Nuclear corrosion: achievements et challenges

D. Feron, F. Legendre

MAIN ACTIVITIES OF

THE “CEA CORROSION UNIT ”

NUCLEAR CORROSION:

ACHIEVEMENTS & CHALLENGES

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Service de la corrosion et du comportement des matériaux dans leur environnement
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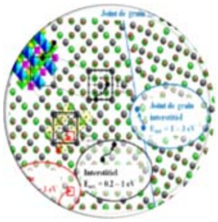
CONTENT

- Introduction: CEA Corrosion Unit
- Gen 2&3 (Pressurized Water Reactor – PWR)
- Gen 4 (Liquid metals, gas & supercritical water cooled reactors)
- Nuclear waste storage
- Decommissioning & conclusive remarks

BACKGROUND

⇒ Complexity of corrosion alteration phenomena



Coupling events

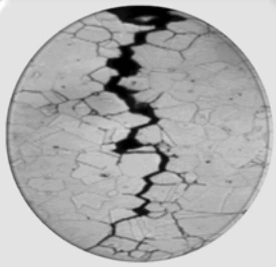
- Electrochemical reactions
- Transport
- Corrosion products
- …

Pluri-physics

Interactions materials/environments

- Several alloys
- Liquids, gas, acids, molten salts and liquid metals
- Solicitations: mechanics, irradiation, bacteria…

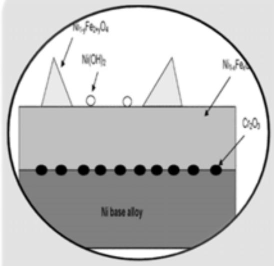
Multi-parameters



Localized phenomena

- Stress corrosion cracking
- Intergranular corrosion
- Pitting
- Crevice corrosion, …

Multi-scales



Interfaces

- Metal/oxides/environ.
- Morphological evolution
- Defects , impurities
- …

Homogenization

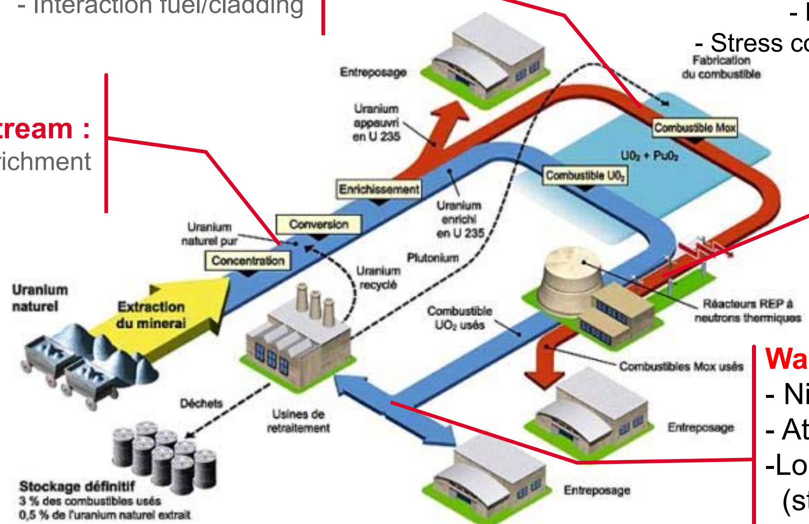
Multi-analyses (observations at the scales adapted to the phenomena)

CORROSION ACTIVITIES: NUCLEAR FUEL CYCLE

Fuel :
- Thermo chemistry
- Cracks & irradiation
- Non equilibrium thermodynamics
- Interaction fuel/cladding

Gen 2, 3 & 4 :
- Safety
- Corrosion in primary and secondary circuits
- H_2 Embrittlement
- Stress corrosion cracking

Upstream :
- Separation & enrichment



Waste management:
- Nitric acid corrosion
- Atmospheric corrosion
- Long term corrosion (storage)
- Thermodynamics

Main Industrial Partners:
- EdF, ANDRA, AREVA, IRSN, CNE, ONDRAF, ENGIE (GdF-Suez), …

« CEA corrosion unit »

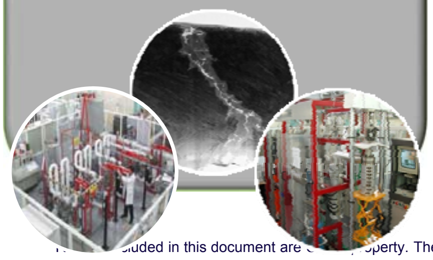
SCCME/DIR

30 students
PhD, post-docs, …

55 permanents
- 1 Director of research
- 2 Professors
- 4 Senior experts
- 12 Experts

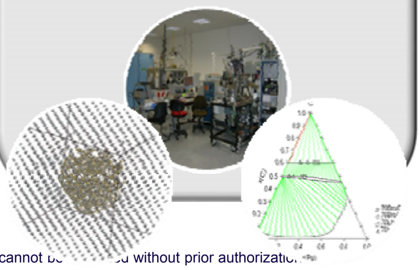
LECA
Laboratory of Aqueous Corrosion

- High temperatures and pressures
- Corrosion in natural environments
- Hydrogen embrittlement
- Stress corrosion cracking



LM2T
Laboratory of Modelling, Thermodynamics and Thermochemistry

- Thermodynamics
- Thermo chemistry
- Atomistic modeling
- Molecular dynamics



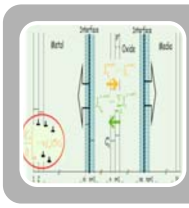
LECNA
Laboratory of Non Aqueous Corrosion

- Corrosion in concentrated acid media
- Corrosion in liquid metals
- Gas oxidation (up to 1450°C)

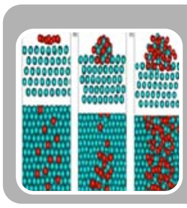
METHODOLOGY

Approach and methodology

Data acquisition & surface analysis
- Specific facilities (autoclaves, loops…)
- **Specific methods (isotopic tracers,…)**
- Surface analyses
- Semi-empirical modeling



