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# Nuclear corrosion and materials: achievements and challenges

D. Feron

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Submitted on 13 Jan 2020

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# NUCLEAR CORROSION & MATERIALS: ACHIEVEMENTS & CHALLENGES

Lee Hsun Lecture Award  
Institut of Metal Research, Chinese Academy of Sciences  
Shenyang  
November 15, 2016

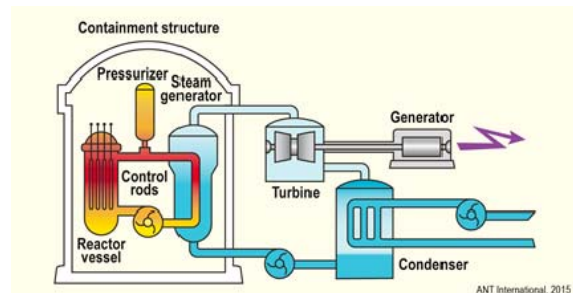
**Damien Féron**

Service de la corrosion et du comportement des matériaux dans leur environnement  
Commissariat à l'énergie atomique et aux énergies alternatives  
*French atomic energy and alternatives energies Commission*  
Saclay, France



## CONTENT

- ❑ Introduction: CEA Corrosion Department
  
- ❑ Gen 2&3 (Pressurized Water Reactor – PWR)
  - ❑ Fuel cladding
  - ❑ Steam generator tubing
  - ❑ Secondary circuits
  
- ❑ Conclusion: multiscale modelling



# « CEA CORROSION DEPARTMENT »

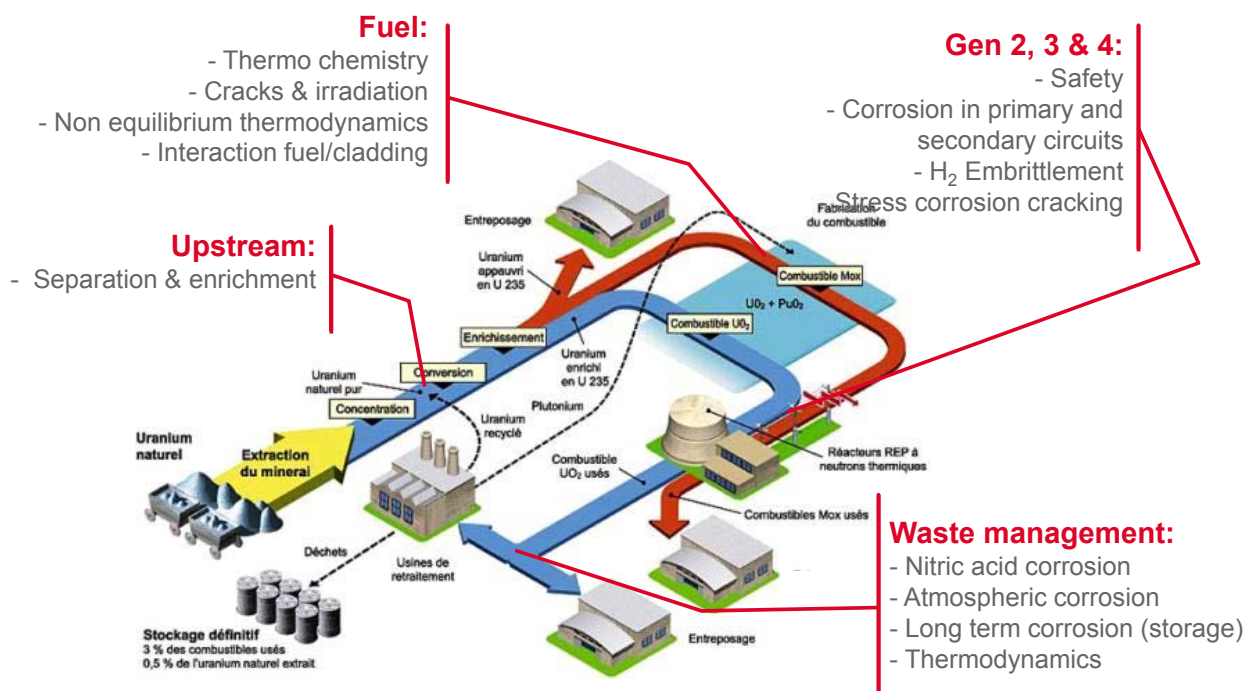
## SERVICE DE LA CORROSION ET DU COMPORTEMENT DES MATÉRIAUX DANS LEUR ENVIRONNEMENT (DEN/DANS/DPC/SCCME)



