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# Corrosion and corrosion mitigation in pressurized water reactors

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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

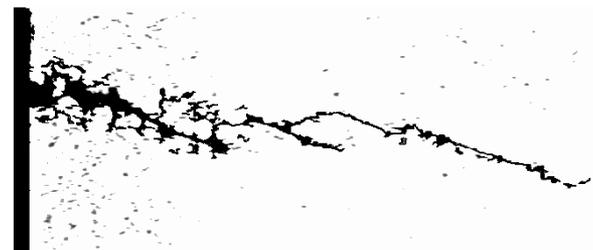


Containers for compacted ILW

- **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 ...



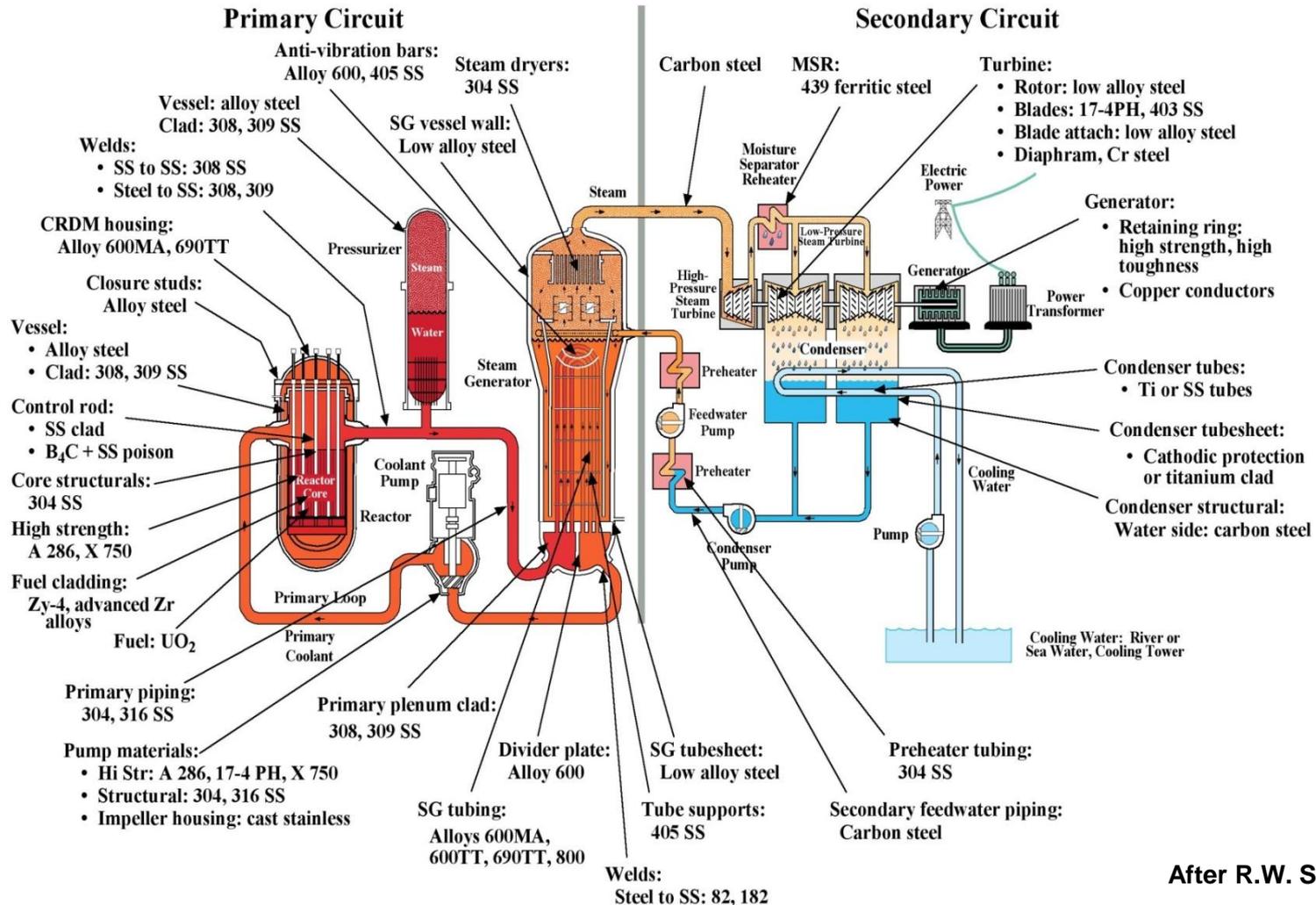
**Corroded steel rebars in concrete structure**



**Crack in steam generator tubing**

# DIVERSITY OF METALLIC MATERIALS IN A PWR

## PWR Materials



After R.W. Staehle

# DIVERSITY OF ENVIRONMENTS IN A PWR

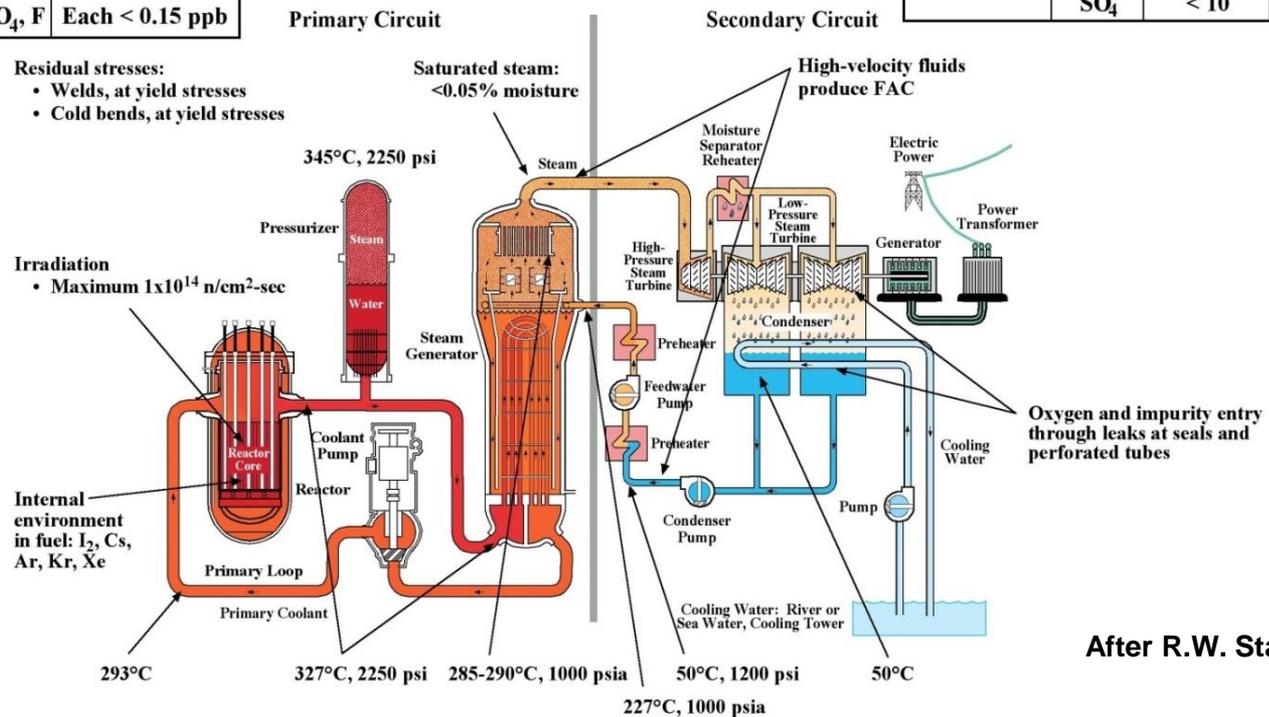
## Primary Water Chemistry

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	$H_2$	$\approx 1$
Corrosion product	Cu	< 1
	Fe	< 5
Contaminant	Na	< 5
	$Cl_2$	< 10
	$SO_4$	< 10

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

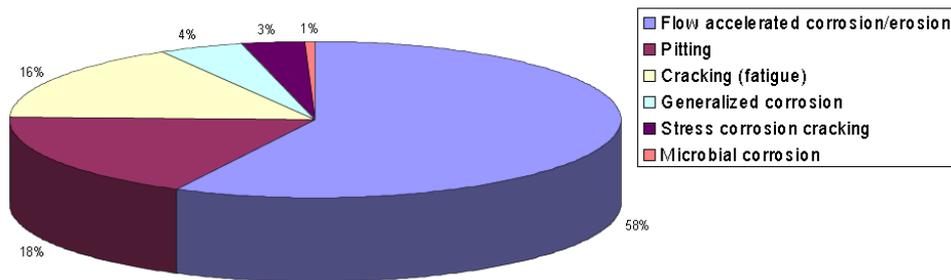


After R.W. Staehle

# DIVERSITY OF CORROSION PHENOMENA IN A PWR

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

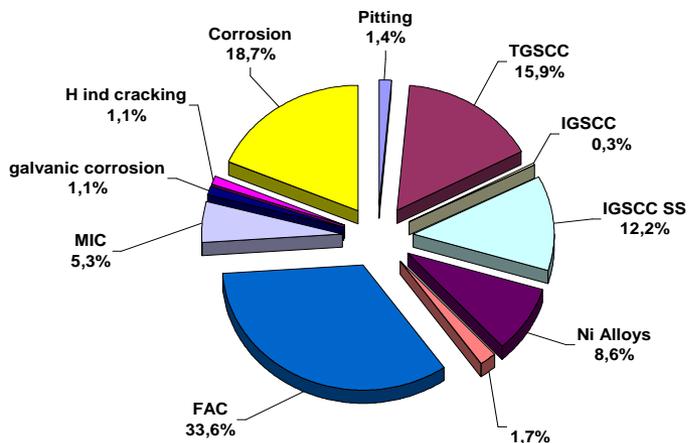
Origin of degradations



### Predominant mechanisms

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

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



### Predominant mechanisms

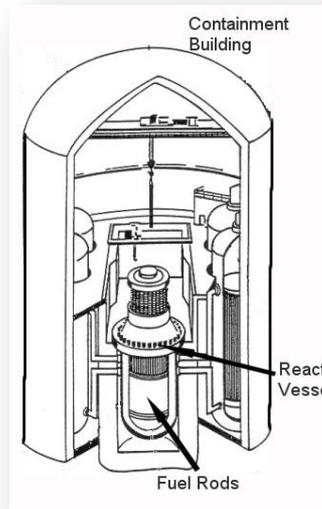
Flow Accelerated Corrosion (FAC)  
Stress Corrosion Cracking (SCC)



