Corr. rate} \implies \text{FAC}$

DOMAIN OF FAC OCCURRENCE



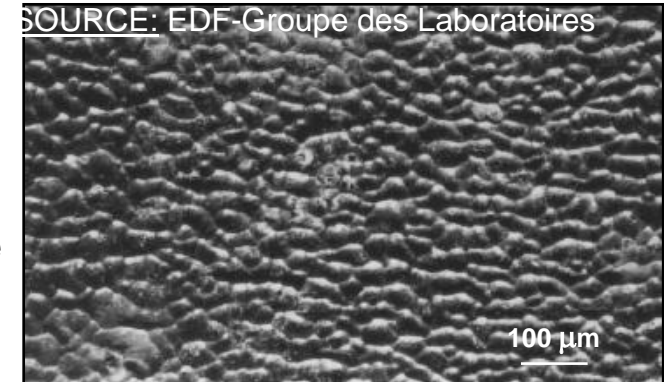
Domains of Corrosion, FAC, and Erosion depending on flow rate

(After S. Trévin, © EDF)

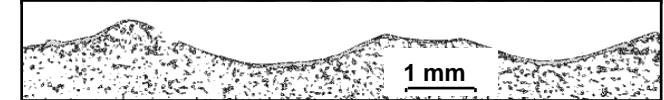
□ Monophasic fluid (liquid water)

- Bugey 5: Valve
Horse shoe pits

SEM view of the surface



Micrographic cut



□ Diphasic fluid (wet vapor)

- Bugey 2: Tubing
Tiger stripping

Internal surface of the corroded tube



❑ 1986: SURRY 2 – 900MW PWR

- Consequences: 4 dead, 4 severely injured

❑ 1995: PLEASANT PRAIRIE 1 – 600MW Coal Plant

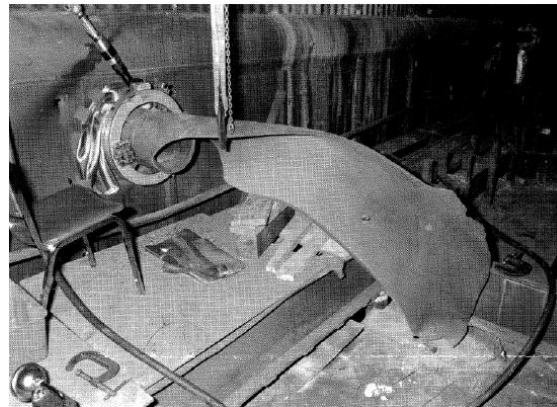
- Consequences: 2 dead

❑ 2004: MIHAMA 3 – 780MW PWR

- Consequences: 5 dead, 6 severely injured



Surry 2: blow up of a 18" elbow



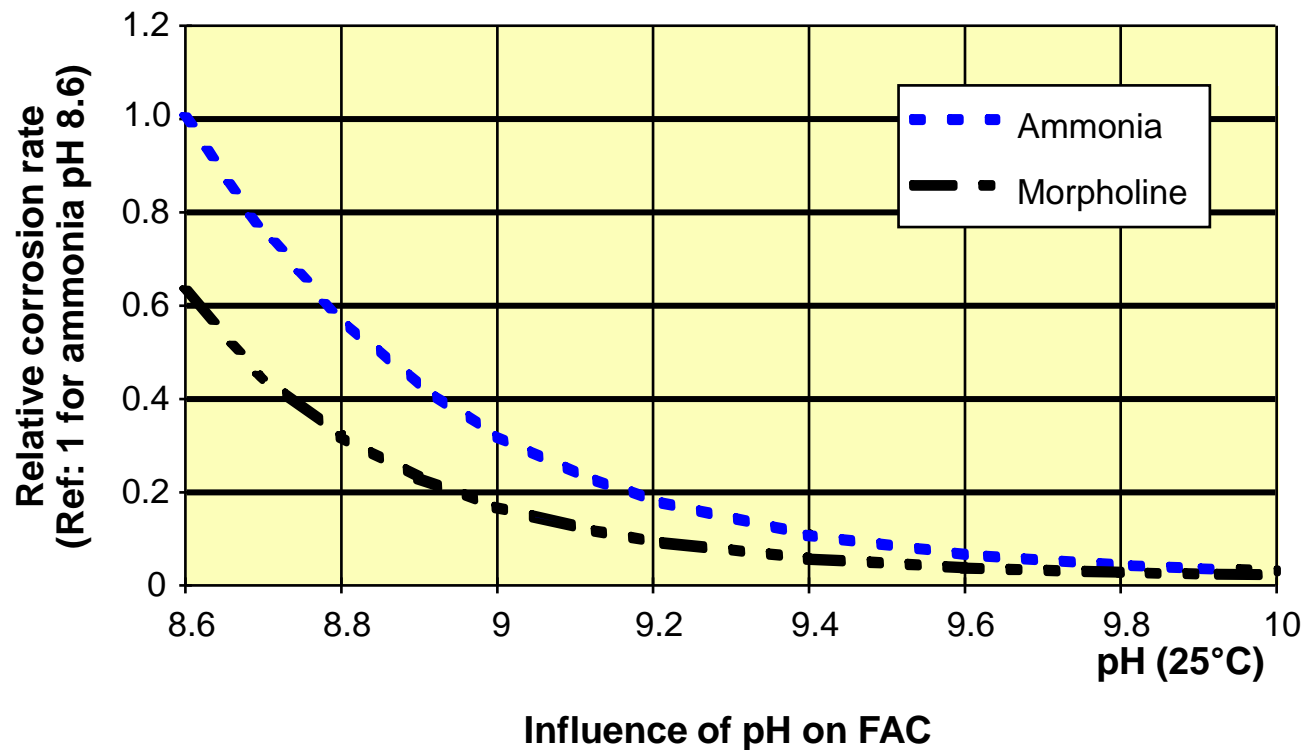
Pleasant Prairie 1: blow up of a straight line after a "T"