Mesoscopic modeling
- Uniform corrosion, Intergranular corrosion…
- Estimation of the Kinetics of Oxidation
- Diffusion Poisson Coupled Model



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

Illustrations

Facilities at the “CEA corrosion department”

View of the corrosion hall at CEA-Saclay (B. 458)

Artist view of the corrosion equipment (Juliette Plisson)

Some specific experimental facilities

Sodium

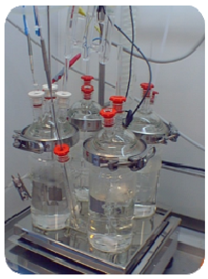
CORRONa 1&2

Stress Corrosion Cracking

VENUS

Autoclaves & loops with tensile machines

HNO_3

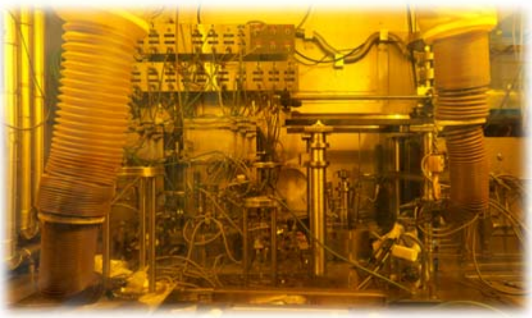


Electrochemical cells

Oxidation & H_2

HAWAI

Irradiated materials (stainless steel & zircaloy)

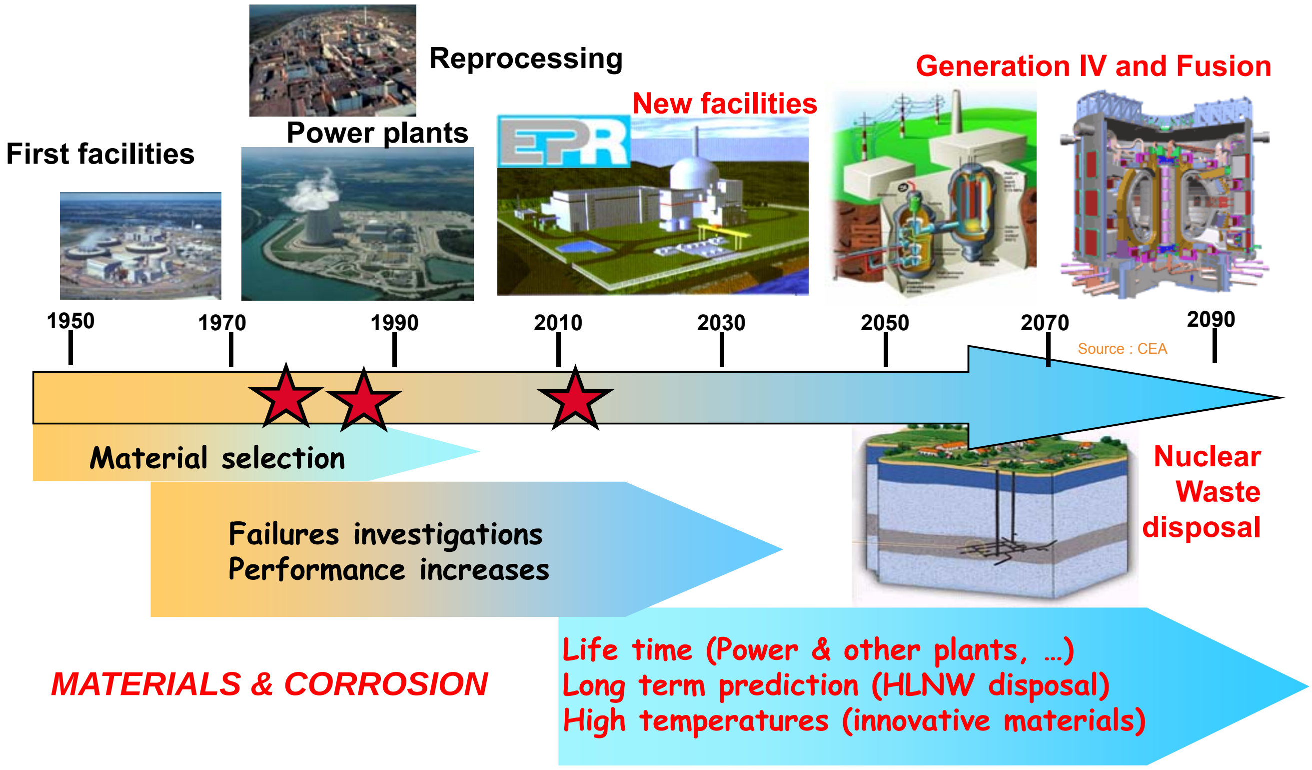


Facility with 3 autoclaves and one tensile machine in hot cell (HP & HT)

Irradiation & electrochemistry

HP & HT cell (e & α irradiations)

NUCLEAR ENERGY & CORROSION: from yesterday to tomorrow



Main Corrosion Challenges

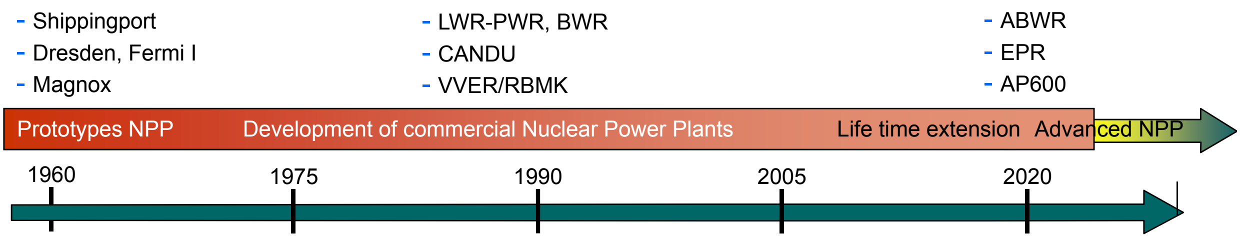
"solved" in Nuclear Power Plants but still occurring