2017

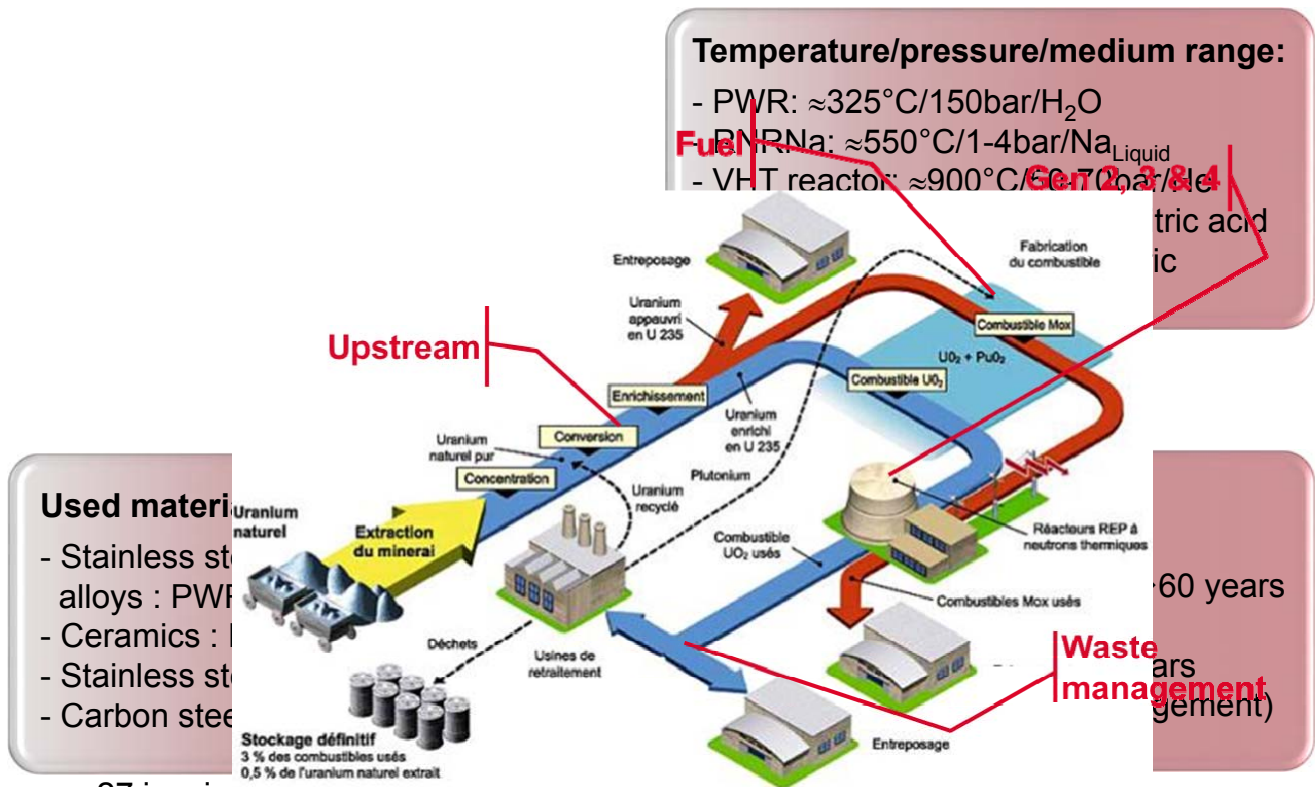


## ACTIVITIES: THE NUCLEAR FUEL CYCLE



27 janvier

2017

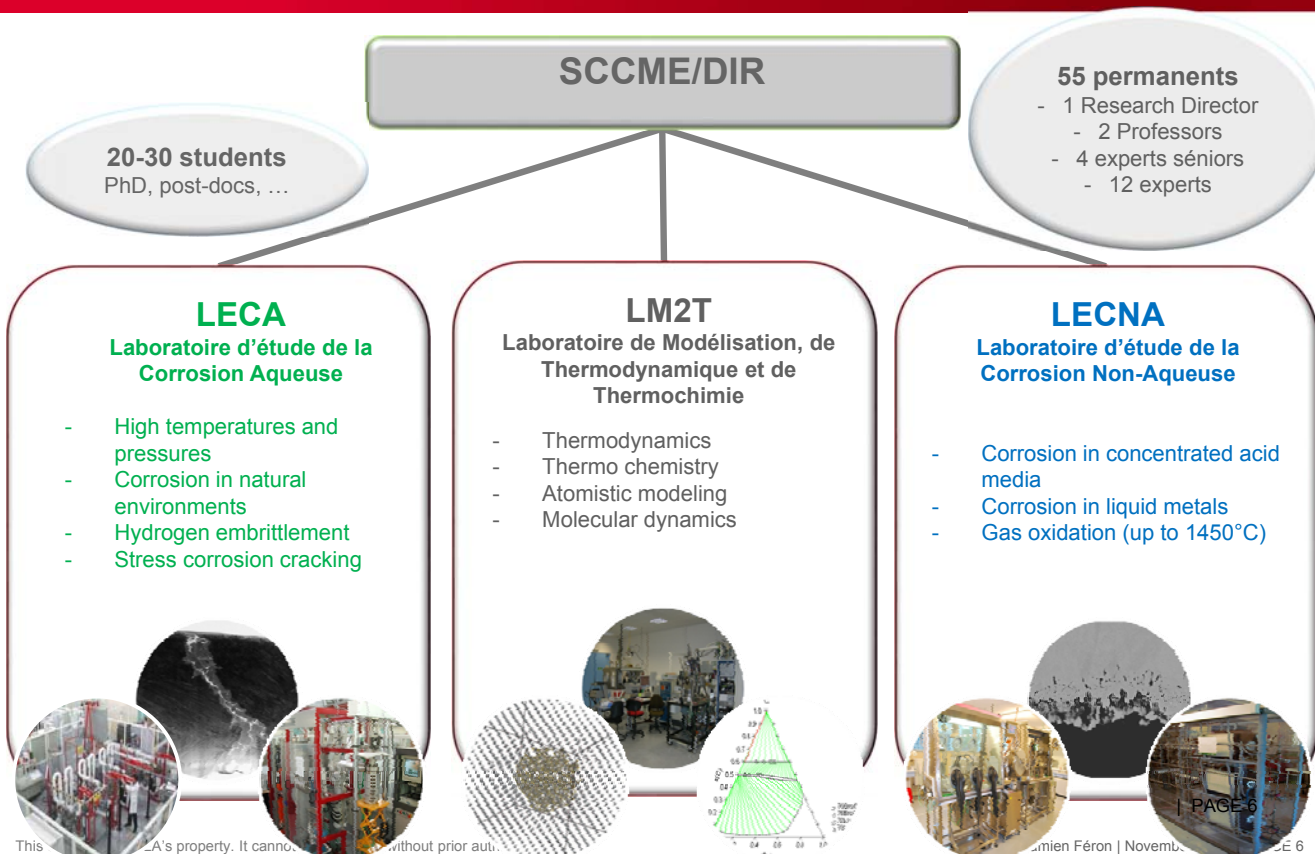


**Used materials**

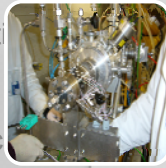
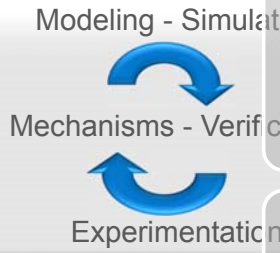
- Stainless steels
- Alloys : PWR
- Ceramics :
- Stainless steels
- Carbon steel

27 janvier 2017

## ORGANISATION

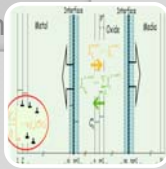






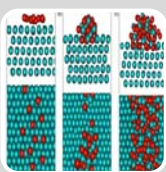
## Data acquisition

- ### Experiments & surface analysis
- Specific facilities (autoclaves, loops...)
  - Specific methods (isotopic tracers)
  - Surface analyses



## Mesoscopic modeling

- Semi-empirical modelling
- Uniform corrosion, Intergranular corrosion...
- Estimation of the Kinetics of Oxidation
- Diffusion Poisson Coupled Model



## Simulations

- Thermodynamics (Calphad, PhreeCea,...)
- Cellular automata
- Atomistic & molecular dynamics

## Evolutions

- From semi-empiricisms to mechanisms
- From large to "smart" experiments
- From macroscopic to multi-scales coupling

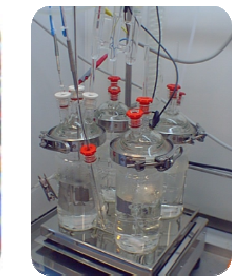


Irradiation facilities: CEA JANNus, and also LSI or CNRS-Orléans in France,...

Stress Corrosion Cracking



Autoclaves & loops with tensile machines

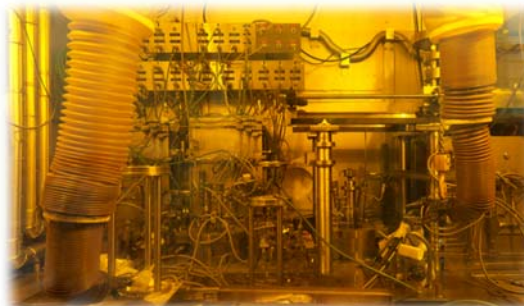


Electrochemical cells

Oxidation & H<sub>2</sub>



Irradiated materials (stainless steel & zircaloy)



Facility with 3 autoclaves and one tensile machine in hot cell (HP & HT)

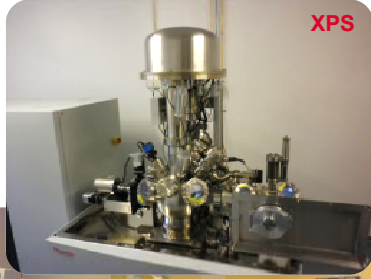
Irradiation & electrochemistry



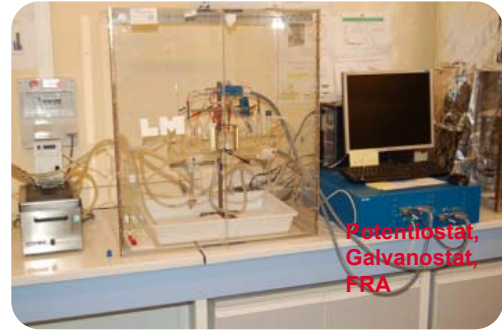
HP & HT cell (irradiations)

## SPECIFIC ANALYTICAL FACILITIES

■ Surface analyses



■ Electrochemistry



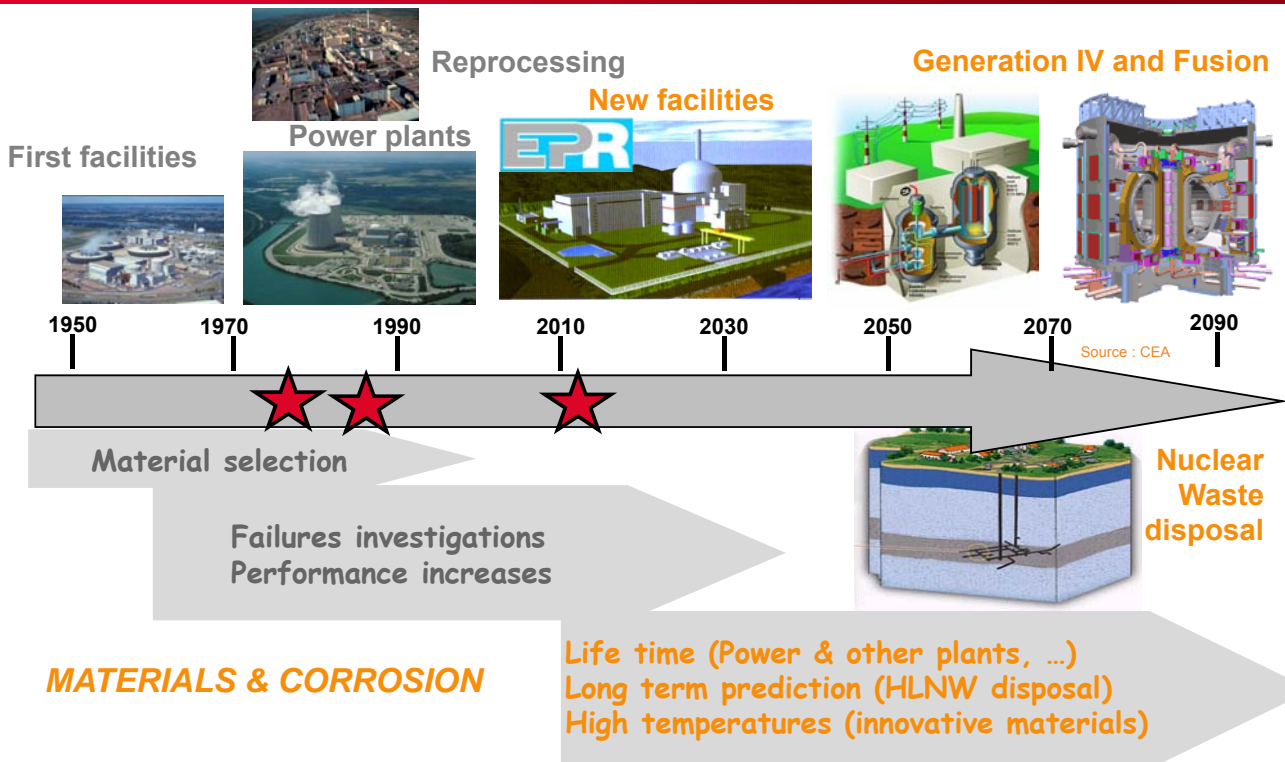
■ Solution analyses



MEB-FEG

Large collaborations with Universities and CNRS for photo-electrochemistry (Grenoble), SIMS (Versailles), TEM (Mines Paris-Tech), TAP (Rouen, Oxford)....