- ❑ **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

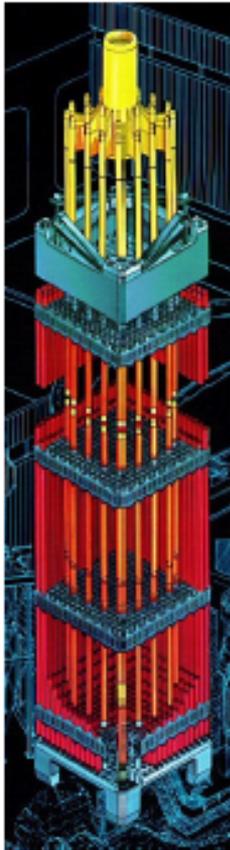


- ❑ **Reactor building:** evolution of concrete and corrosion of rebars

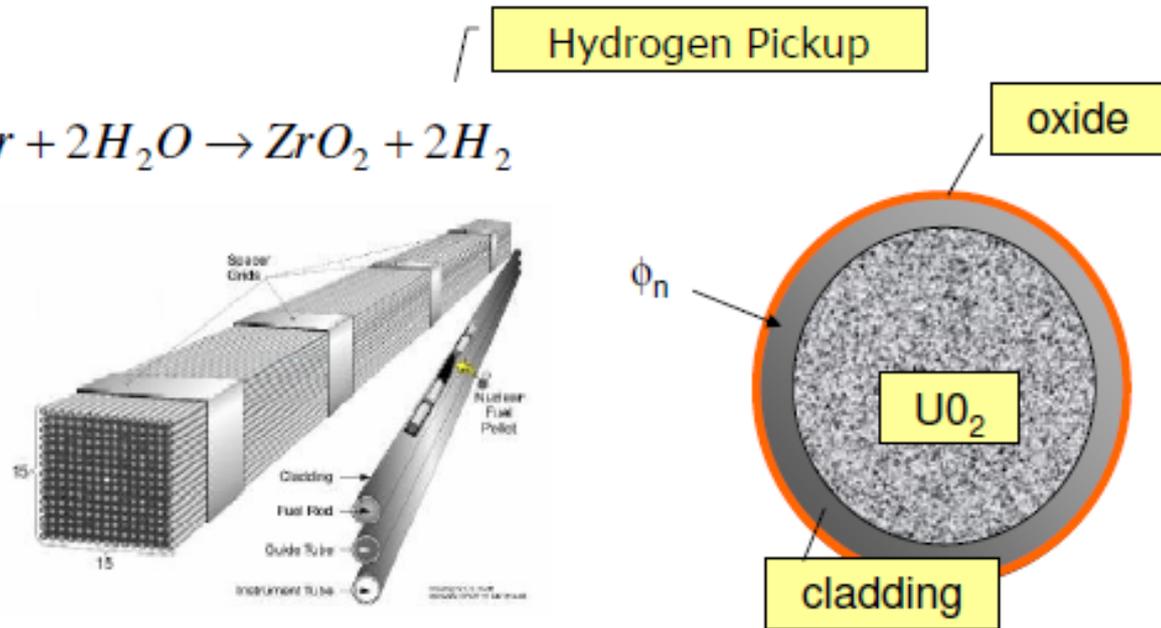
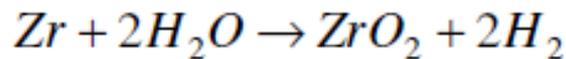


## Light Water Reactor Nuclear Fuel

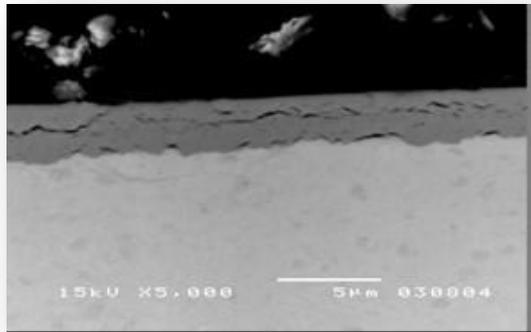
Immersed in water in reactor core, Zr alloy cladding undergoes hydriding and uniform corrosion on its outer diameter, and iodine SCC on its inner diameter



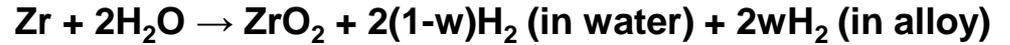
After A. Motta



# ZIRCALLOY: UNIFORM CORROSION IN PRIMARY MEDIUM



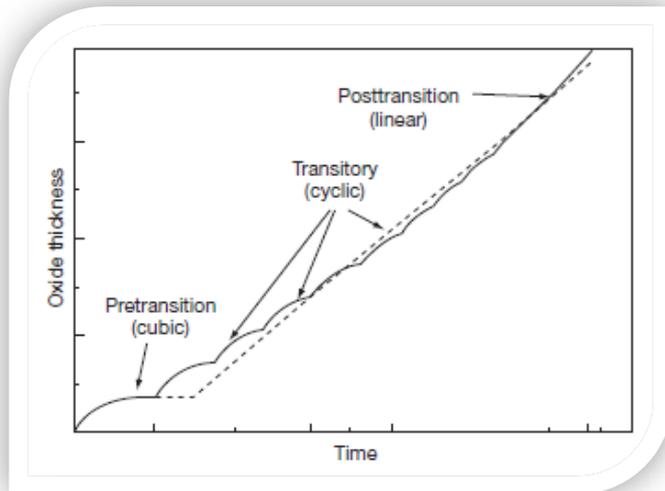
In primary conditions, the corrosion reaction is as follows:



$w$  = fraction of  $\text{H}_2$  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**