Pioneer period

Flow accelerated Corrosion (FAC)
BWR, Magnox, PWR, VVER, ….
All components and tubing with one (liquid) or two phases (liquid and vapor)

Selection of appropriate materials

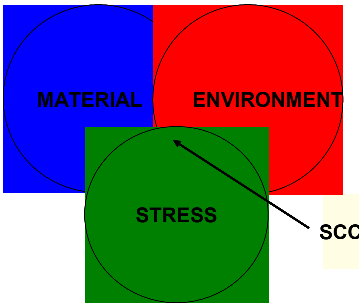
Stress corrosion cracking (SCC)
BWR
Stainless steels in recalculating loops (70s) and vessel weldings
PWR
Alloys 600 tubing (80s) & Vessel head penetrations (90s)

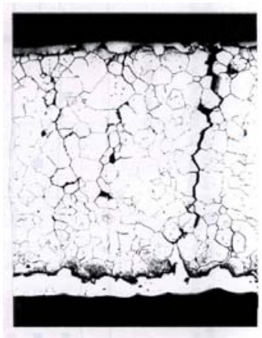


<u>Gen 2&3 illustrations</u>

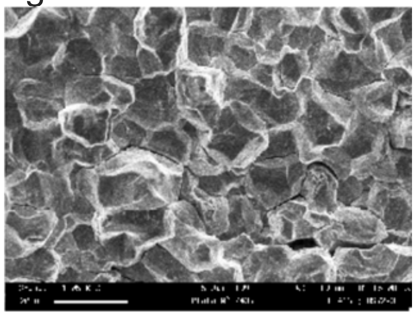
- ~~Flow accelerated corrosion~~
- Stress corrosion cracking
- Zirconium oxidation

STRESS CORROSION CRACKING



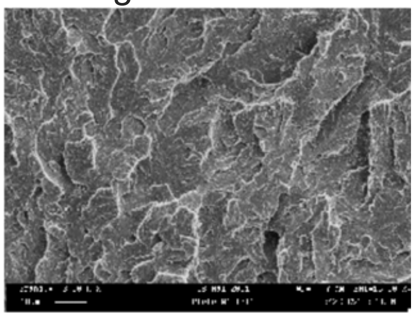


Intergranular SCC

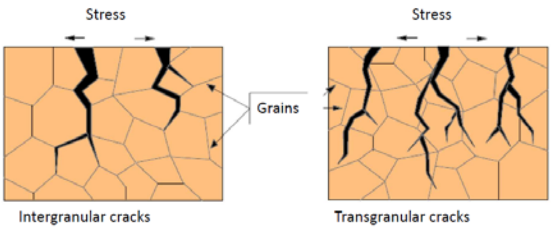


Alloy 600, SG tube, primary water

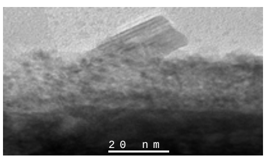
Transgranular SCC



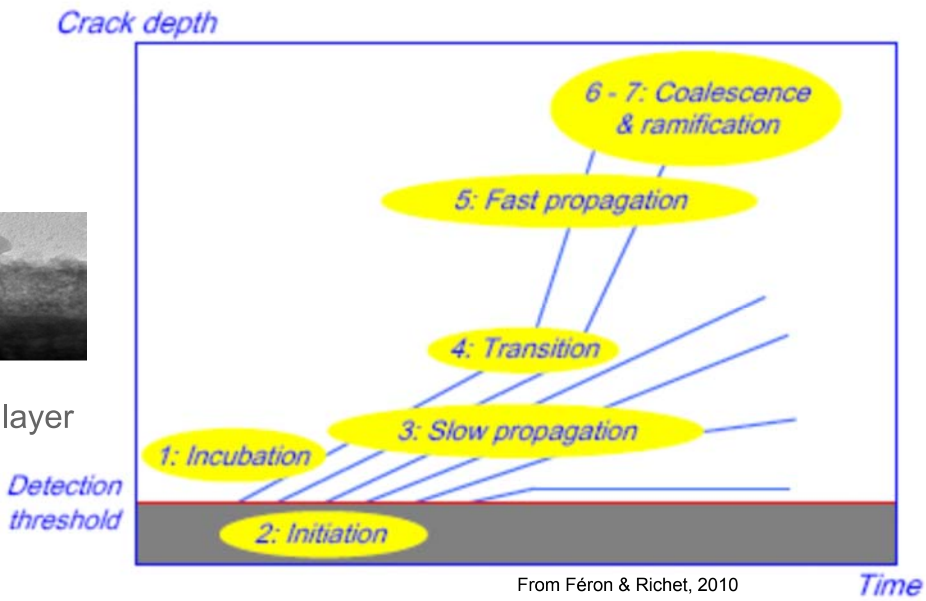
17-4 PH Stainless steel, 300°C



STRESS CORROSION CRACKING



1: Passive layer



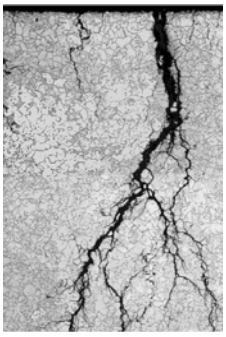
From Féron & Richet, 2010

2: Breakdown of the passive layer

3-4: Inside and outside cracks (anodic and cathodic reactions)

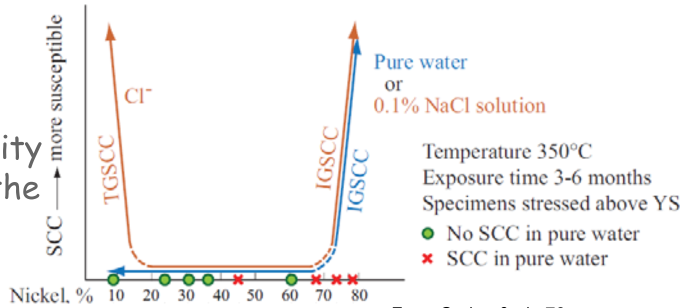
STRESS CORROSION CRACKING OF NI ALLOYS

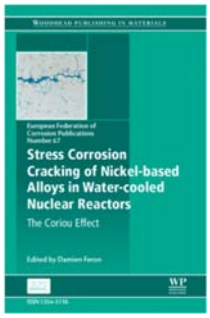
Historical background
SCC of Alloy 600 or the *"Coriou effect"*