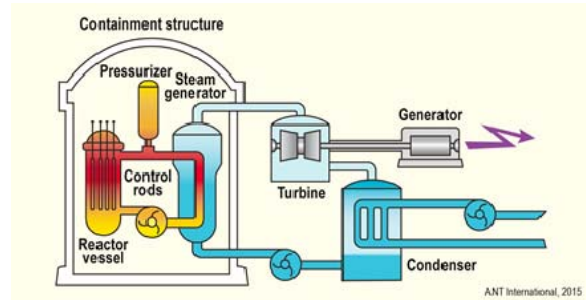
## NUCLEAR MATERIALS: from yesterday to tomorrow



❑ Introduction: CEA Corrosion Department

❑ Gen 2&3 (Pressurized Water Reactor – PWR)

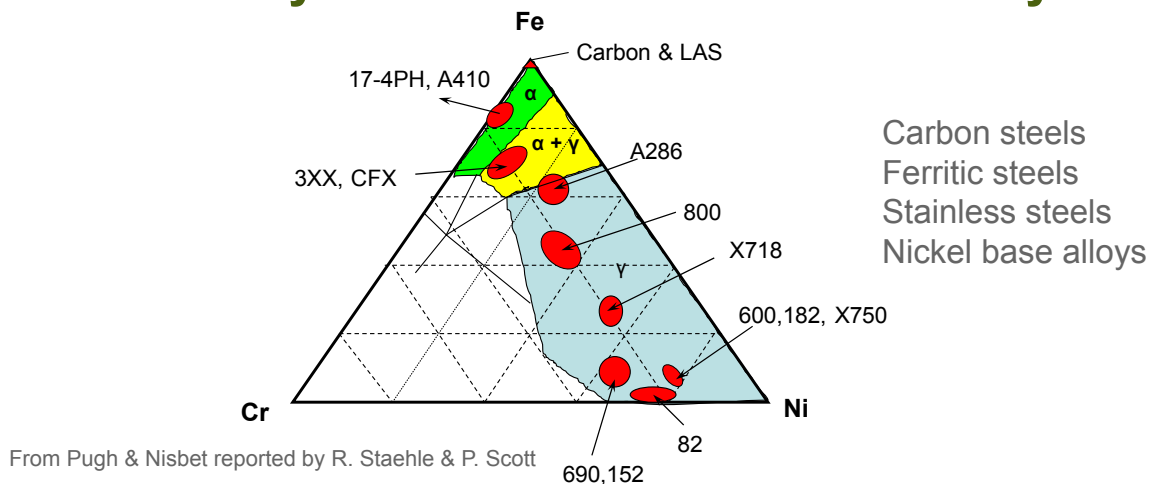
- ❑ Fuel cladding
- ❑ Steam generator tubing
- ❑ Secondary circuits



❑ Conclusion: multiscale modelling

**Cladding: Zirconium alloys**

**Structural alloys: steels and nickel base alloys**



**Evolution of the alloys due to corrosion issues**



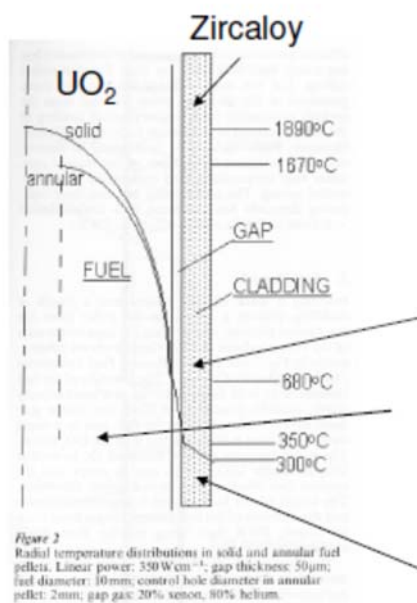
## FUEL CLADDING

## EVOLUTIONS OF ZR ALLOYS LINKED TO CORROSION ISSUES



## PWR FUEL CLADDING

### SOLLICITATIONS & EXPECTATIONS



From A. Motta

Pressure vessel: 40-60 years operation,  $< 1 \text{ dpa}$

Fuel: 3-5 years in reactor

About 20-40 displacements per atom (dpa)

About 40,000 dpa, highly radioactive

ZrO<sub>2</sub> oxide layer up to 120 micron and [H] content up to 700 wt ppm



| 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 1

|  | BWR                    | PWR                    | WER                    | CANDU                |
|--|------------------------|------------------------|------------------------|----------------------|
| Coolant  | H <sub>2</sub> O       | H <sub>2</sub> O       | H <sub>2</sub> O       | D <sub>2</sub> O     |
| 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* (ncm <sup>-2</sup> s <sup>-1</sup> ) | 4-7 × 10 <sup>13</sup> | 6-9 × 10 <sup>13</sup> | 5-7 × 10 <sup>13</sup> | 2 × 10 <sup>12</sup> |
| Coolant chemistry                                  |                        |                        |                        |                      |
| [O <sub>2</sub> ] (ppb)                            | ~200                   | <0.05                  | < 0.1                  | <5                   |
| [H <sub>2</sub> ] (ppm)                            | ~0.03                  | 2-5                    | -                      | 0.5-1                |
| pH   | 7                      | 6.9-7.4                | -                      | 10.2-10.8            |
| B (as H <sub>3</sub> BO <sub>3</sub> ) (ppm)       | -                      | 0-2200                 | 0-1400 <sup>16</sup>   | -                    |
| 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 <sub>3</sub> (ppm)                              | -                      | -                      | 6-30                   | -                    |

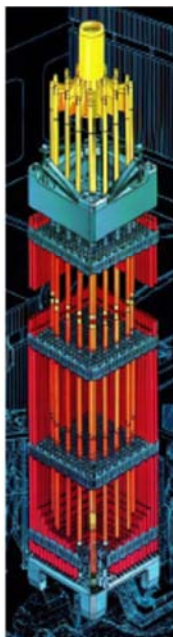
Typical reactor environments to which zirconium alloys are exposed

\*E > 1 MeV.

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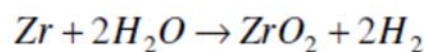
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## Ligh water reactor nuclear fuel cladding

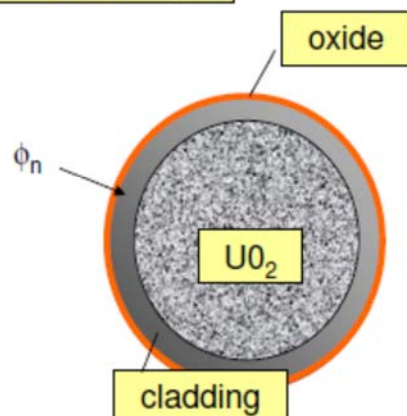
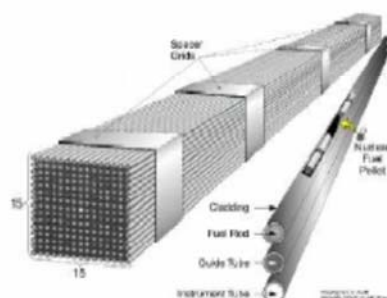


In reactor, Zr alloy cladding undergoes

- on the outer surface (water side)
  - General corrosion from primary water
  - Hydriding
- on the inner surface (oxide side)
  - Stress corrosion cracking (iodine)