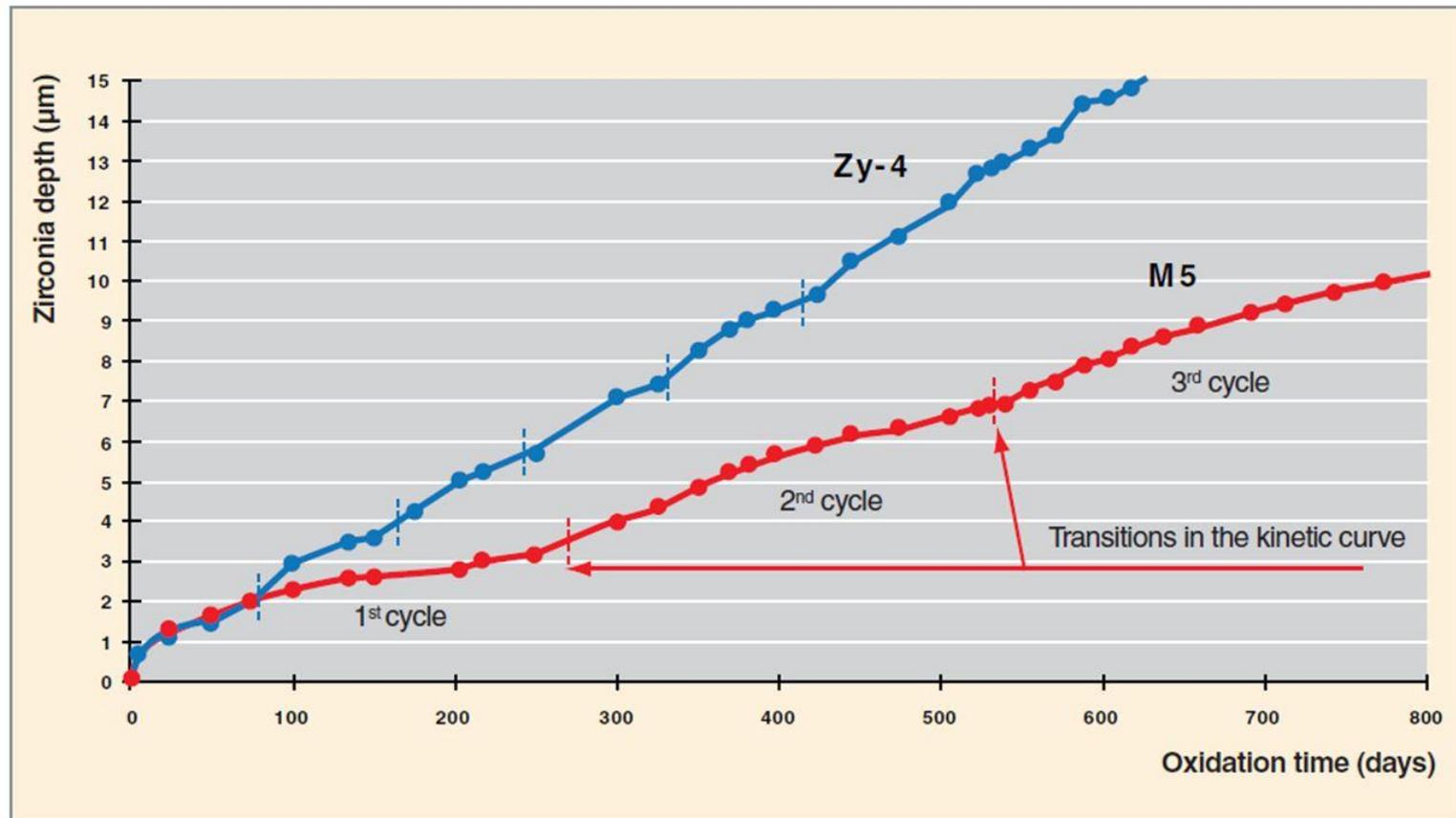


**Hydrides**

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

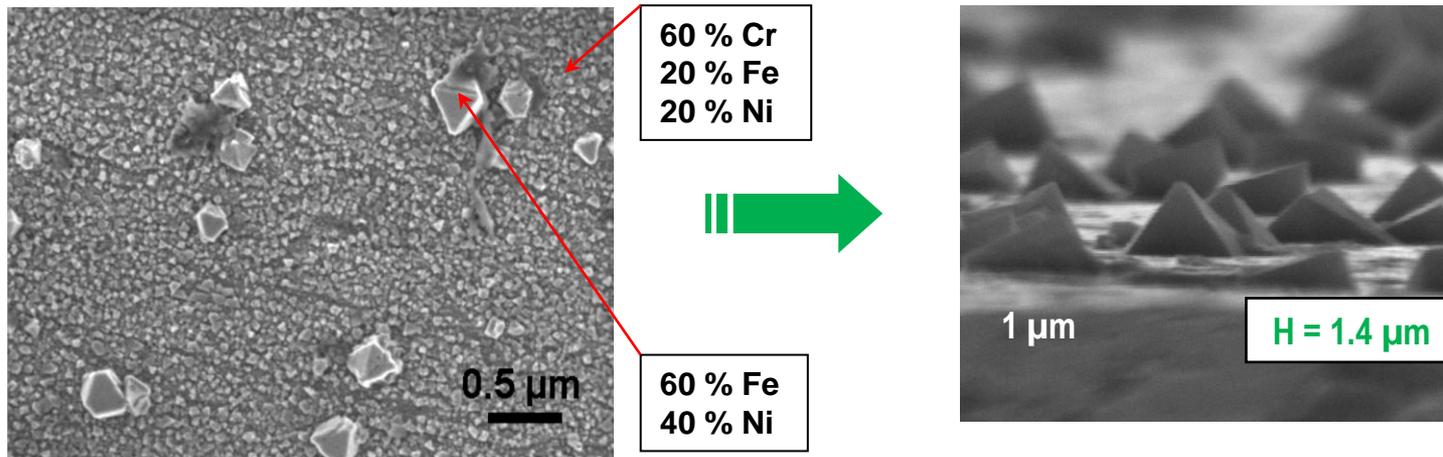
After P. Bouffioux & B. Cheng

## 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  $\Rightarrow$   $^{58}\text{Co}$   $\Rightarrow$   $^{60}\text{Co}$  in the core : **Dose rate increase**
- Intergranular oxidation – selective chromium oxidation

## □ Mitigation

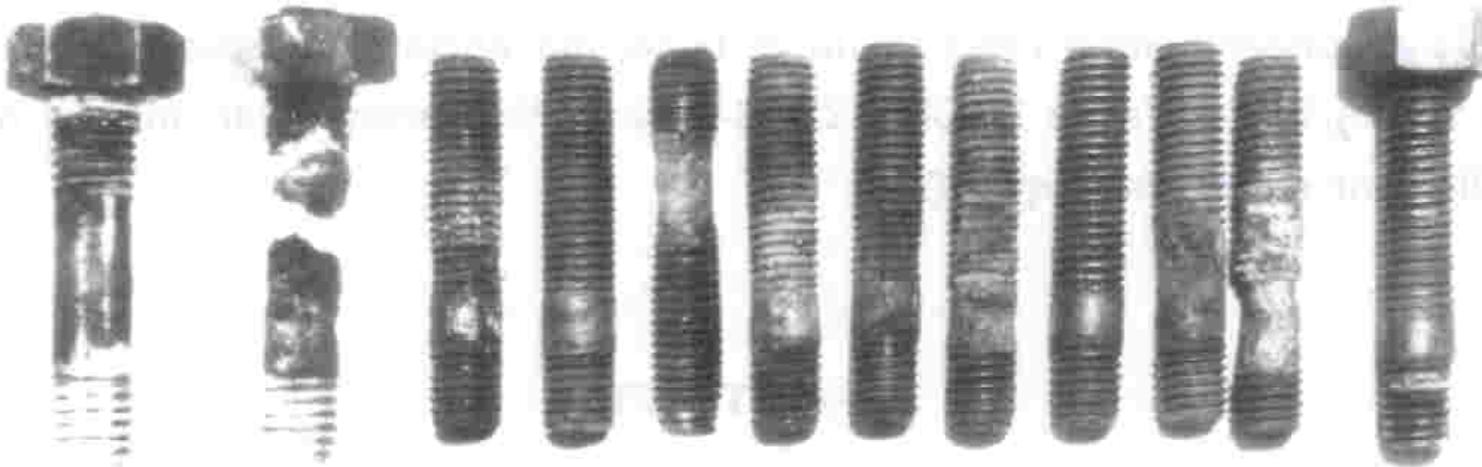
- pH adjustment to minimize oxide solubility. Zn addition to replace Ni in oxide ?

## ❑ 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**



## Boric acid deposit due to leaks



**South Texas (USA)**

**Vessel bottom**

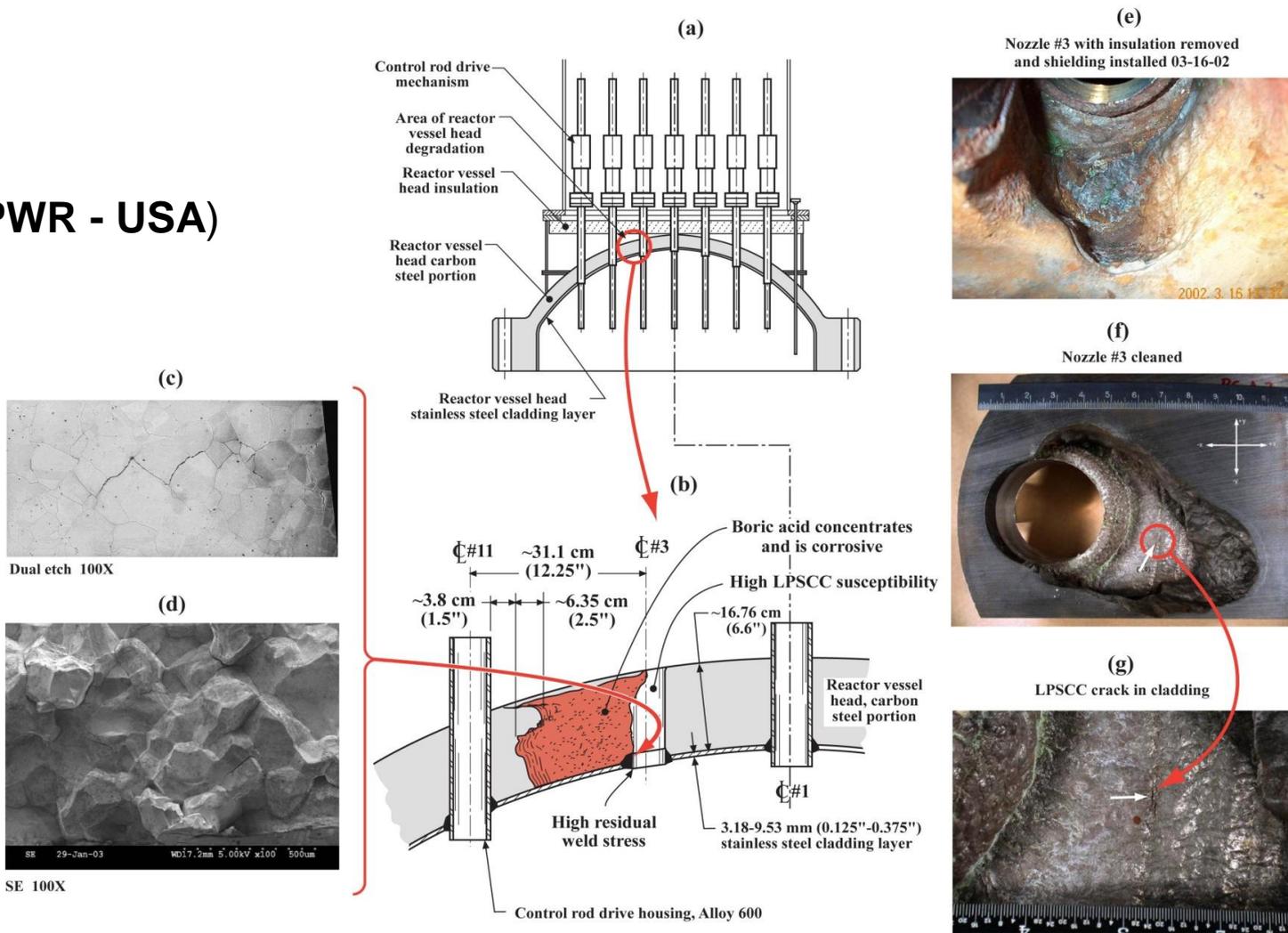


Nozzle 3 with insulation removed and shielding installed 03-16-02

**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)

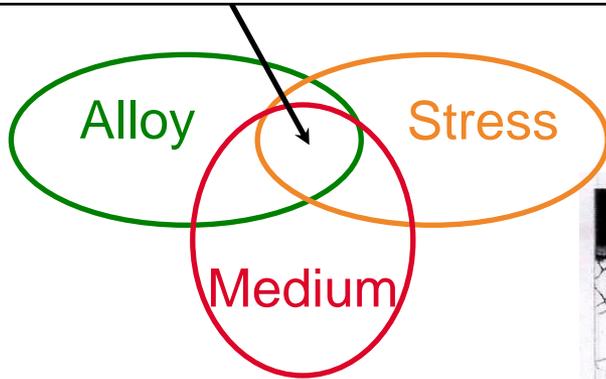
## ❑ Stainless steel

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

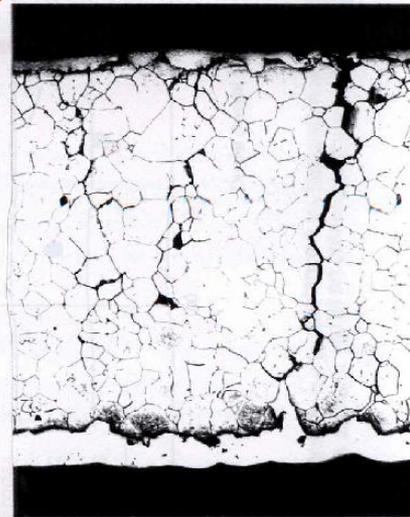
## ❑ Other alloys prone to SCC

- Brass (vapor or liquid polluted with  $\text{NH}_3$  or sulfide) in condensers
- Low alloy or carbon steel for bolting and auxiliary circuits (sodium hydroxide, nitrates, chlorides,  $\text{H}_2\text{S}$ )
- Titanium in condensers (cathodic potential ( $\text{H}_2$  embrittlement), hot medium with chloride)