Mihama 3: blow up of a 22" straight line

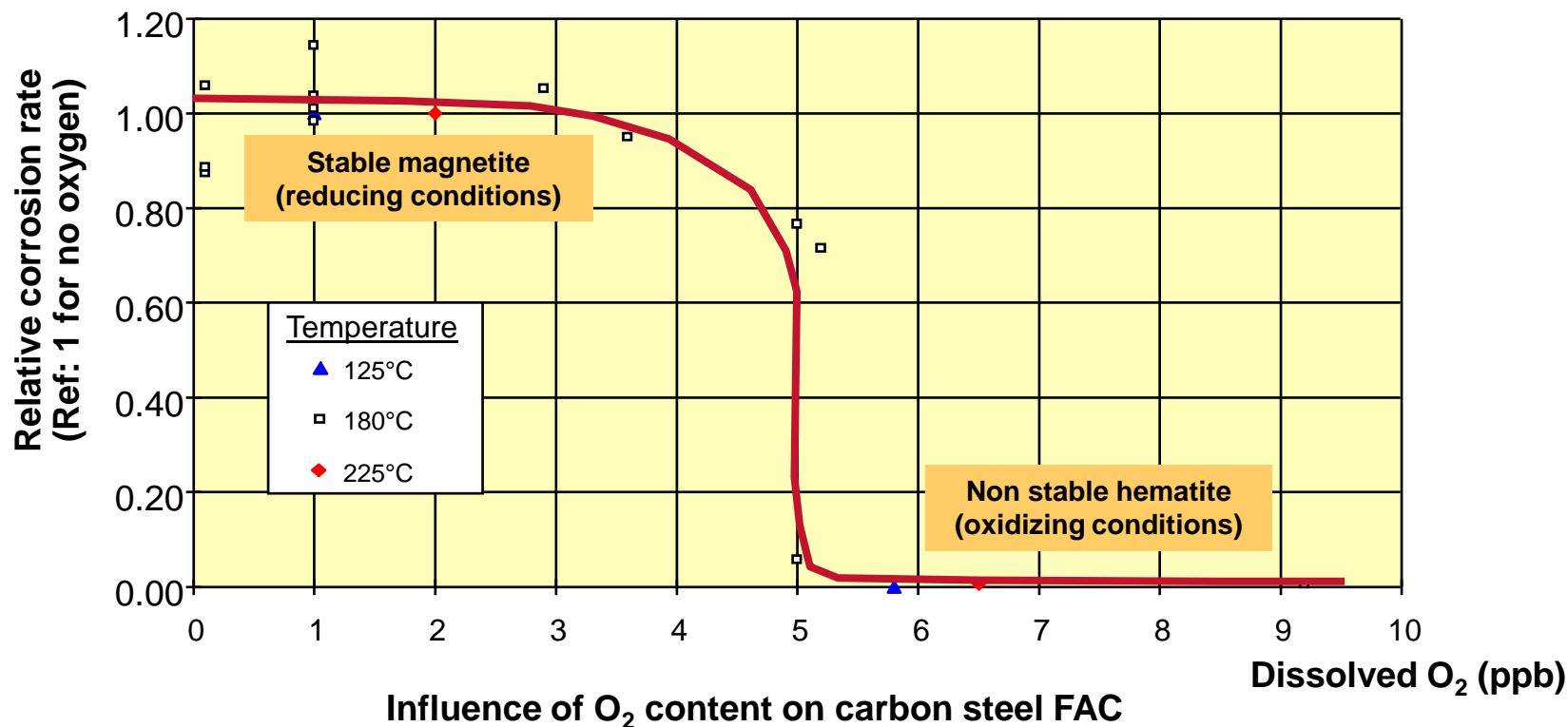
- pH has an important influence since it affects the solubility of metallic elements