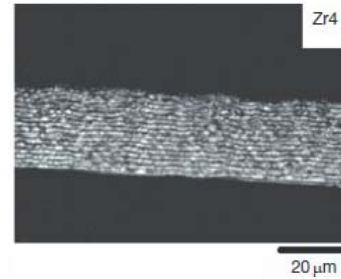
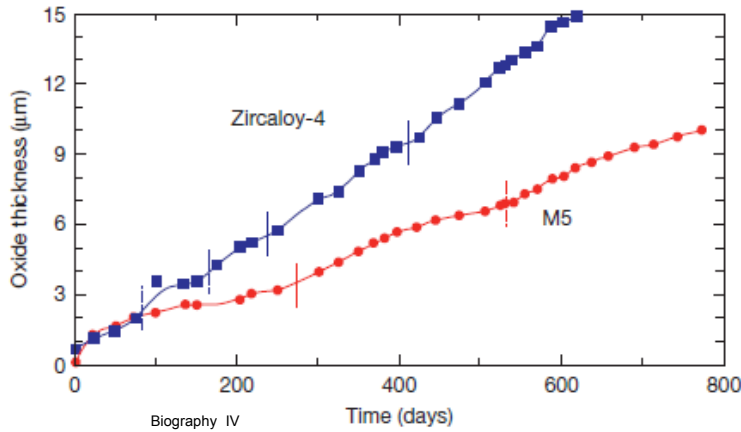
Hydrogen Pickup



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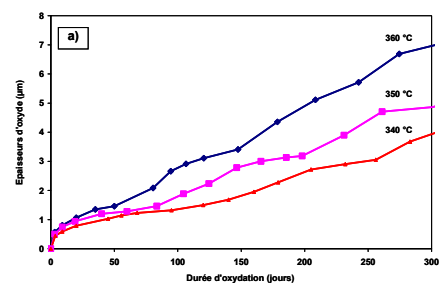
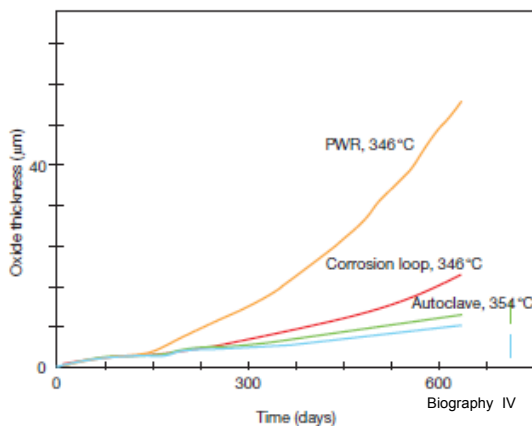
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**Oxidation rates of Zircaloy-4® and M5®**  
*measured in primary water conditions by autoclave tests  
 (at 360°C, with 10 ppm of Li and 650 ppm of B in water).  
 Cycles appear with transitions*



Bibliography IV

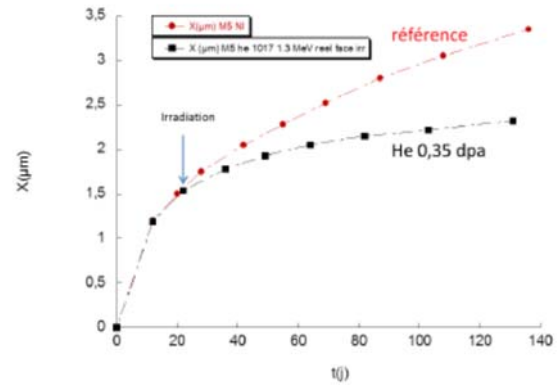
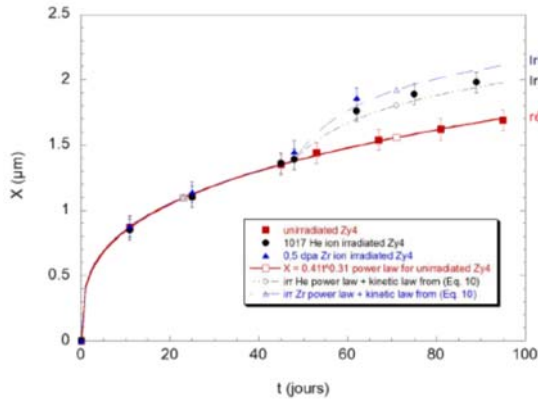
**Influence of the exposure conditions  
 (major influence of irradiation)**



Increase of the corrosion rate  
 with the temperature

Zircaloy-4®

## Influence of the irradiation



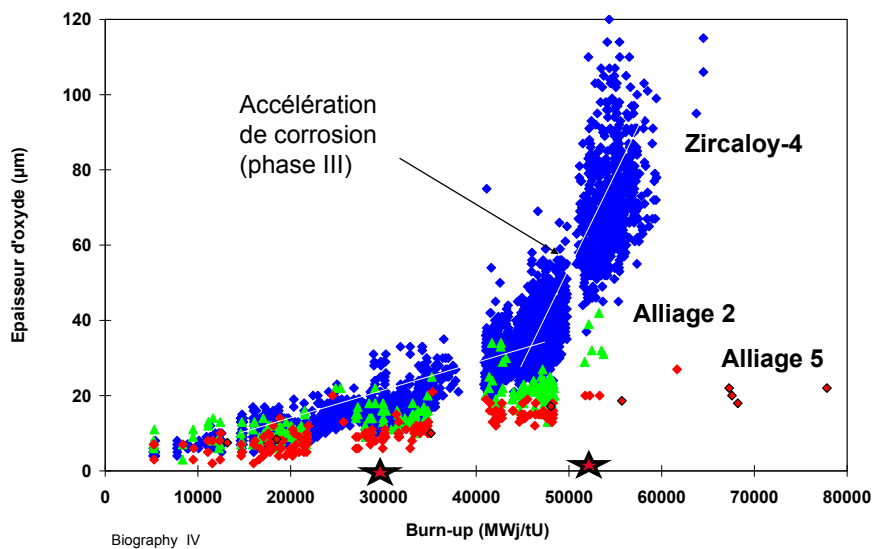
R. Verlet, Phd thesis, Mines de Saint-Etienne, December 3, 2015

**Zircaloy-4®**  
360°C / primary water  
Corrosion higher with irradiated Zy4

**M5®**  
360°C / primary water  
Corrosion lower with irradiated M5®

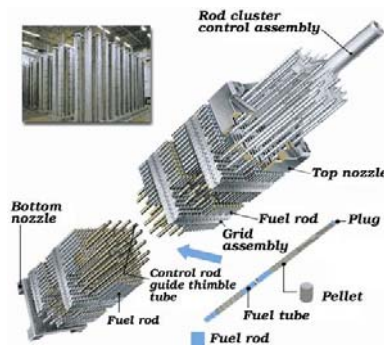
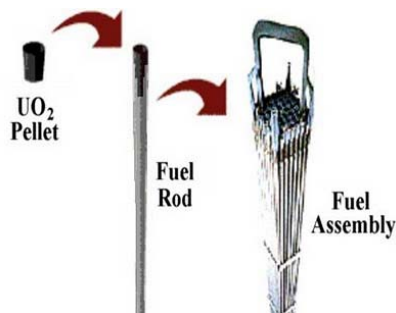
**Thickness of the oxide measured by Foucault currents, on site and in hot laboratories on claddings made of Zircaloy-4® (1.3 % Sn), M5® (alliage 5) and alliage 2 (0.5 % Sn)**

Data obtained on French PWRs



## Evolution and challenges

- ❑ Chemistry: lithium /boron & hydrogen (Zn injection)
- ❑ Total residence time: 3 years increased to 5 years
- ❑ Burnup: from 30 (52) GWd/t to 75-100 GWd/t
- ❑ Fuel cycles increased from 18 to 24 month cycle
- ❑ From Zircaloy4® to M5®



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Bibliography IV

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From <http://de.aveva.com>

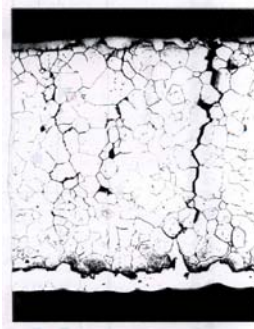
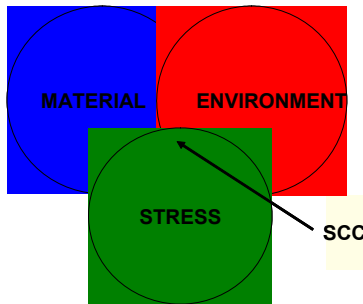
## STEAM GENERATOR TUBES

### EVOLUTION OF THE MATERIAL LINKED TO CORROSION ISSUES

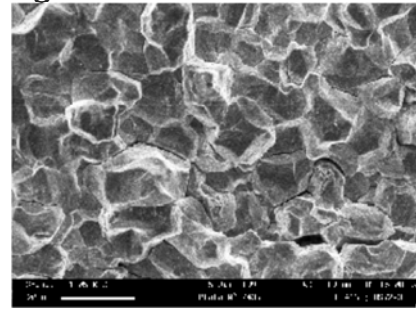
## ALLOY 600

|    |            |              |             |         |            |           |
|----|------------|--------------|-------------|---------|------------|-----------|
| 27 | C ≤ 0,15 % | Cr = 14-17 % | Fe = 6-10 % | Mn ≤ 1% | Si ≤ 0,5 % | Ni > 72 % |
| 20 |            |              |             |         |            |           |