## Stress Corrosion Cracking

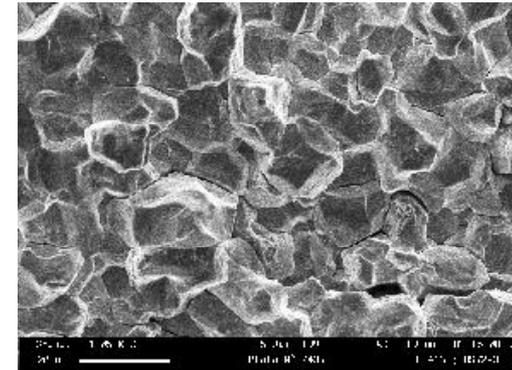


Lowering of  $R_m$ , A%  
Rupture through  
crack propagation



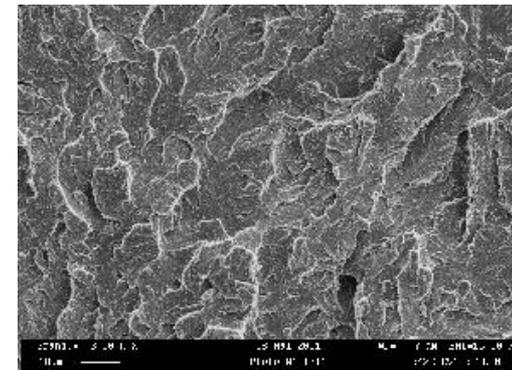
Welded alloy 600, SG tubing  
Saint-Laurent-des-Eaux 1  
(French PWR)

## Intergranular Cracking



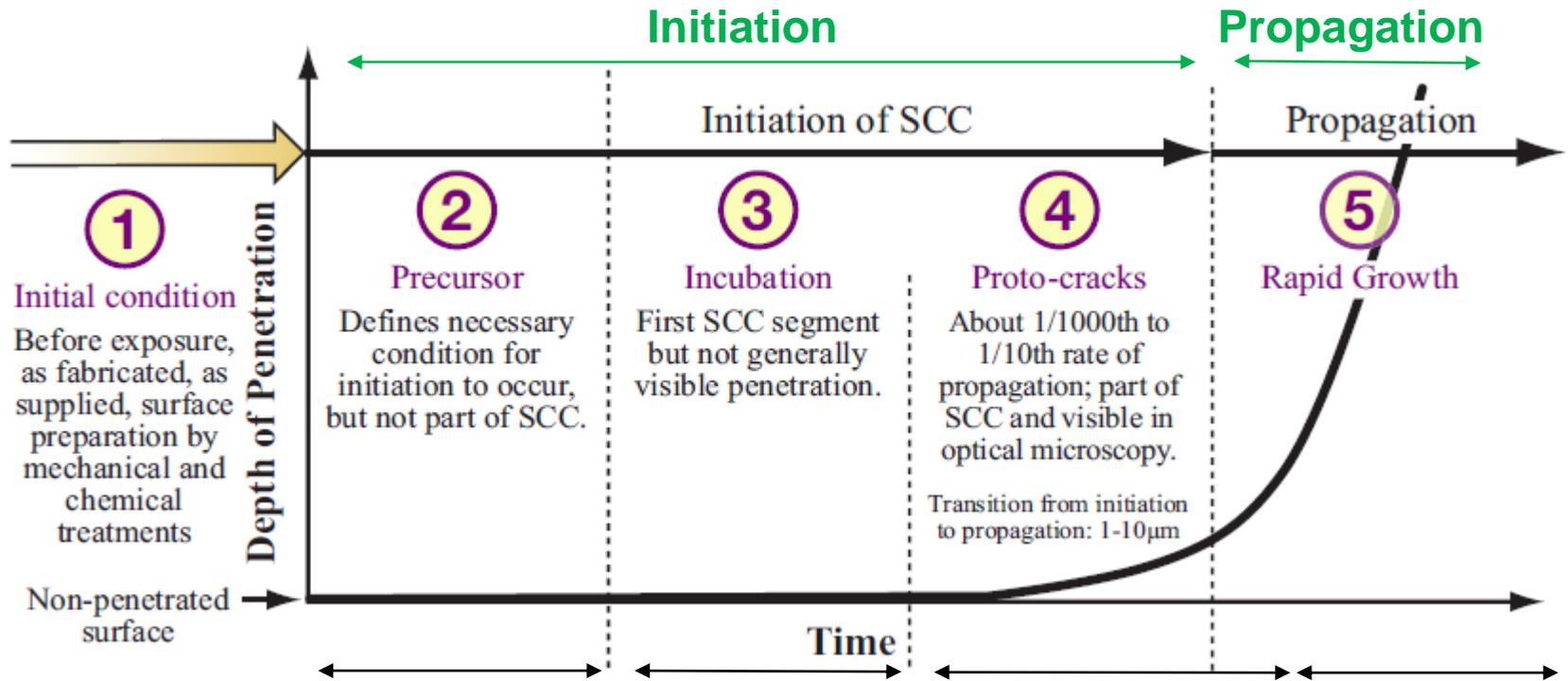
Alloy 600, SG tubing, primary water

## Transgranular Cracking



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

# DIFFERENT STAGES OF STRESS CORROSION CRACKING

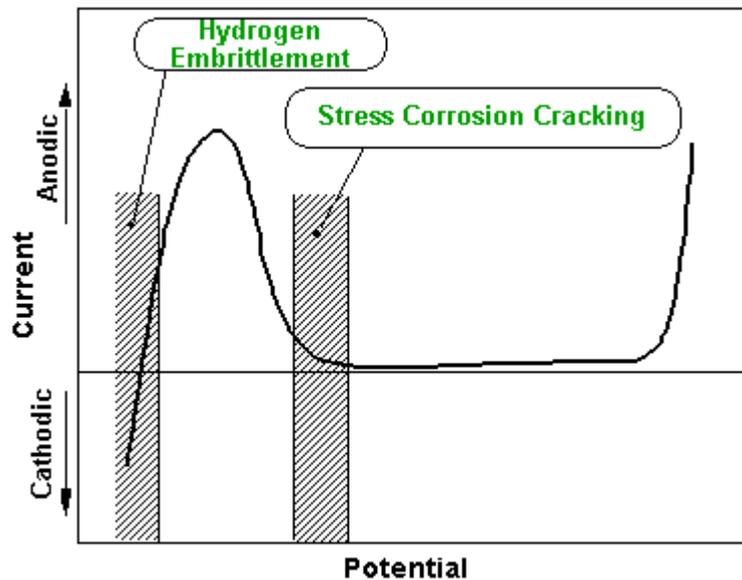


**For Ni base alloys :** Incubation      Initiation      Slow propagation      Rapid propagation

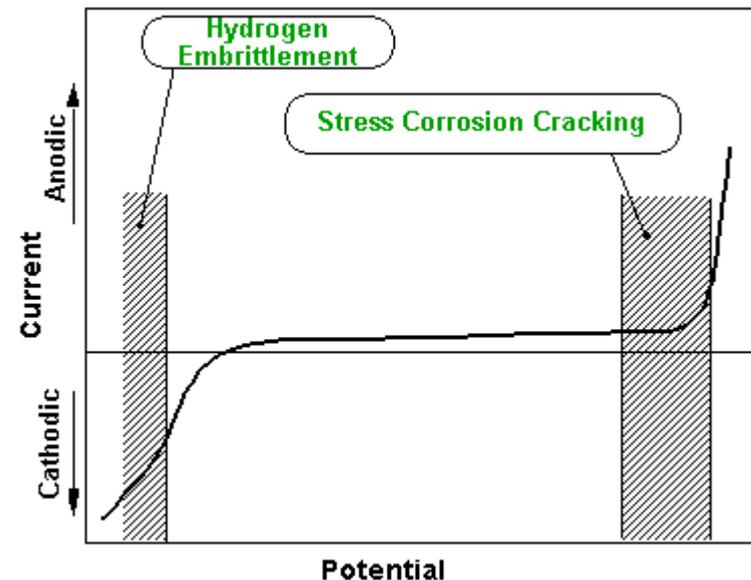
- (1) Importance of initial conditions
- (2) Preparatory phase (incubation)
- (3) Initiation phase followed by slow (4) and rapid propagation (5)