● Increasing pH decreases FAC

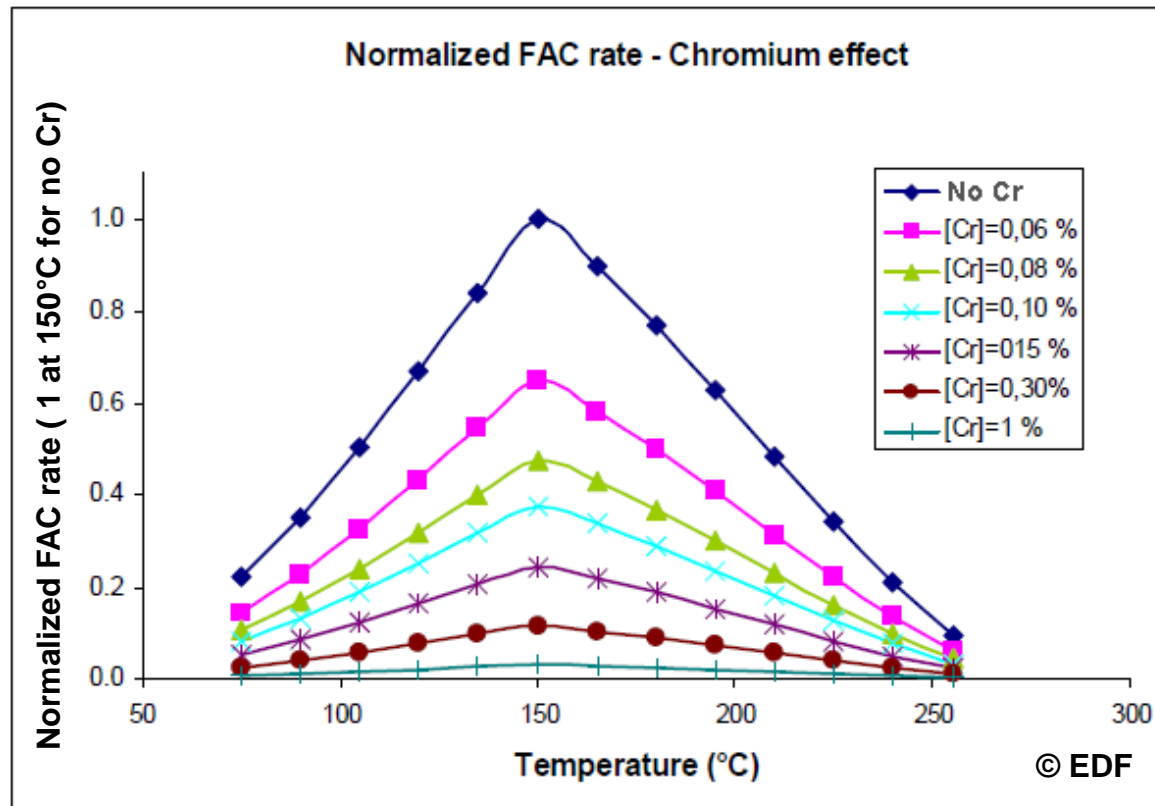


□ O_2 content has an important influence on FAC since it affects the oxide nature and properties