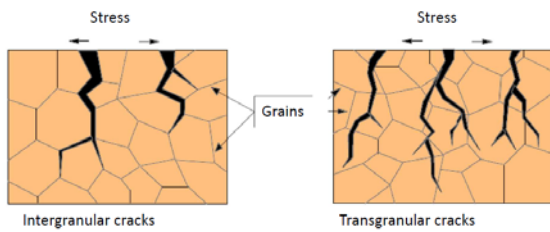




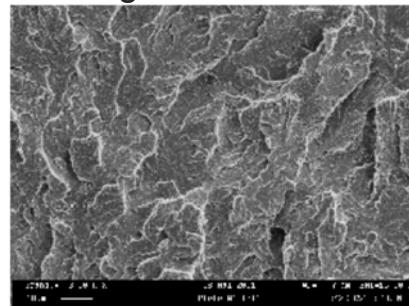
Intergranular SCC



Alloy 600, SG tube, primary water



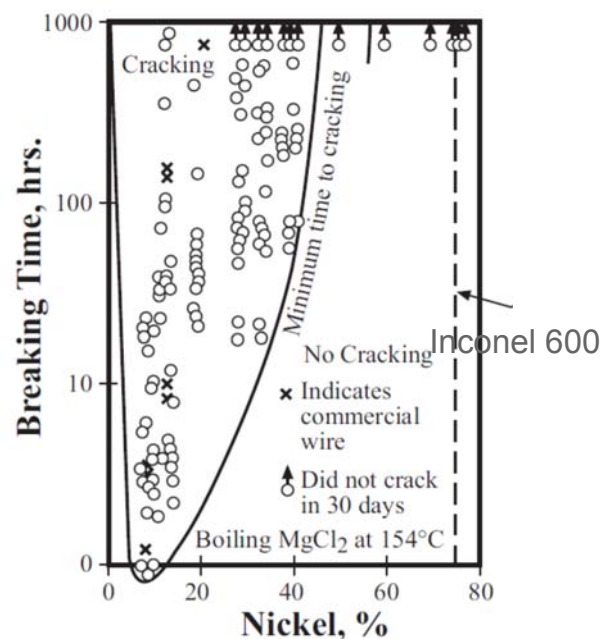
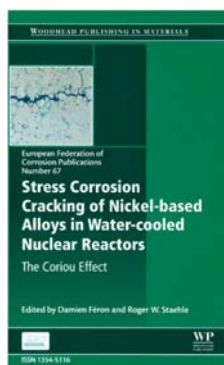
Transgranular SCC



17-4 PH Stainless steel, 300°C

1953: Stress Corrosion Cracking occurred in the stainless steel tubing of the steam generator of the prototype for the Nautilus. SCC failures occurred on the secondary surfaces of the tubes.

By 1957, H. Copson at INCO had demonstrated that the Stress corrosion cracking of Fe-Cr-Ni alloys, when exposed to boiling  $MgCl_2$ , would stop above about 40% Ni.

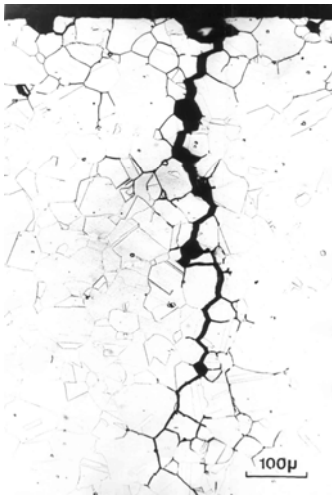


Time to failure of laboratory alloys (1963)

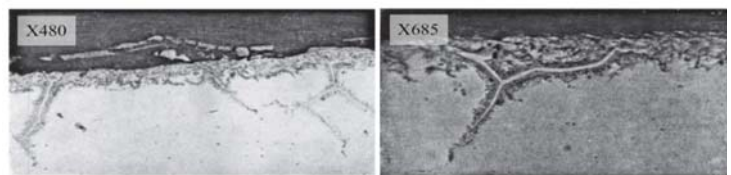
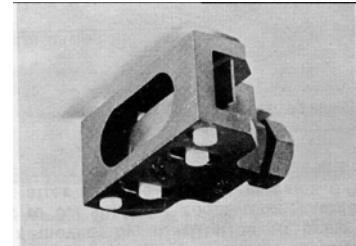
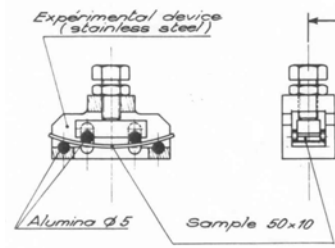
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2017

“Coriou effect”

1959: Coriou et al. published that Alloy 600 (75% Ni & 15% Cr) is sensitive to SCC in “pure” water at 350°C.

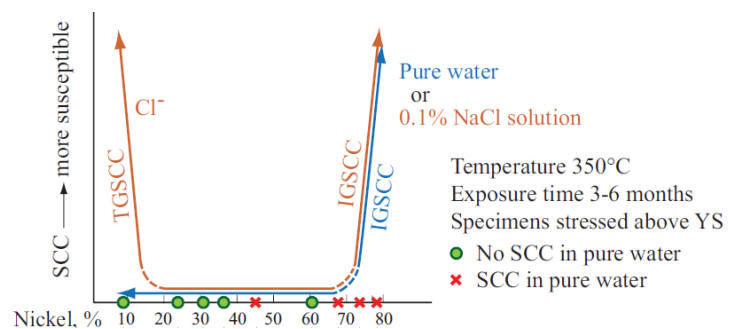
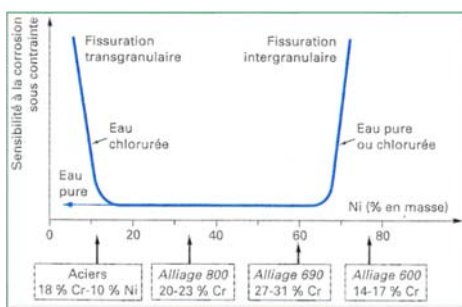


Intergranular SCC of Alloy 600 (350°C, pure deoxygenated water) – 3 months



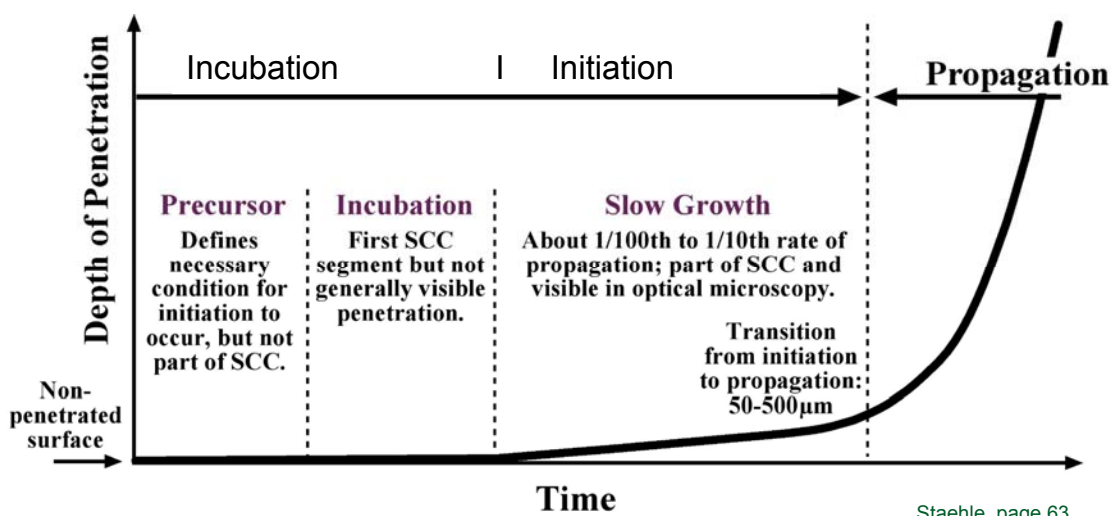
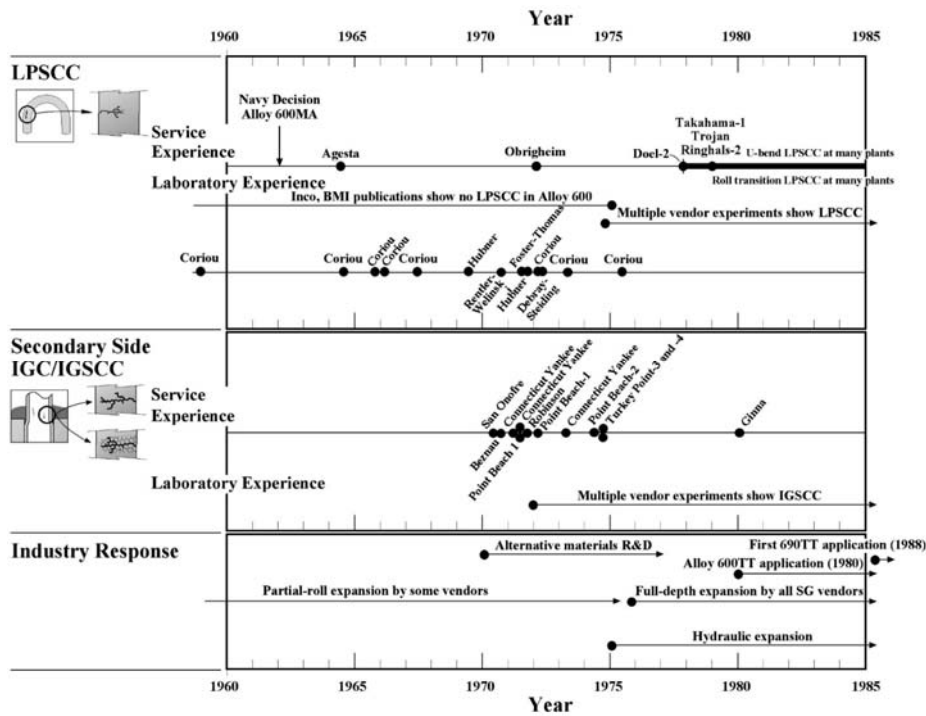
Intergranular oxidation on Alloy 600 (350°C, pure deoxygenated water, 3 months)