## Zones of relative "instability" of protective layers

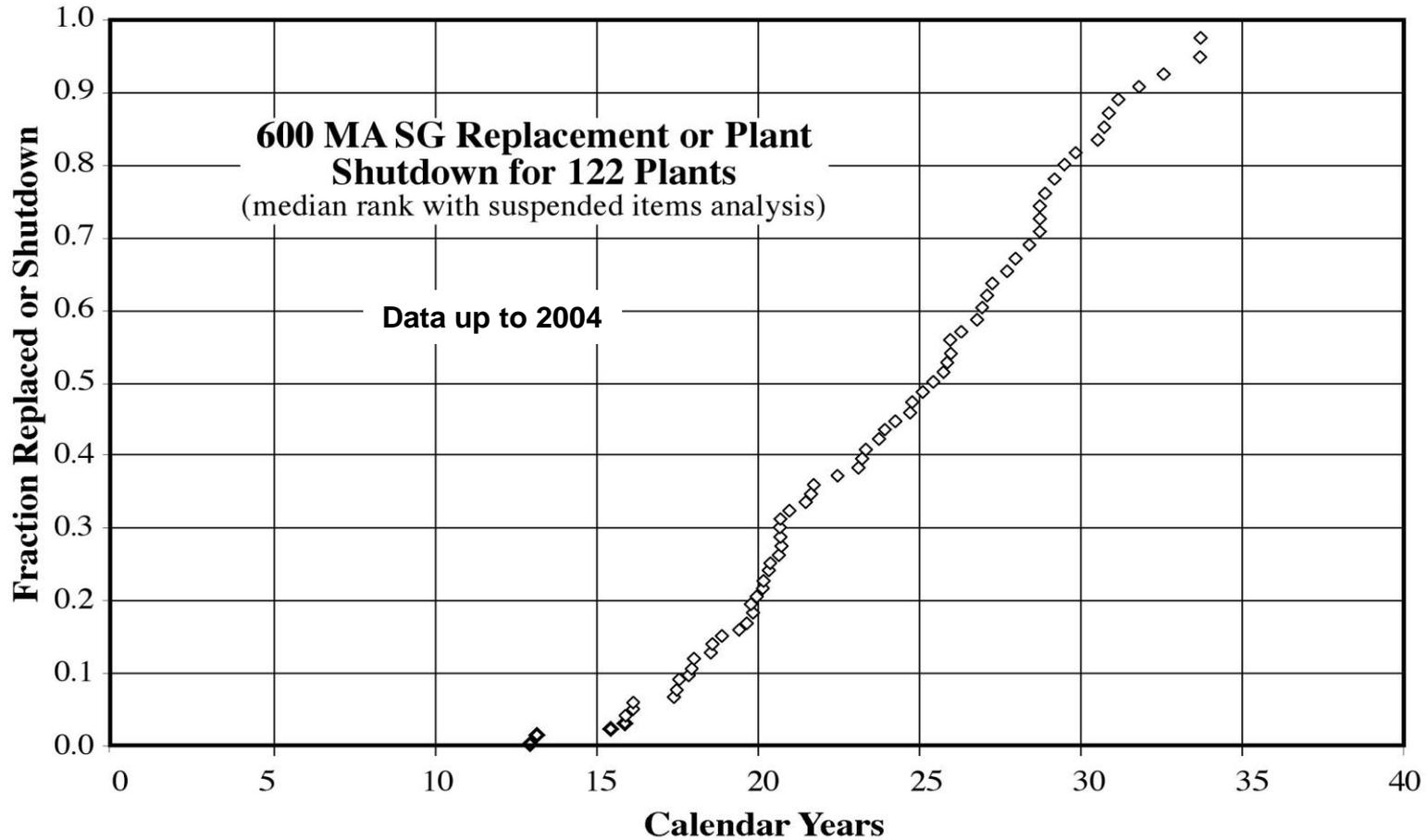
Systems with poor ability to passivate  
cracking in the active/passive transition



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



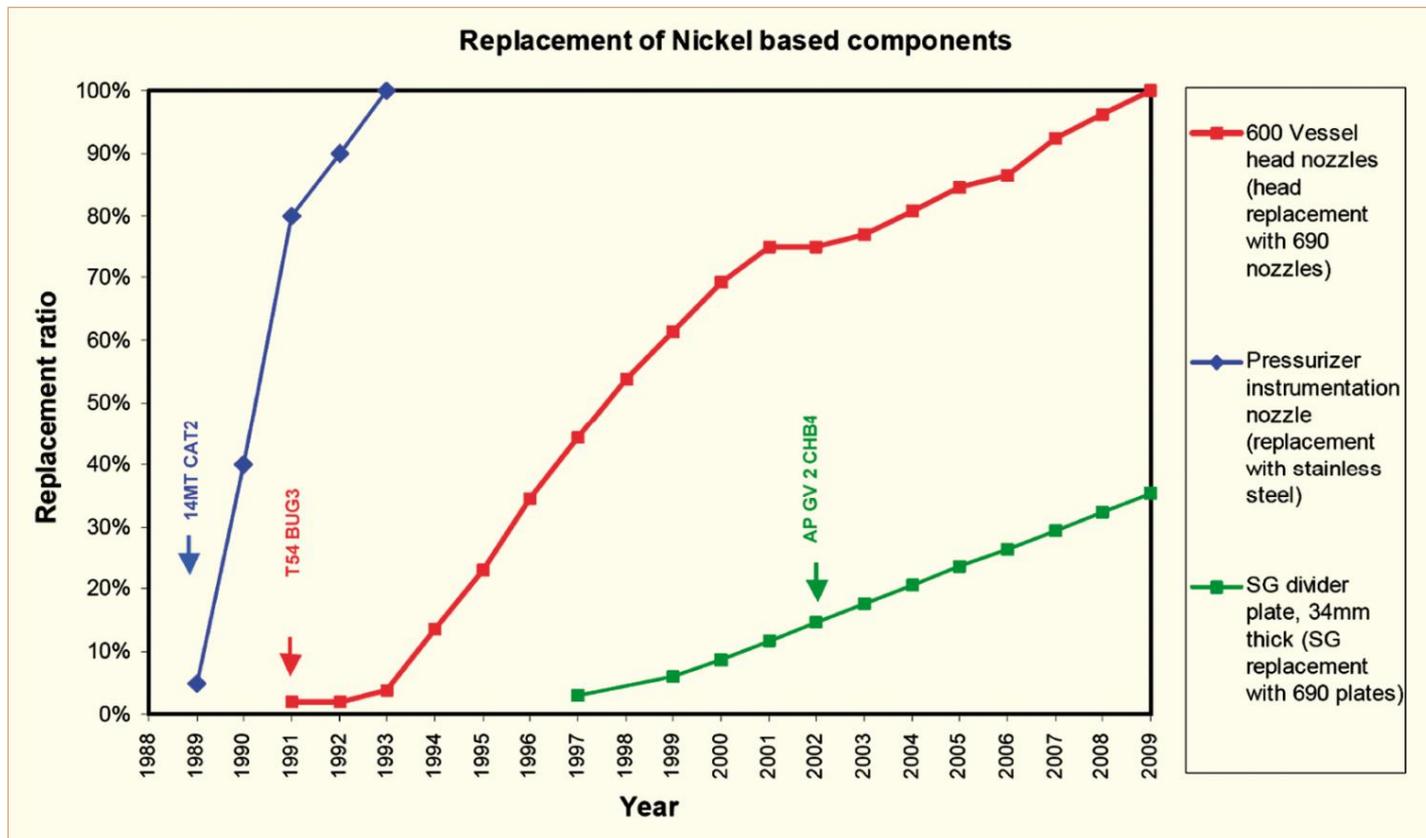


Replacement of a Steam Generator

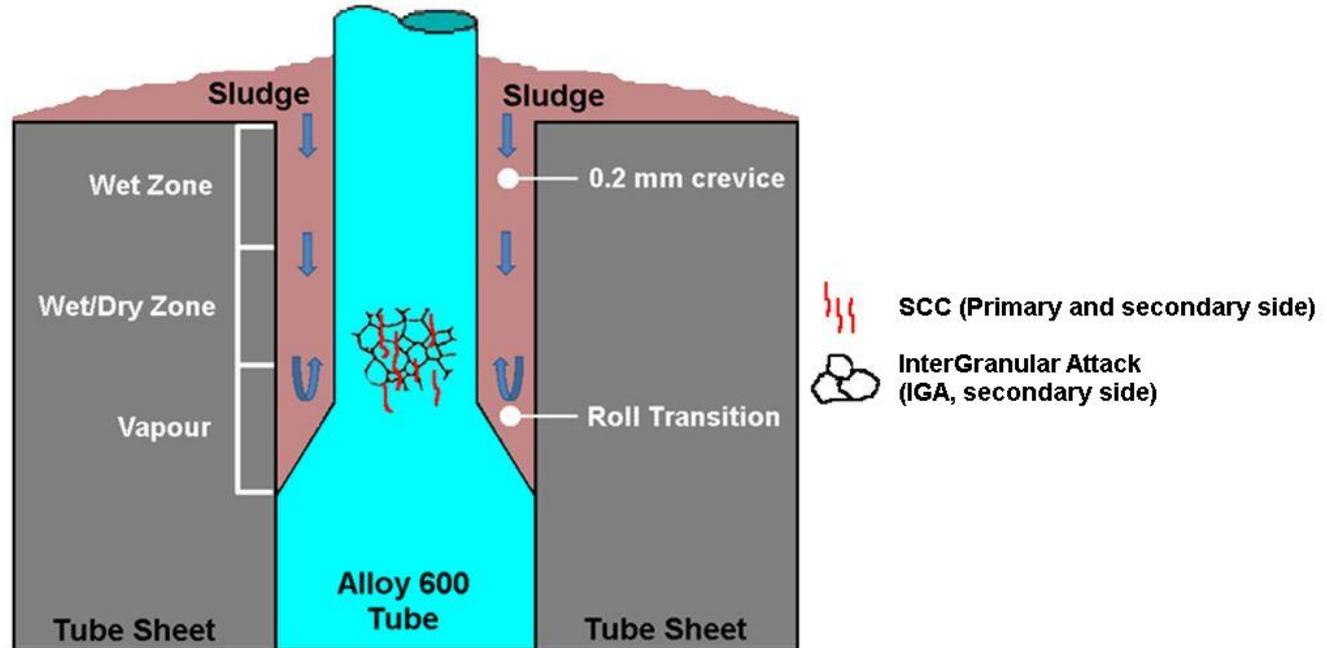
**Since 1998, AREVA has carried out more than 80 steam generator replacements, covering half of the market in the United States**