- ✓ 1959: *Coriou et al.* published that Alloy 600 (nickel based alloy (75% Ni & 15% Cr) is sensitive to SCC in pure water at 350°C.
- ✓ 1959 – 1980s: Confirmation of the phenomena in pure water and in PWR primary water, named also "PWSCC" for Pure *or Primary* Water Stress Corrosion Cracking".
- ✓ 1980s – 1990s: generic phenomena occurring on Alloy 600 components and particularly on SG tubes.
- ✓ 1991 (in France) – 2002 (US, then Japan …): cracking of vessel head penetrations (Alloy 600 tubes, Weld made of Alloy 182 or 82).

SCC susceptibility as function of the nickel content

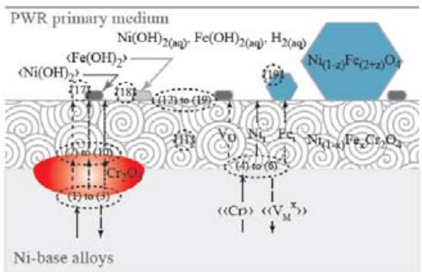




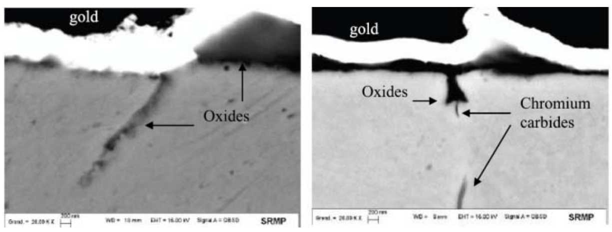
From Coriou & al., 70s

STRESS CORROSION CRACKING OF NI ALLOYS

Incubation



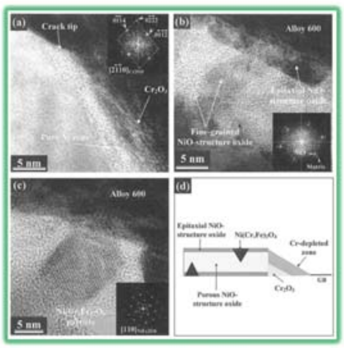
Initiation



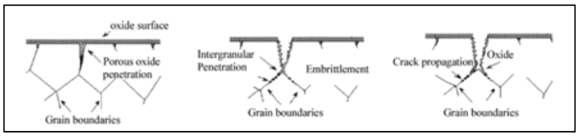
On model alloy with intergranular carbides, intergranular oxidation much shorter

P. Laghoutaris & al. , JNM 393 (2009) 254–266
M. Sennour & al., JNM, 402 (2010) 147-156
C. Guerre & al., Environmental Degradation, TMS, 2011, 1477-1488
M. Dumerval & al., Corrosion Science 85 (2014) 251–257,
L. Marchetti & Al., *Corrosion Science, 102 (2016) 24-35*

Propagation



Internal oxidation model

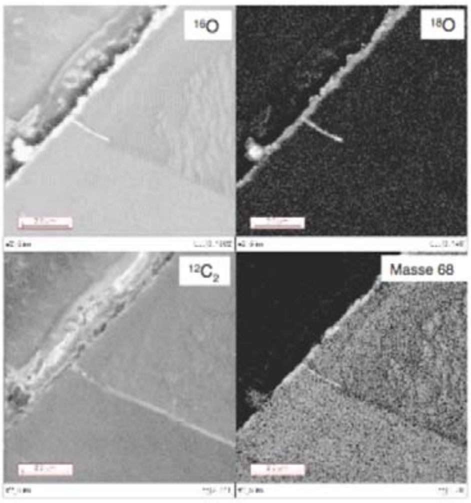


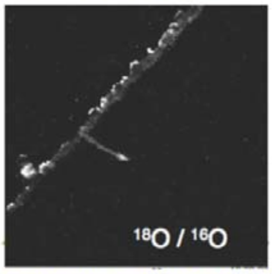
Crack propagation: oxidation & hydrogen

STRESS CORROSION CRACKING OF NI ALLOYS

Use of tracers (^{18}O) to investigate the growth of the oxide of the passive film and in the crack

Evidence and role of oxide at the crack tip (1)





^{18}O is located at the tip of the IG penetration and in the outer part of the oxide surface layer

=> Oxygen and hydrogen can diffuse in the crack and in an IG attack

P. Laghoutaris & Al., 2009-2016

Pre-exposure in primary water conditions followed by an exposure period in H_2O_{18} under same conditions

STRESS CORROSION CRACKING OF NI ALLOYS

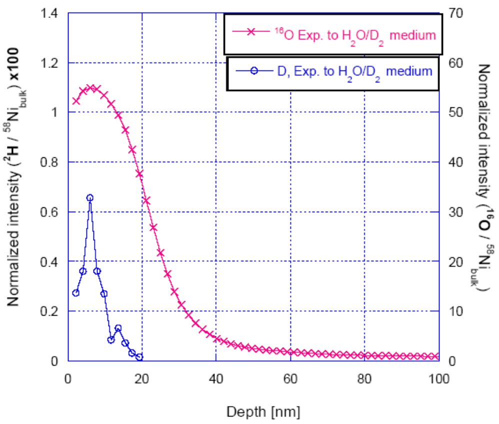
Hydrogen origin

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

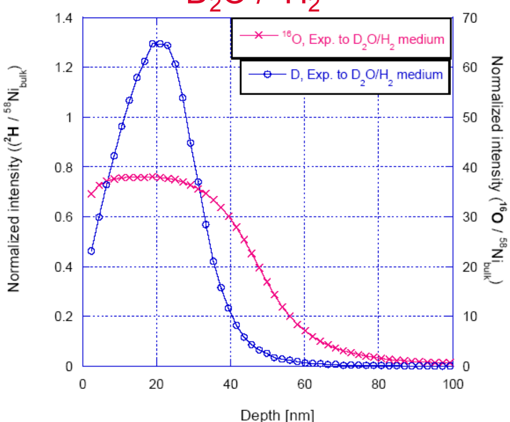
– a classical primary medium (with H_2O), pressurized by deuterium gas (D_2).