Stress corrosion cracking susceptibility by CORIOU



SCC susceptibility as function of the nickel content (Coriou’s work – summary 1967)

Work done with a series of laboratory alloys Fe-18%Cr-Ni with various Ni content  
Pure water and solution with 0.1% NaCl / 350°C / 6 months / 1.2 and 1.7 E<sub>0.2</sub>



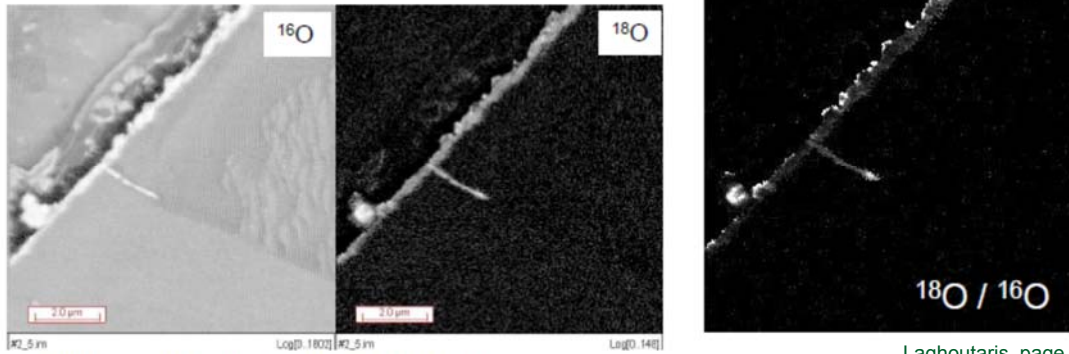
**Incubation:** Passive film formation and evolution

**Initiation:** Film rupture & Intergranular oxidation

**Propagation:** Internal oxidation & Hydrogen

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## Oxygen transport in the crack tip (nano-SIMS and tracers)



Solution-annealed material (no intergranular carbide)  
1340 hr in nominal primary water + primary water containing tracers (deuterium and  $^{18}\text{O}$ ) for 67 hr

Laghoutaris, page 319

- >  $^{18}\text{O}$  is located at the tip of the IG penetration and in the outer part of the surface oxide layer, where the oxide growth occurs.
- >  $^{18}\text{O}$  diffusion occurs during the second stage of the test in 67 hr
- > estimate of the oxygen transport coefficient :  $> 10^{-13} \text{ cm}^2 \cdot \text{s}^{-1}$
- Oxygen transport up to the crack tip is not a rate limiting step.

27 janvier  
2017

M. Sennour & al., JNL, 393 (2009) 254-266  
P. Laghoutaris & al., JNM 393 (2009) 254-266  
C. Guerre & al., Environmental Degradation, TMS, 2011, 1477-1488

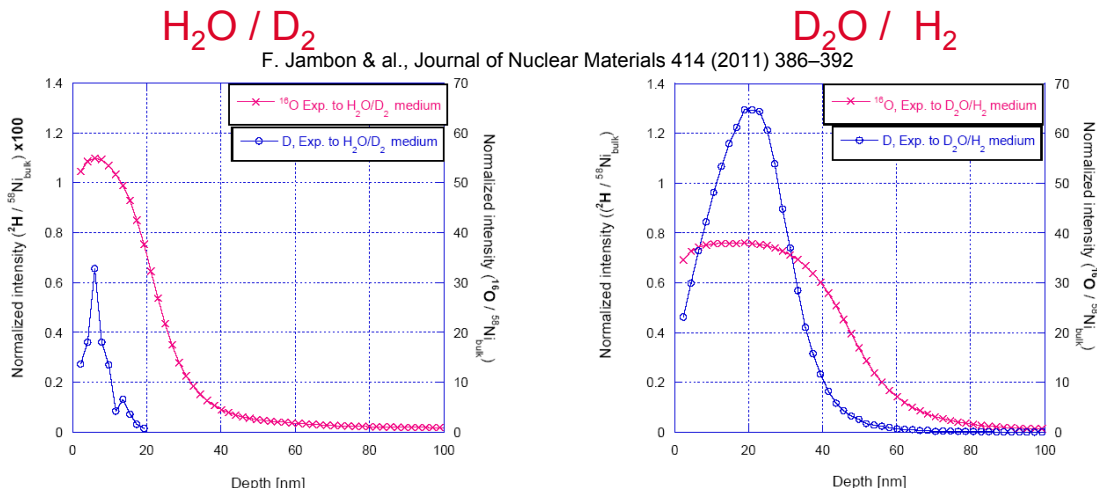
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# ORIGIN OF THE ABSORBED HYDROGEN IN NI ALLOYS

Two series of experiments were done, in which the specimens are exposed to:

- a PWR primary medium in which the water is replaced by deuterated water  $\text{D}_2\text{O}$  (D content 97.90%), pressurized by classical hydrogen gas ( $\text{H}_2$ )
- a classical primary medium (with  $\text{H}_2\text{O}$ ), pressurized by deuterium gas ( $\text{D}_2$ ) (D content 99.05%).



F. Jambon & al., Journal of Nuclear Materials 414 (2011) 386-392

Hydrogen absorption is associated with the cathodic reaction  
( $\text{H}_2\text{O} + \text{e}^- \rightarrow 1/2\text{H}_2 + \text{OH}^-$ )

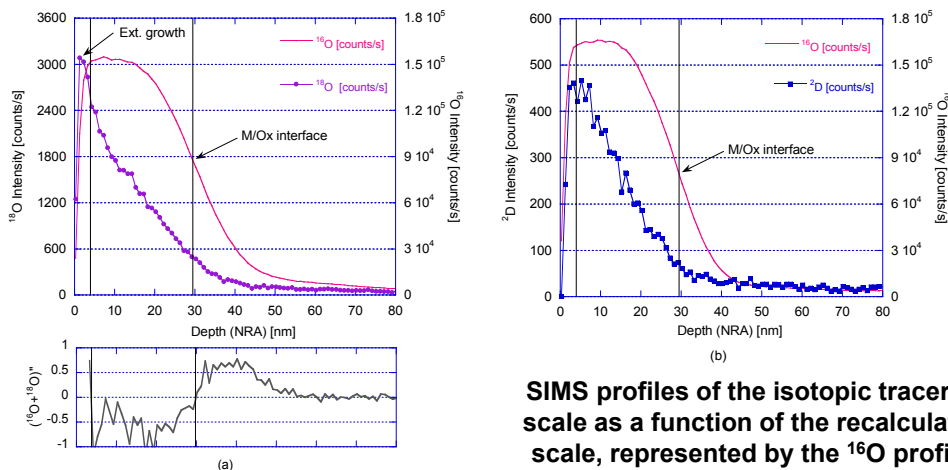
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## VALIDATION OF OH<sup>-</sup> MIGRATION IN THE OXIDE