## □ 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



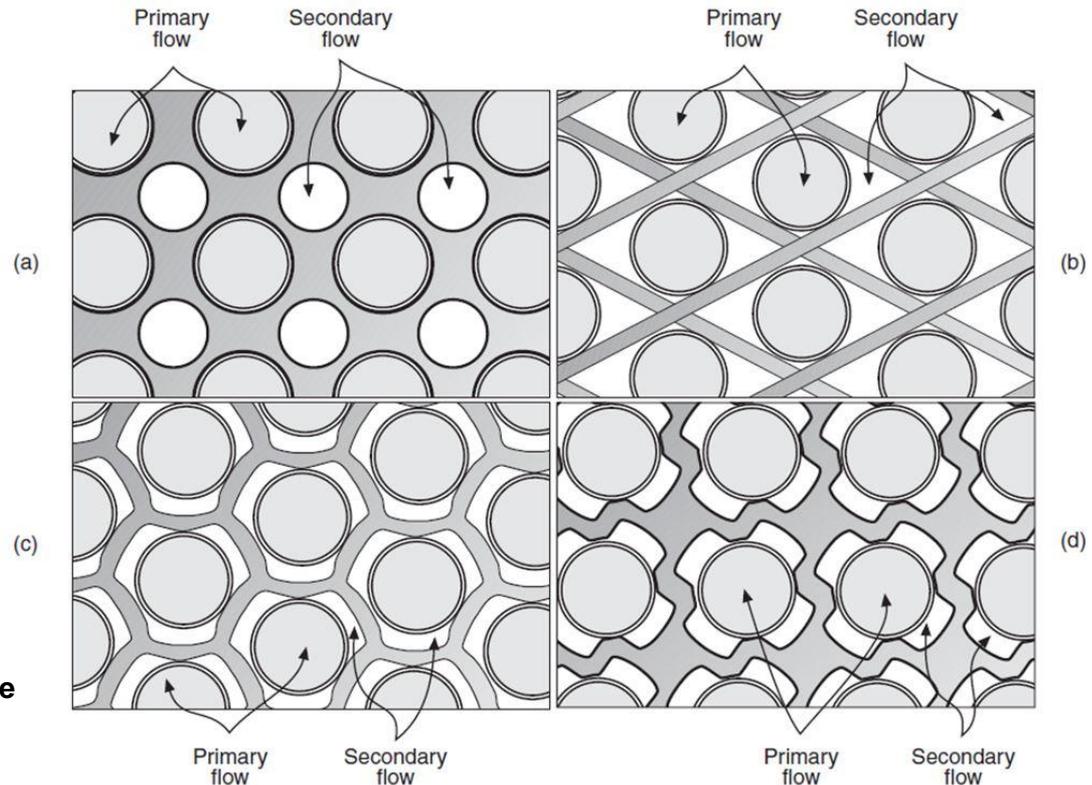
□ Accumulation of corrosion products at the interface causing stresses

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

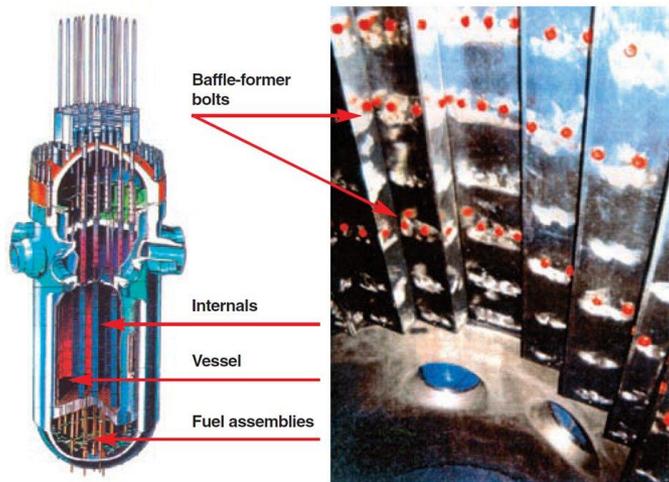
● Evolution of TSP geometry

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

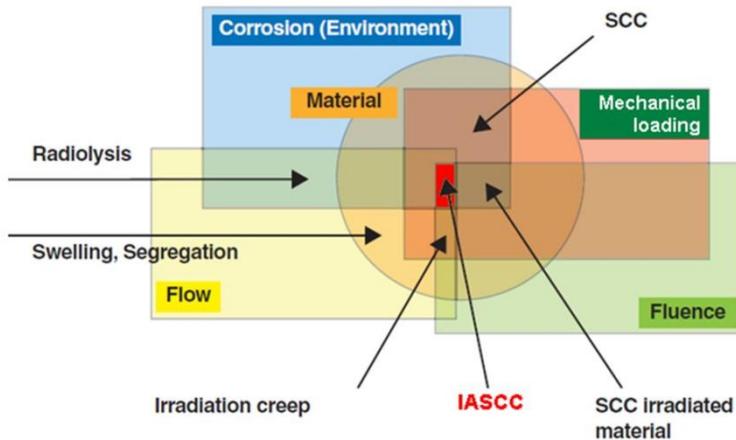
After R.W. Staehle



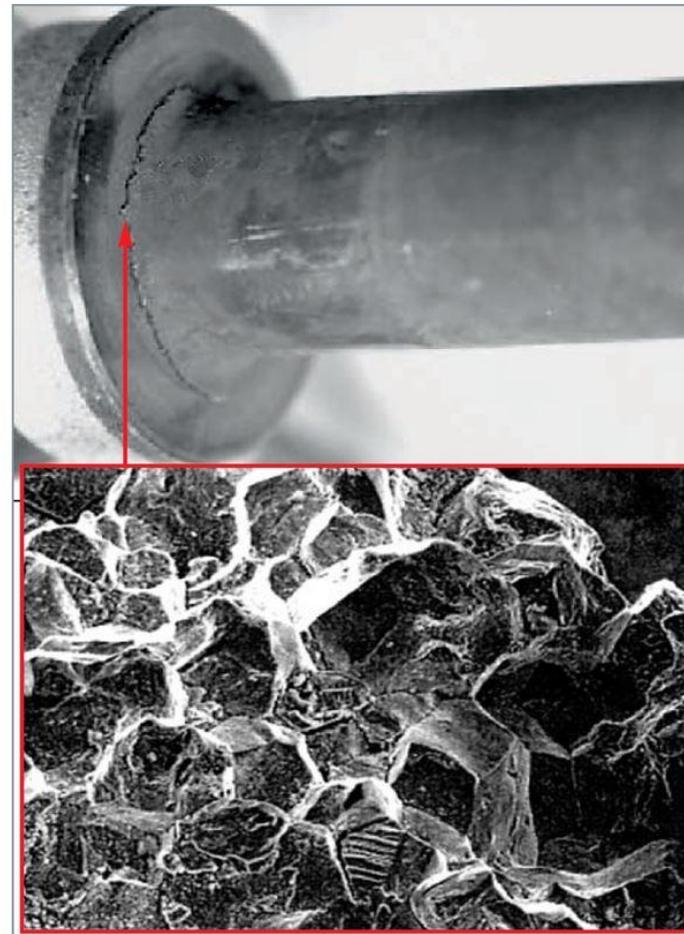
# IASCC OF STAINLESS STEEL VESSEL INTERNALS



PWR vessel internals



Sinergy factors involved in IASCC

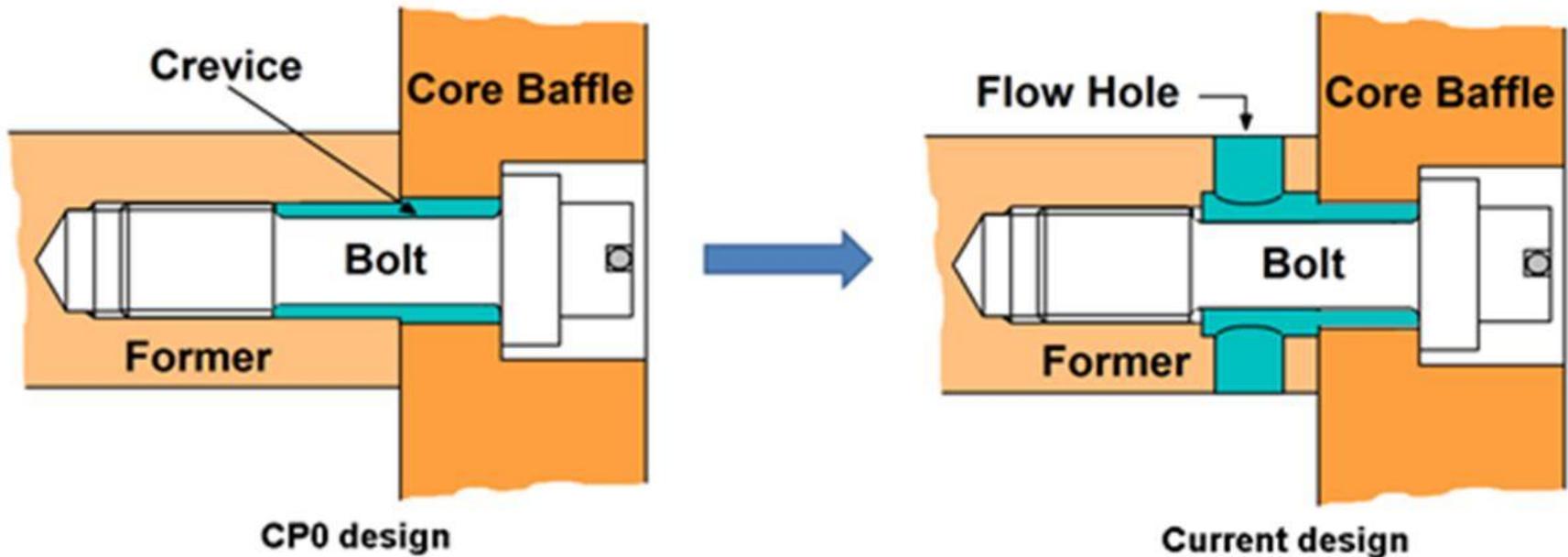


IASCC on an internal bolt of the French CPO series

### ❑ Crevice around the bolt shank

- Local boiling due to  $\gamma$  heating of the bolt
- LiOH, H<sub>3</sub>BO<sub>3</sub> 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