- Increasing O_2 content decreases FAC
- No FAC above 5 ppb O_2



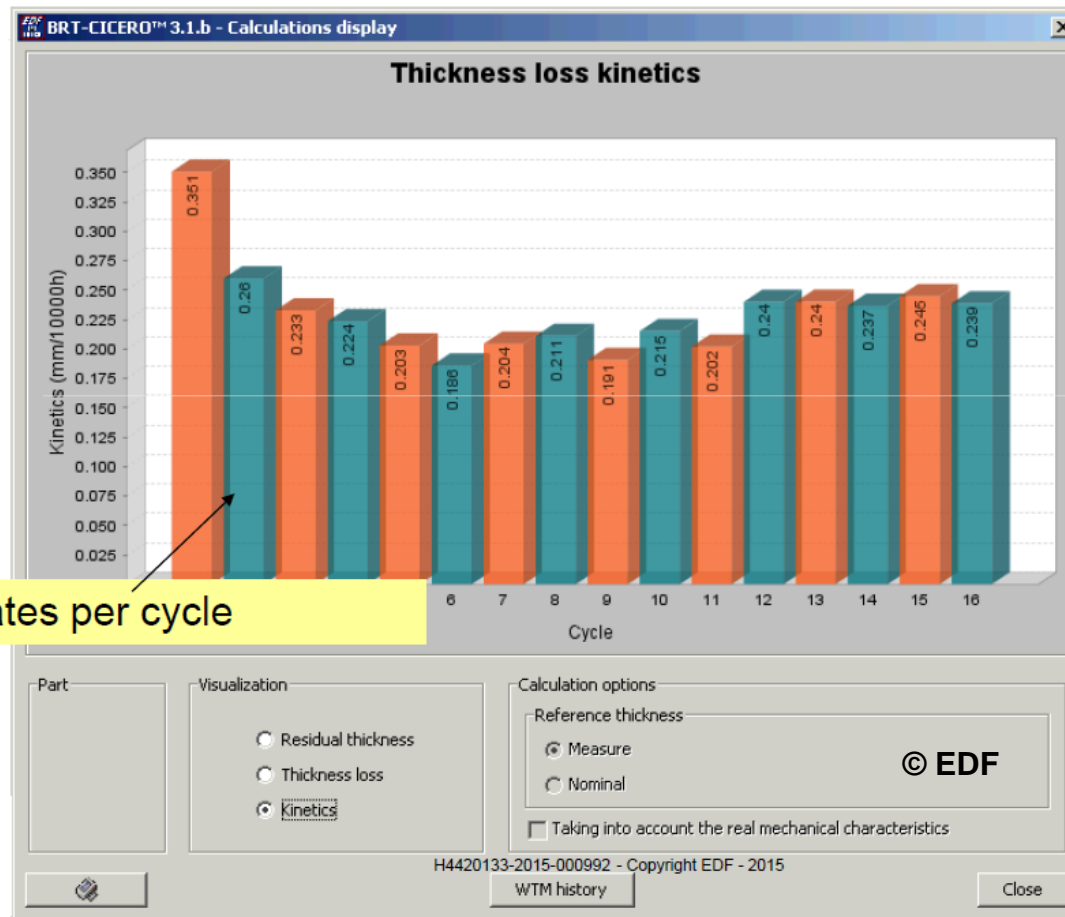
- Cr content has an important influence on FAC since it affects the oxide nature (formation of Fe_2CrO_4 of poor solubility)
 - Increasing Cr content decreases FAC
 - No FAC above 1% Cr whatever the temperature



- ❑ **Objective : to predict wall thickness loss due to FAC in order to be able to replace a component before rupture**

- ❑ **Prediction based on :**
 - **Physicochemical model**
 - **Laboratory experiments**
 - **In service data (real time monitoring of selected portion of circuits) to adjust the results**
 - **Database involving results of all affiliated utilities in the world**

□ Example of result given by BRT CICERO™ on a portion of circuit



FAC rates per cycle

- The use of BRT CICERO™ is mandatory for the 58 French PWRs by decision of the Nuclear Safety Authority (ANS)**

- Also used by Daya Bay and Ling Ao plants in China**

- Also used by Koeberg plant in South Africa**

THANK YOU FOR YOUR ATTENTION

Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Saclay | 91191 Gif-sur-Yvette Cedex
T. +33 (0)1 69 08 54 83 | F. +33 (0)1 69 08 15 86

Etablissement public à caractère industriel et commercial | RCS Paris B 775 685 019

Direction de l'énergie nucléaire
Département de physico-chimie
Service de la corrosion et du comportement
des matériaux dans leur environnement
Laboratoire d'étude de la corrosion aqueuse