F. Jambon & al., Solid State Ionics, 231 (2013) 69-73

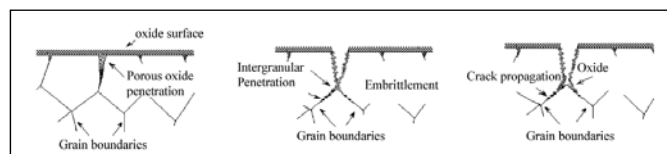
**SIMS profiles of the isotopic tracers through the oxide scale as a function of the recalculated depth (the oxide scale, represented by the <sup>16</sup>O profile is displayed as a guide to the eyes): (a) <sup>18</sup>O tracer (subplot: total oxygen signal's second derivative used to identify the domains); (b) <sup>2</sup>D tracer.**

respectively  $D_{sc}=(4.6\pm 0.9) \times 10^{-17} \text{ cm}^2/\text{s}$  for <sup>18</sup>O, and  $D_{sc}=(5.2\pm 1.2) \times 10^{-17} \text{ cm}^2/\text{s}$  for <sup>2</sup>D

⇒ **diffusion of OH<sup>-</sup> in the oxide layer**

## STRESS CORROSION CRACKING OF NI ALLOYS

❑ Large progress on mechanisms

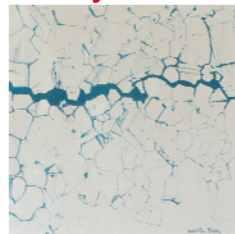


Internal oxidation model with an eventual influence of the cathodic hydrogen in grain bound

❑ Steam generator tubes are no longer made of Alloy 600 MA or alloy 600TT

❑ Good behavior of Alloy 690 and Alloy 800 linked to the higher chromium content

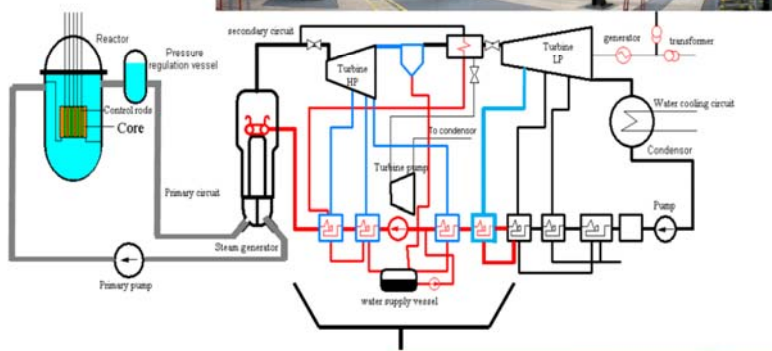
Artist's view of the Coriou's crack,  
by Juliette Plisson



# PWR SECONDARY CIRCUITS

## FLOW ACCELERATED CORROSION (FAC) & CARBON STEELS

Main susceptible FAC systems



2017



## BRIEF HISTORICAL BACKGROUND OF FAC

### INTERNATIONAL



**12/02/1995**  
**Pleasant Prairie**  
(Fossil Plant 600 MW, USA)

**2 persons died**

**09/08/2004 - MIHAMA 3 (Japon)**  
Tube leakage downstream diaphragm



**5 persons died**

**09/05/2007 – IATAN**  
(Fossil Plant, USA)

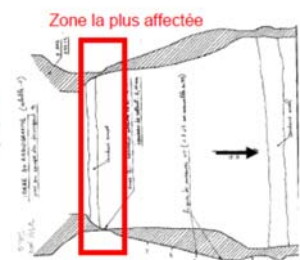
**2 persons died**



### FRANCE

(No death)

**2000**  
**Fessenheim 2**  
Important wear on expander downstream regulating valve on low Flow Rate Feedwater lines

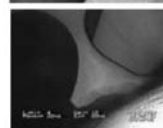


Since 2001

BRT-CICERO™ is used on all units in France



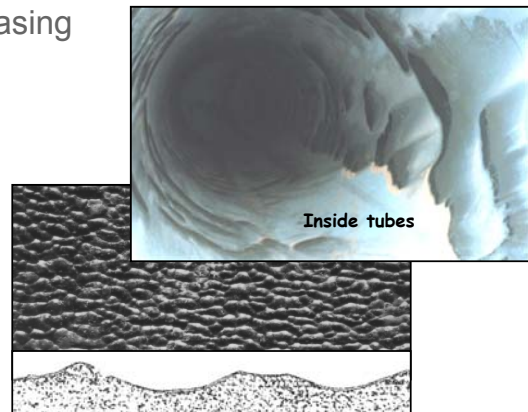
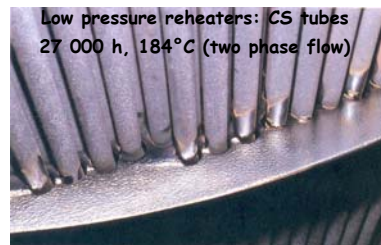
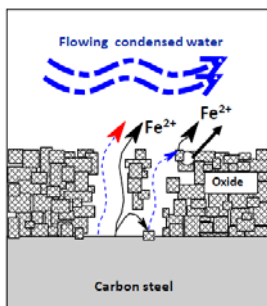
**2002**  
**Flamenville**  
Tube support plates degradation on AHP 500 heaters



# FLOW ACCELERATED CORROSION - FAC "BASIC UNDERSTANDING"

Electrochemical based phenomena accelerated by flow rate  
(and not mechanically – erosion / abrasion)

- Metallic materials in contact with liquid water at high flow rates
- Carbon steels (CS) or low Alloyed Steels (LAS) covered with a protective layer magnetite / hematite (passive layer)
- Stationary conditions:  $V_{\text{film formation}} = V_{\text{oxide dissolution}}$
- High flow rate
  - Oxide dissolution is faster
  - Oxide film thickness is decreasing
  - Corrosion rate is increasing

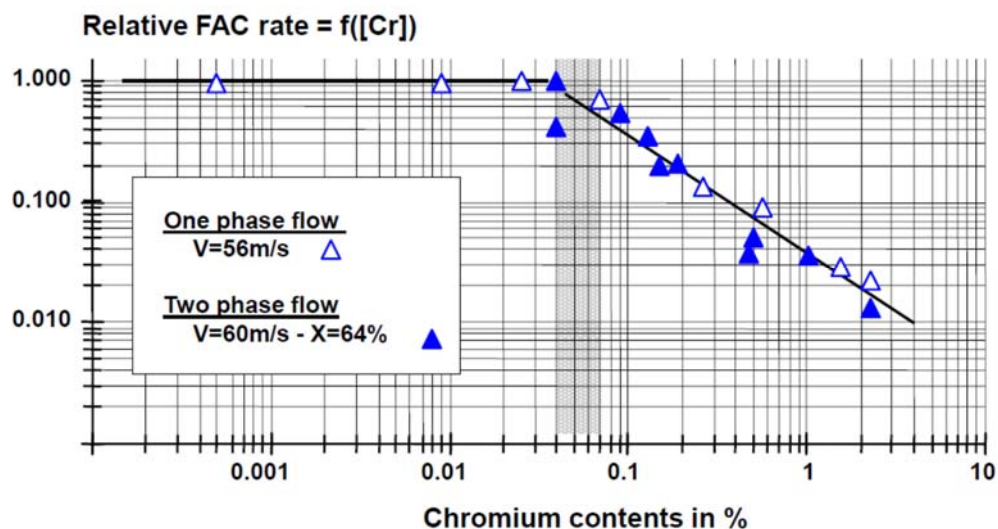


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# IMPORTANCE OF THE CHROMIUM IN THE STEEL

With only 0,5% of chromium in the steel, the FAC rates are decreased by a factor of 10 at least

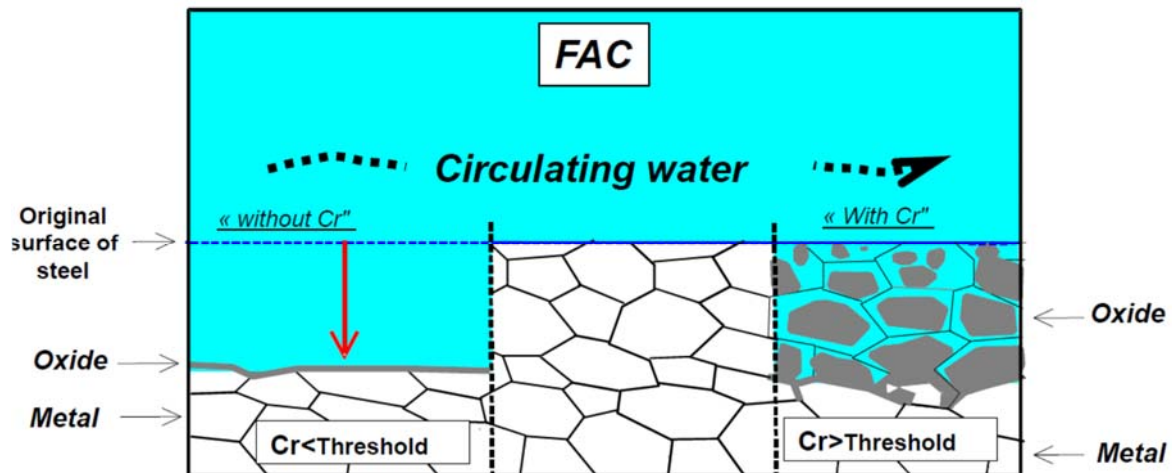


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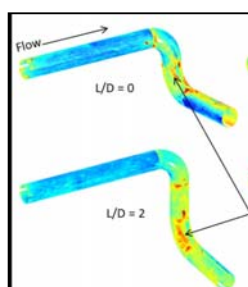
Without Cr: the FAC rate is high due to the solubility of magnetite  $Fe_3O_4$