– a PWR primary medium in which the water is replaced by deuterated water D_2O, pressurized by classical hydrogen gas (H_2).

H_2O / D_2



D_2O / H_2

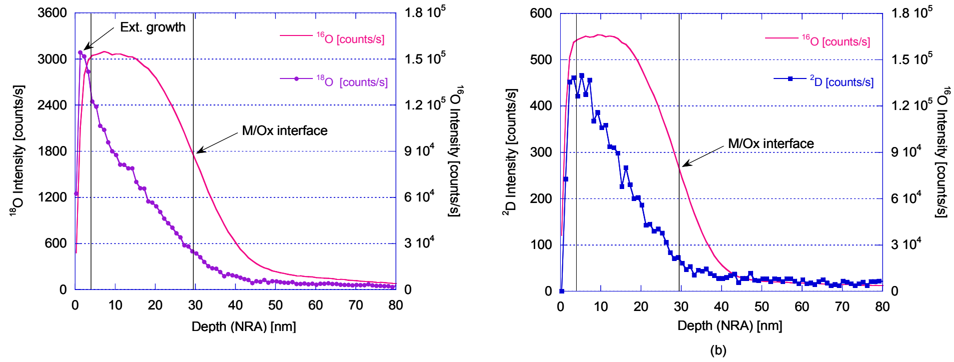


F. Jambon & al., J. Nuclear Materials 414 (2011) 386–392

Hydrogen absorption is associated with the cathodic reaction
($H_2O + e^- \rightarrow H^* + OH^-$)

STRESS CORROSION CRACKING OF NI ALLOYS

^{18}O



^{2}D

SIMS profiles of the isotopic tracers through the oxide scale as a function of the recalculated depth (the oxide scale is represented by the ^{16}O): (a) ^{18}O tracer (subplot: total oxygen signal's second derivative used to identify the domains); (b) ^{2}H tracer.

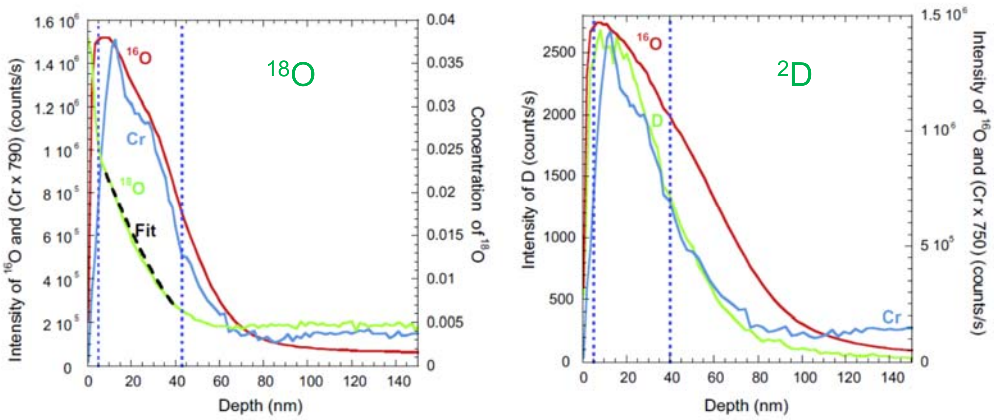
respectively D_{sc}=(4.6±0.9) x10^{-17} cm²/s for ^{18}O, and D_{sc}=(5.2±1.2) x10^{-17} cm²/s for ^{2}H

⇒ **diffusion of OH^- in the oxide layer**

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

STRESS CORROSION CRACKING OF STAINLESS STEELS

SIMS profiles of the isotopic tracers through the oxide scale as a function of the recalculated depth: 2-stages (600h+16h) corrosion experiments , 325°C, with ^{18}O tracer and ^{2}H tracer during the second stage.



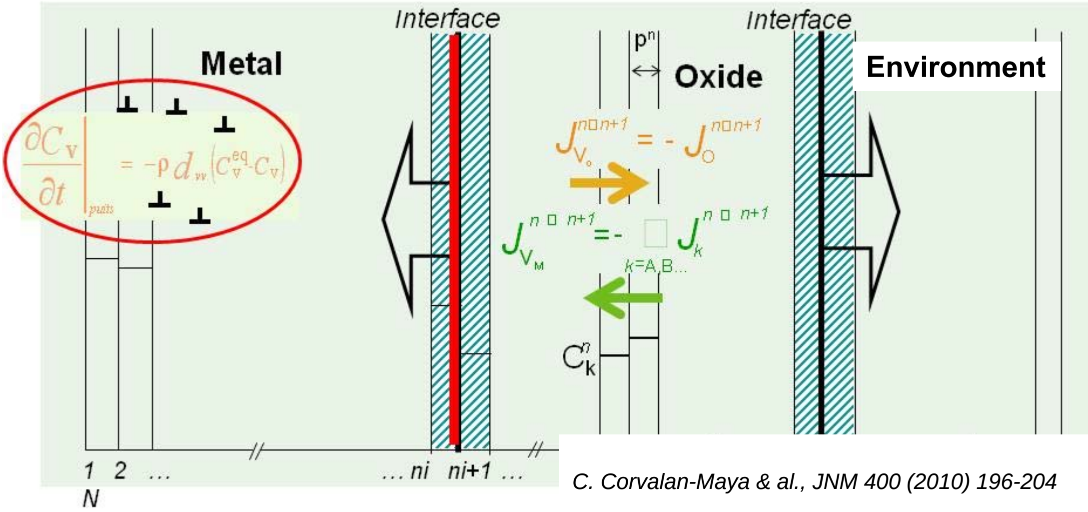
- ❑ Oxygen and hydrogen transport is not coupled
- ❑ Short-circuit diffusion coefficient of ^{18}O: D_{sc}=(9±&) x10^{-17} cm²/s