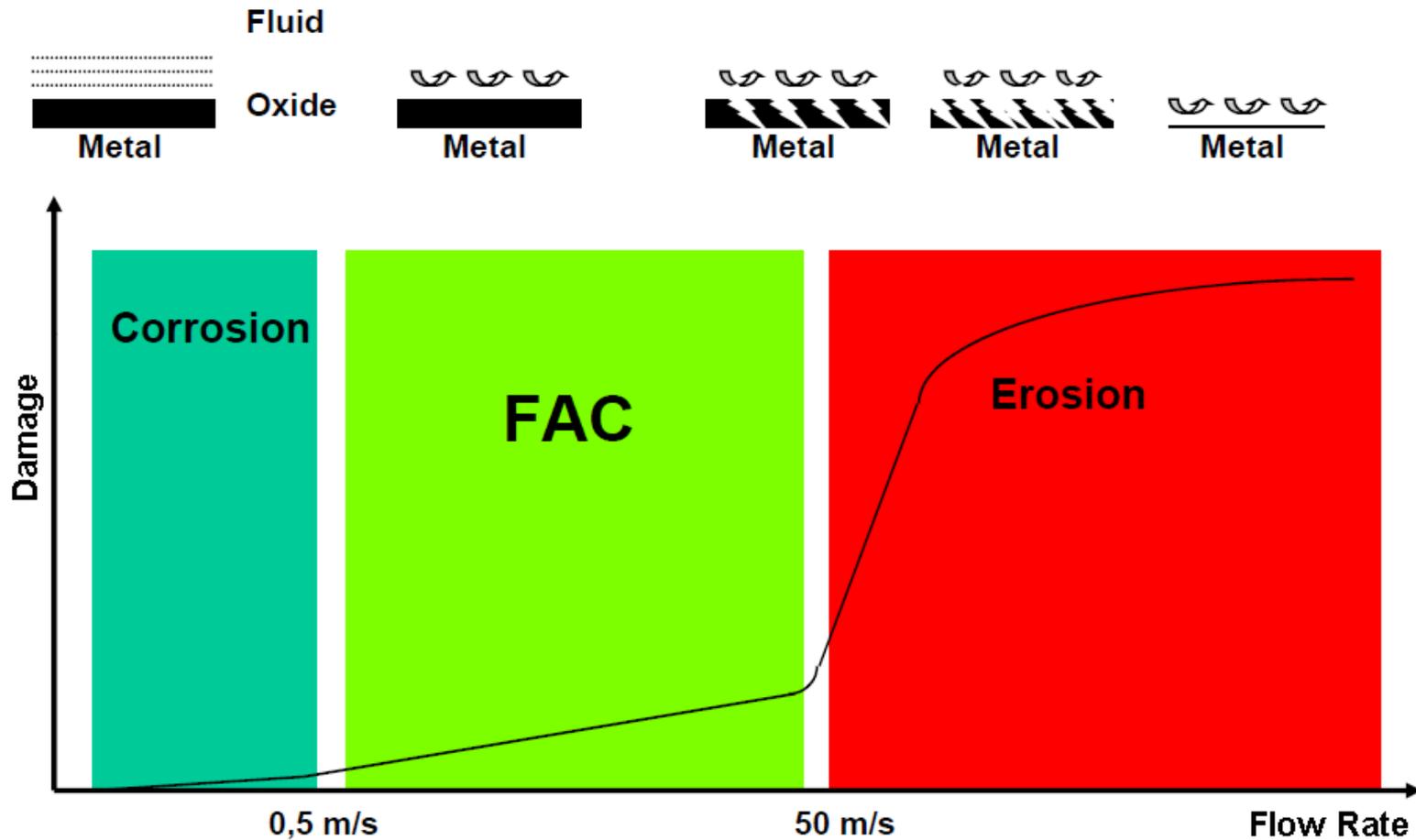
### □ Chemical stationary conditions

- 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



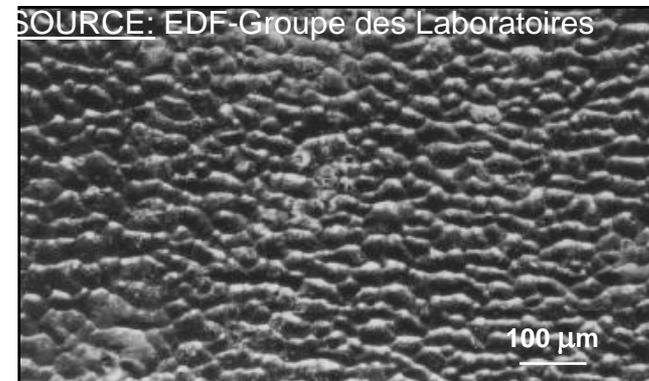
Domains of Corrosion, FAC, and Erosion depending on flow rate

(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

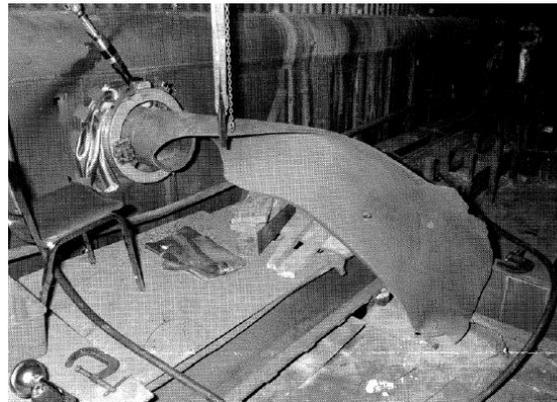
- Consequences: 2 dead

## ❑ 2004: MIHAMA 3 – 780MW PWR

- Consequences: 5 dead, 6 severely injured



**Surry 2: blow up of a 18" elbow**



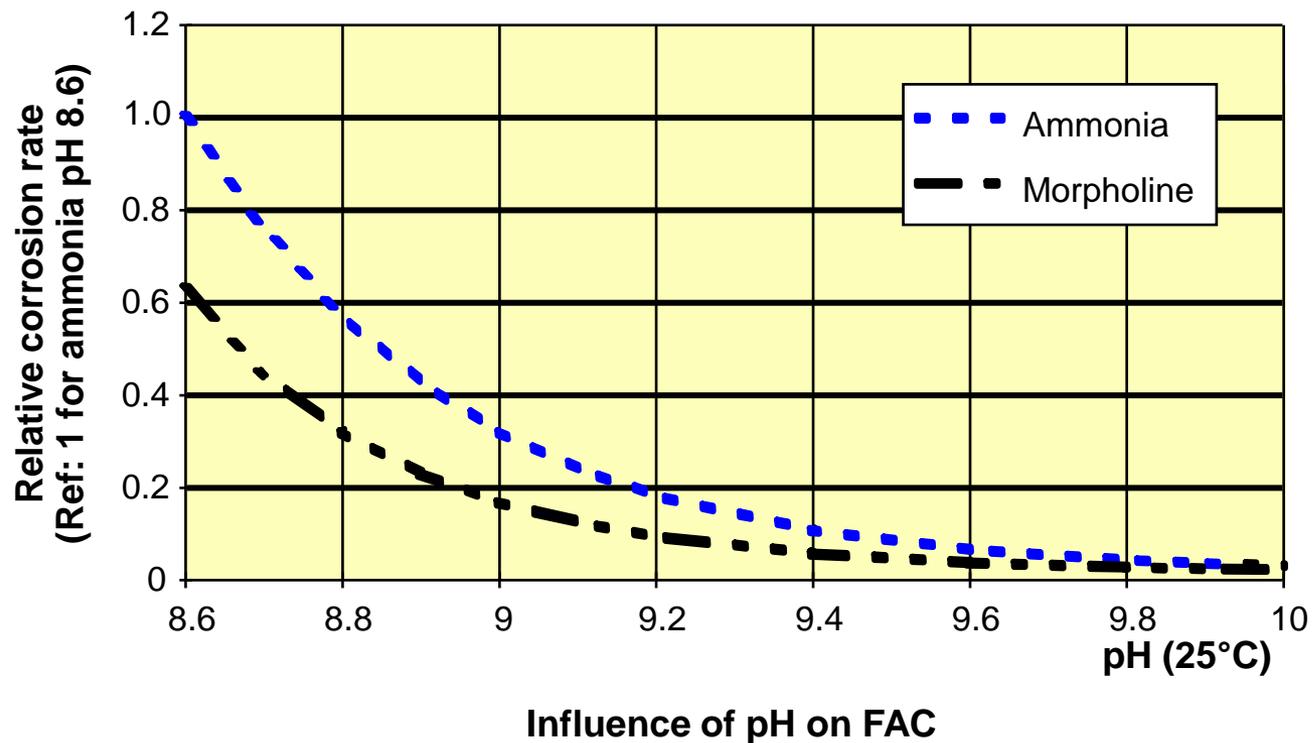
**Pleasant Prairie 1: blow up of a straight line after a "T"**