With Cr in the steel: formation of a  $Fe_2CrO_4$  oxide with very low solubility



| Plants | equipment where the feed water flows in | material improvement | water chemistry<br>pH | improvement<br>[O <sub>2</sub> ] | remarks                                       |
|--------|---|----------------------|-----------------------|----------------------------------|---|
| PWR    | steam generator                         | increasing [Cr]      | increasing pH         | AVT(H&O)                         | minimizing [O <sub>2</sub> ] at SG inlet      |
| BWR    | reactor core                            | increasing [Cr]      | - (neutral)           | oxygen injection                 | [O <sub>2</sub> ] generated due to radiolysis |
| Fossil | boiler                                  | increasing [Cr]      | increasing pH         | AVT(O)<br>OT                     | From S. Uchida & al., FAC2013                 |

⇒ Importance of the design of the components, **modeling and prediction of degradations (COMSY, BRT-CICERO, WATHEC, CHECWORKS...)** coupled with non-destructive examinations.





# CONCLUSION

## Corrosion issues lead to evolutions of materials

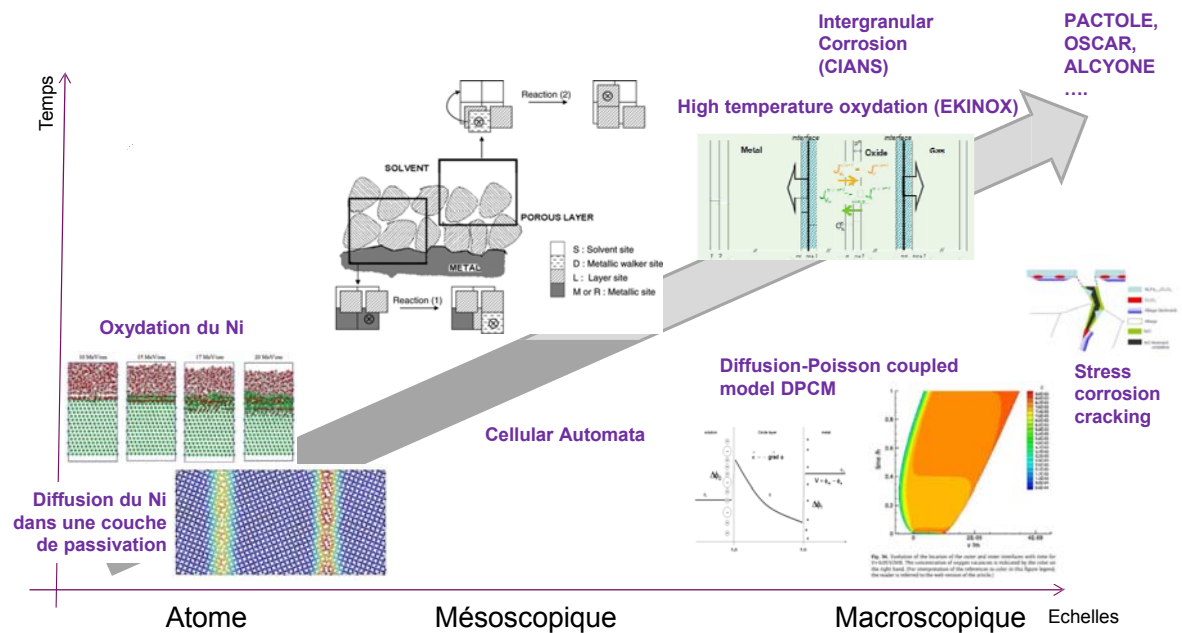
- Cladding: Zircaloy-4 to M5
- SG tubes: Alloy 600 to Alloy 690
- FAC: from carbon steels to low alloyed steels (LAS – less than 1%Cr)

# MODELLING & SIMULATION



DE LA RECHERCHE À L'INDUSTRIE

## MULTISCALE MODELING

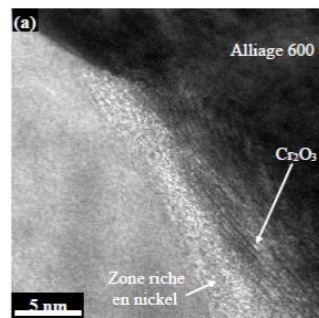
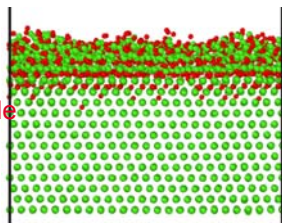


- ⇒ Needs to replace semi-empirical models by more phenomenological models
- ⇒ Multiscale modeling is then needed
- ⇒ Strategy for homogenization & harmonization

Why do we performed (need) atomic simulation?

- Verifications of ideas/mechanisms
- Identification, **comprehension** and characterization of **microscopic mechanisms**
- **Data production** (thermo, transport, structure) → mesoscopic codes
- Interpret experimental results (observations at the same scale – Tomography atom probe)

Growth of the oxide layer on Nickel surfaces



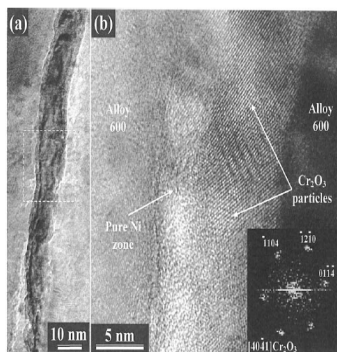
Diffusion of <sup>54</sup>Cr (green) and <sup>52</sup>Cr (red) / TAP

Chromium oxide and nickel rich zone observed at a crack tip/ HRTEM

O. Assowe et al, JPC 116 (2012) 11796  
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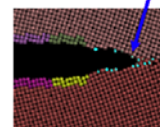
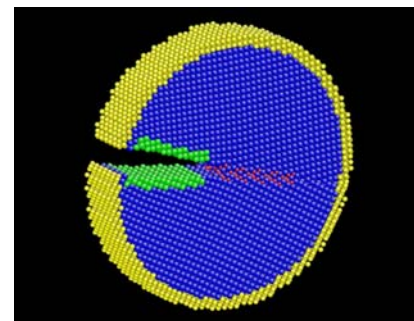
Bogdan thesis, 2015  
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SCC: Influence of hydrogen on crack propagation



P. Laghoutaris & al. , JNM 393 (2009) 254–266

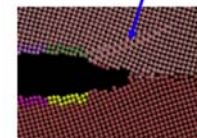
- Molecular dynamic simulation: LAMMPS
- Interatomic potential: EAM (type)
- 750 000 atoms (Ni)  
Ductile crack without H  
Brittle crack with H



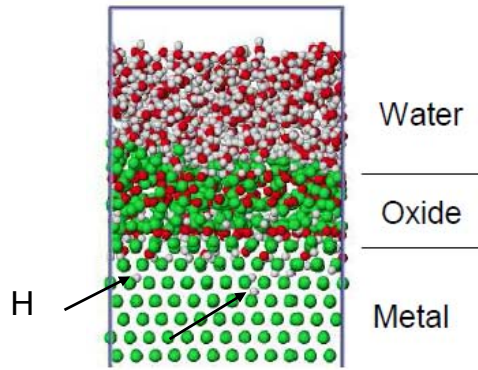
Brittle crack without dislocation nor anorophization

Dislocation

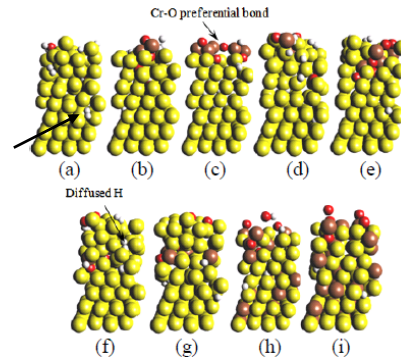
P. Arnoux, Corrosion Science 52 (2010) 1247–1257  
Confirm by Cornell & Zamora, Physical Review B, 060101 (R) 2012,



## Molecular simulation of the oxidation by water of Ni (hydrogen in the metal from the cathodic reaction)



From B. Diawara & Al., Winter School, Modelling of corrosion, December 2011



Same results on Cr  
N.K. Das & T. Shoji, SNA-MC, Paris, November 2013

### Atomistic simulation of oxidation & experimental observations in agreement

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Atoms & molecules  
by Juliette Plisson

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**Thank you**