M. Dumerval & al., Corrosion science 85 (2014) 251-257

FUEL CLADDING EVOLUTION DURING LOCA

Zircaloy oxidation at high temperature

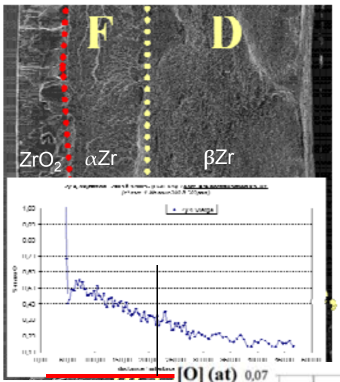
EKINOX (Estimation of the Kinetics of Oxidation)
Calculations to anticipate the evolution in the substrate during alloy oxidation



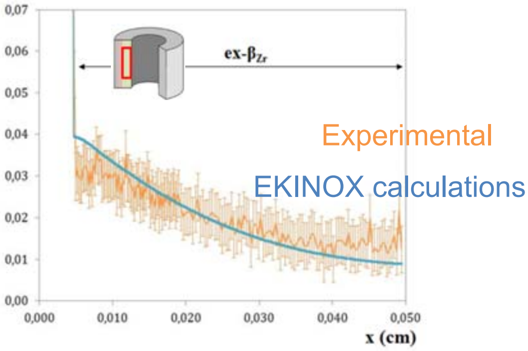
C. Corvalan-Maya & al., JNM 400 (2010) 196-204

FUEL CLADDING EVOLUTION DURING LOCA

Numerical tool: EKINOX-Zr



Steam oxidation, 1200°C, 187s, Zy4



B. Mazeres & al., Ox. Metals (2013)

Steam oxidation, 1200°C, Zy-4

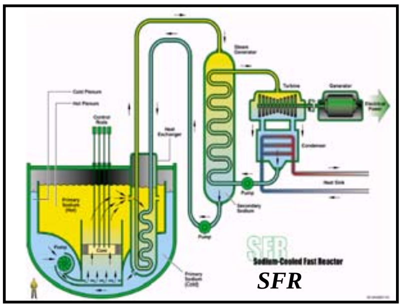
Critical duration leading to overall ductile to brittle		
Analytical solution	EKINOX Zircobase	Experimental
41 min.	17.8 min.	17 min.

C. Corvalan-Maya & al., JNM 400 (2010) 196-204

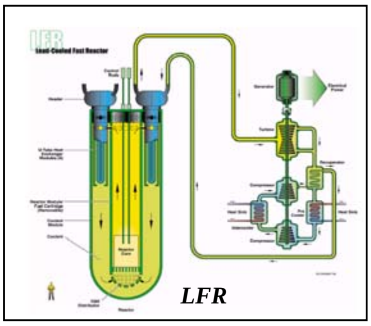
CONTENT

- Introduction: CEA Corrosion Unit
- Gen 2&3 (Pressurized Water Reactor – PWR)
- **Gen 4**
- Nuclear waste storage
- Decommissioning
- Conclusion: modelling