**Mihama 3: blow up of a 22" straight line**

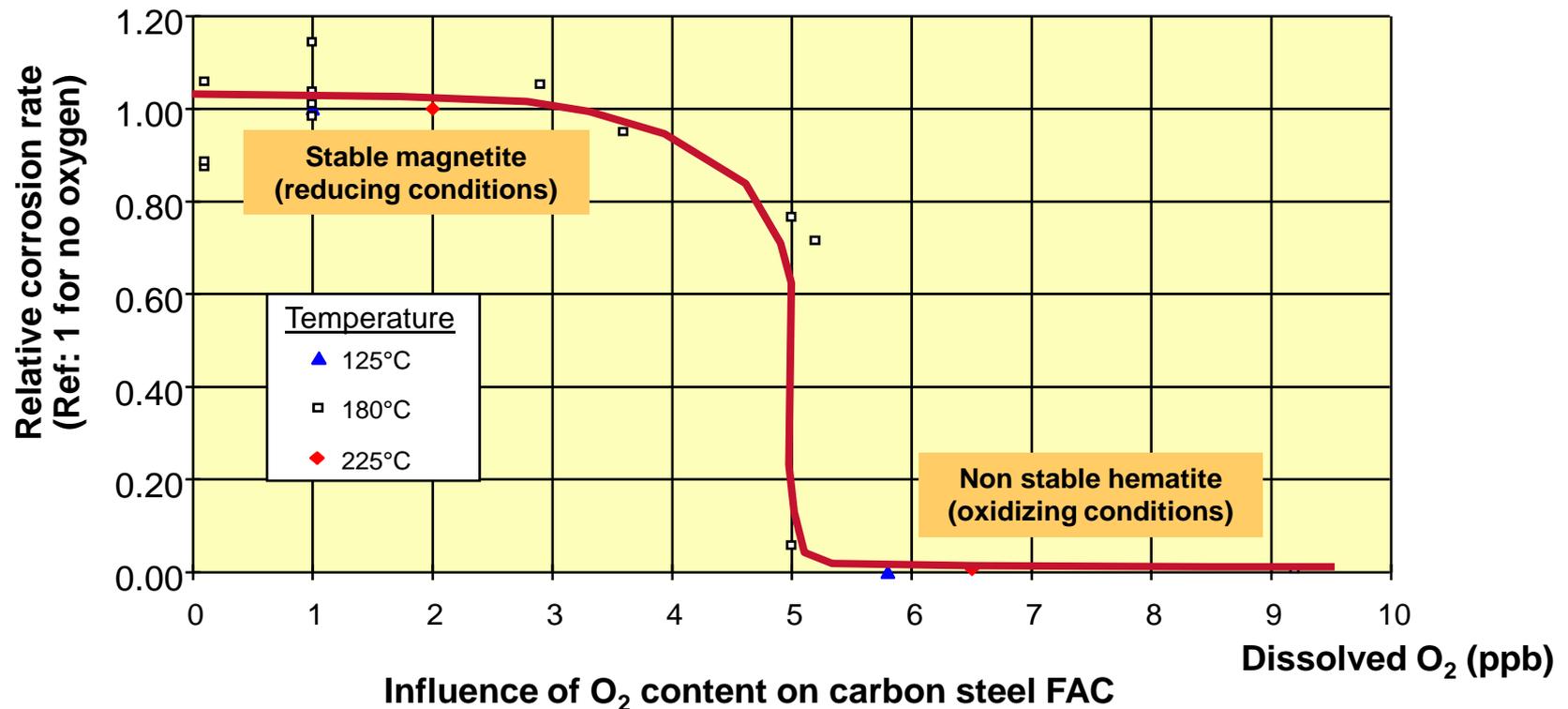
- pH has an important influence since it affects the solubility of metallic elements

● Increasing pH decreases FAC

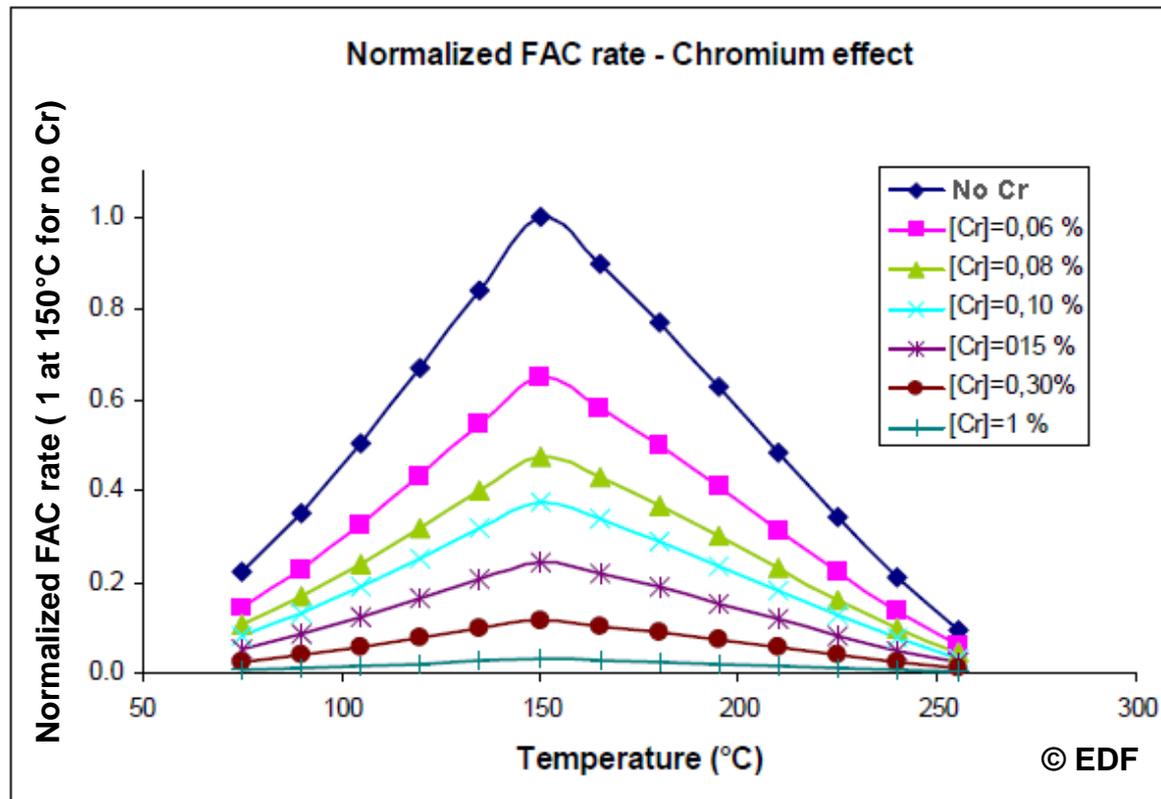


## □ O<sub>2</sub> content has an important influence on FAC since it affects the oxide nature and properties

- Increasing O<sub>2</sub> content decreases FAC
- No FAC above 5 ppb O<sub>2</sub>

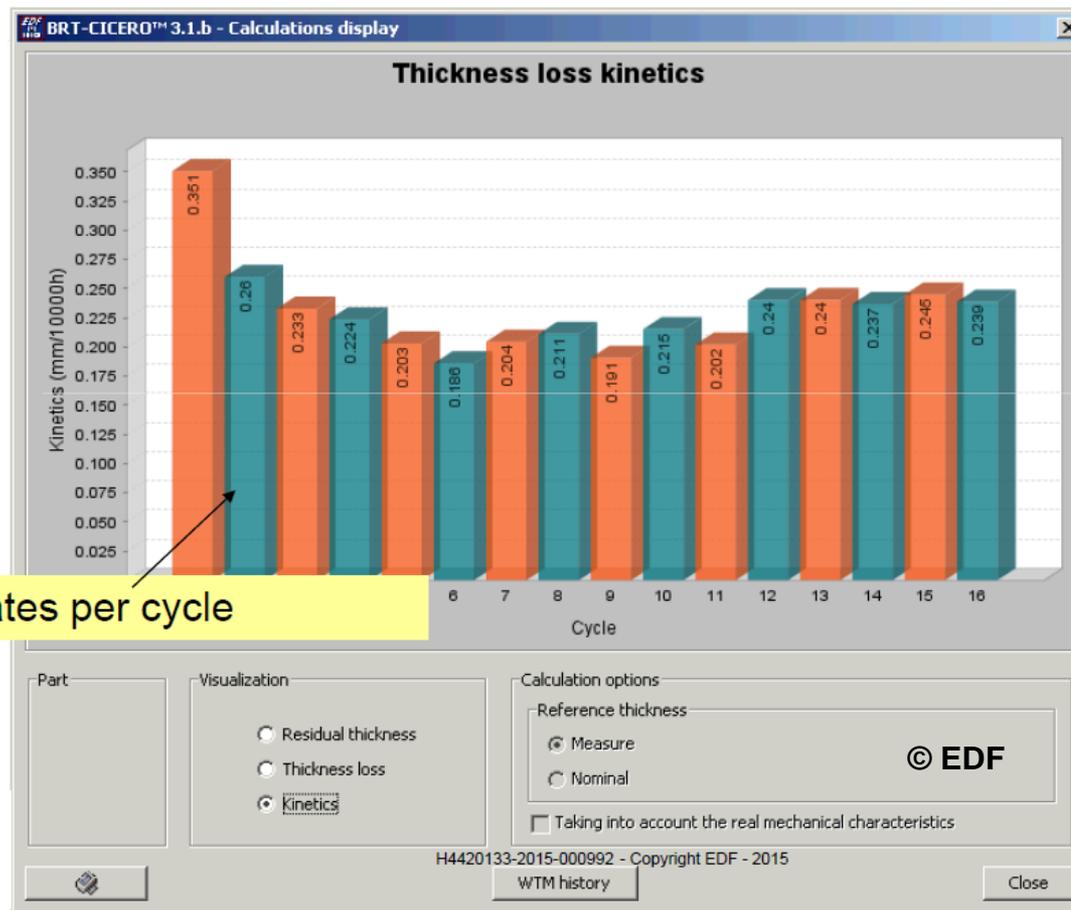


- Cr content has an important influence on FAC since it affects the oxide nature (formation of  $\text{Fe}_2\text{CrO}_4$  of poor solubility)
  - Increasing Cr content decreases FAC
  - No FAC above 1% Cr whatever the temperature



- ❑ **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



- 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

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Service de la corrosion et du comportement  
des matériaux dans leur environnement  
Laboratoire d'étude de la corrosion aqueuse