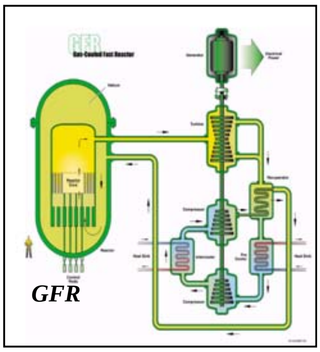
GENERATION IV CONCEPTS



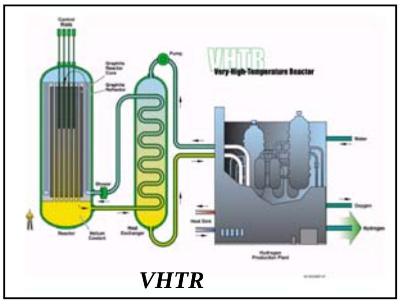
Sodium Fast reactor



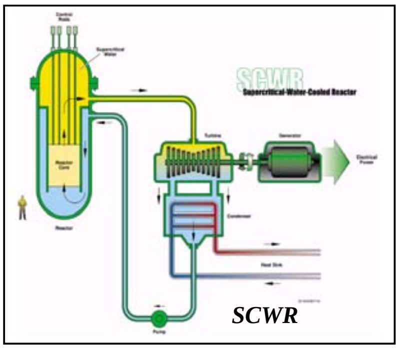
Lead Fast Reactor



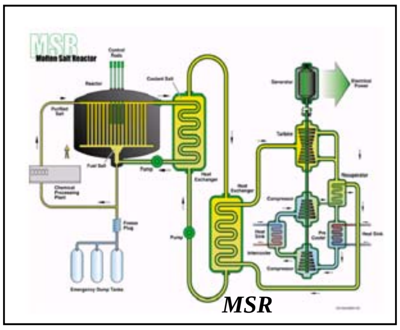
Gas Fast Reactor



Very Higth Temperature Reactor



SuperCritical Water Reactor

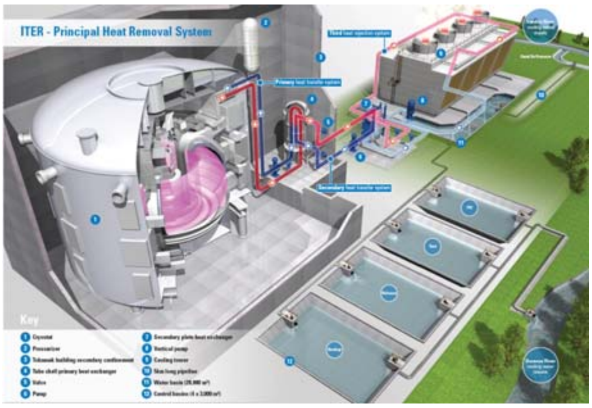


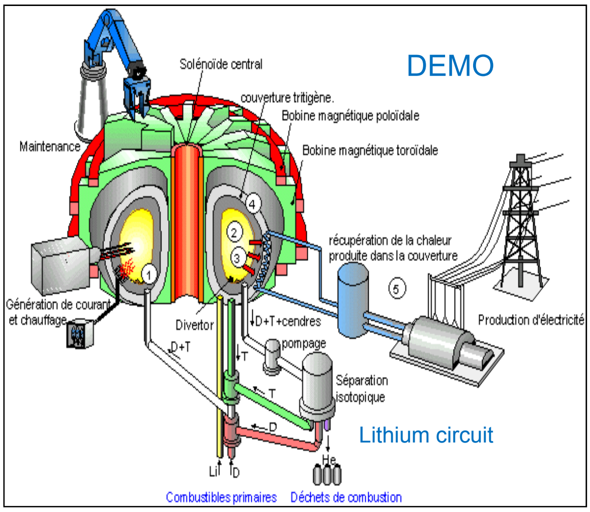
Molten Salt Reactor

Source : AIEA

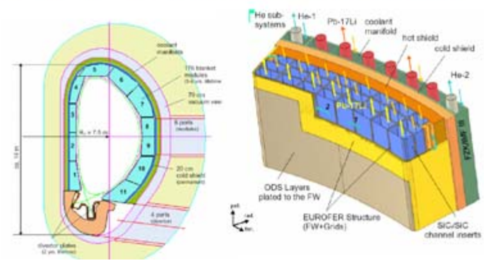
Characteristics: high and very high temperatures / Corrosive environments

Sodium & lead Fast reactor (SFR and LFR) & fusion (ITER)





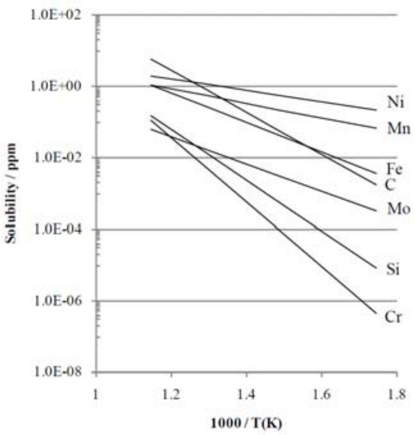
Pb-17Li/Helium Dual Coolant Blanket



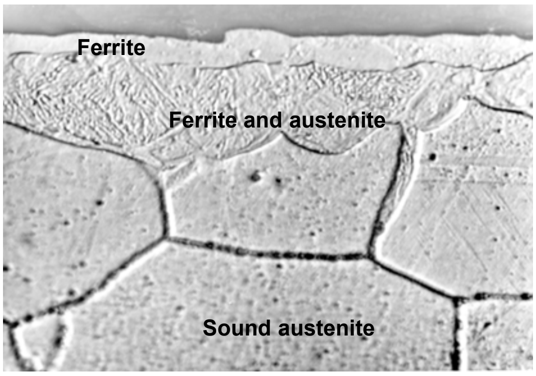
Liquid metals or gas (helium)
High dose rates
High temperatures

LIQUID METAL CORROSION

Corrosion in reducing liquid metals: dissolution
(Li, Pb-Li, Na & Pb with low oxygen content)



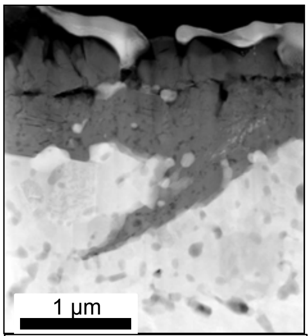
Solubility of alloy elements in liquid sodium



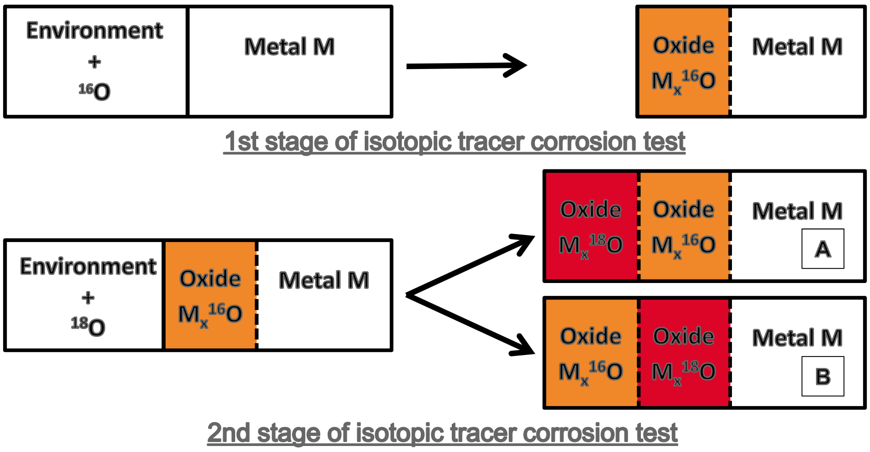
Austentic stainless steel
in liquid sodium with low level of oxygen
-preferential dissolution of nickel-

Corrosion in “oxidising” liquid metals: oxidation & dissolution

(Na, with high oxygen content)



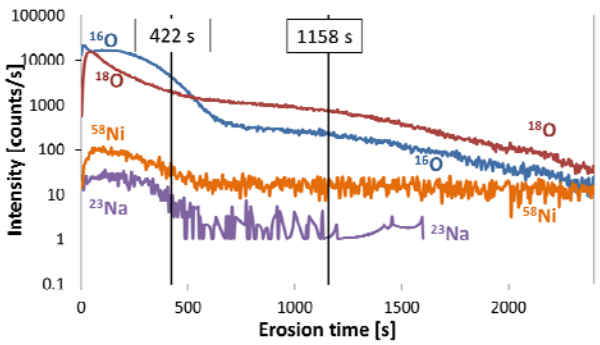
316L, 4241 h in liquid Na at 550 °C, [O]= 200 µg.g^{-1}



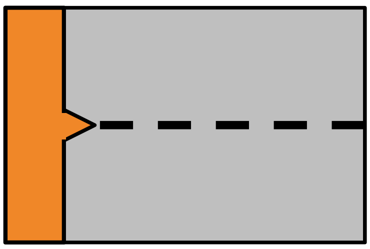
“Two stages” Experiments with oxygen 18
to know where the oxide growth occurs

Corrosion in “oxidising” liquid metals: oxidation & dissolution

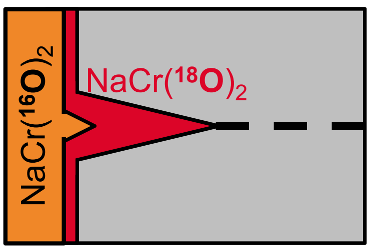
(Na with high oxygen content)



^{18}O profile on grain boundary
550 °C
[O] = 200 µg.g^{-1}
(^{16}O: 500 h,
^{18}O: 960 h)



Initial stage(^{16}O, 500h)

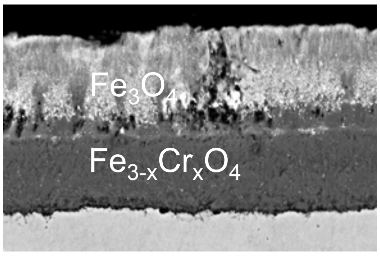


Final stage (^{18}O, 960h)

LIQUID METAL CORROSION

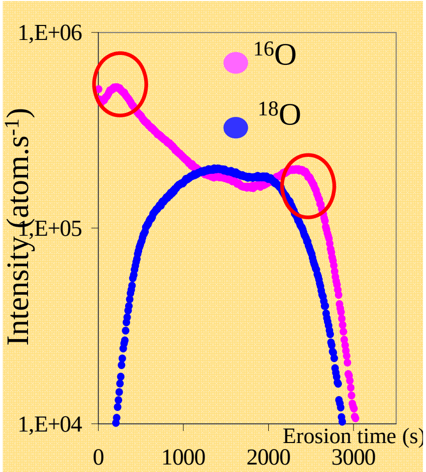
Corrosion in "oxidising" liquid metals: oxidation & dissolution

(Pb-Bi with high oxygen content)



Ferritic steel (9% Cr) in Pb-Bi at 500°C with oxygen : formation of two oxide layers (protective)

Use of tracors to determine the growth mechanism (^{16}O and ^{18}O)
First with ^{16}O and ^{18}O dissolved in liquid Pb-Bi, followed by an exposure only with ^{16}O.



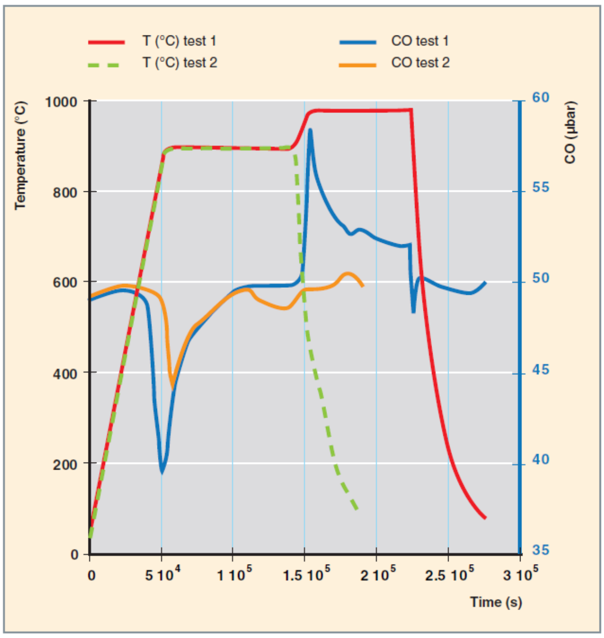
From L. Martinelli & al.

SIMS analysis : peaks of ^{16}O at the external interface and at the metal interface

>> Growth of magnetite layer at the interface with Pb-Bi
>> Growth of the spinel layer at the metal/spinel interface

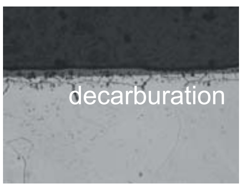
High temperature corrosion in helium systems

(major role of the impurities / example with CO)



Evolution of CO concentration with time and temperature during the exposure of a nickel base alloy in an helium flux (other impurities constant)

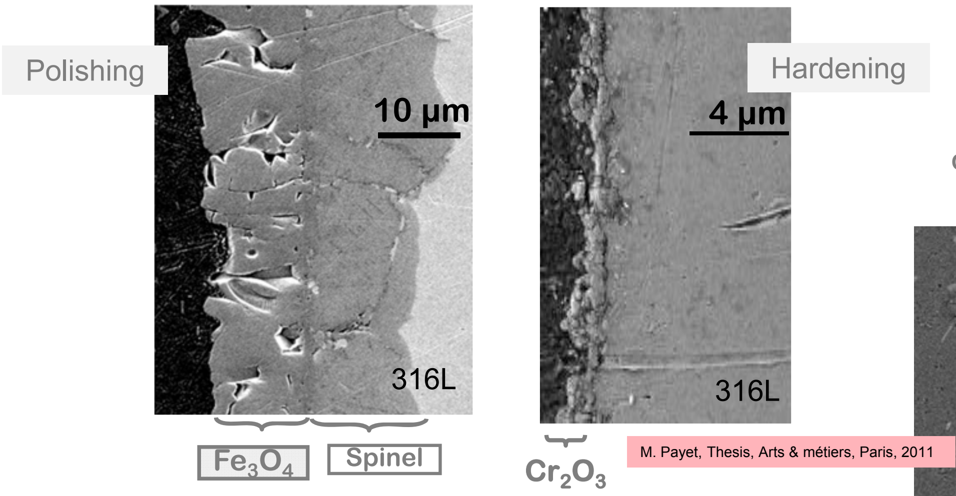
- Carburation between 650 and 900°C
- Decarburation at 980°C

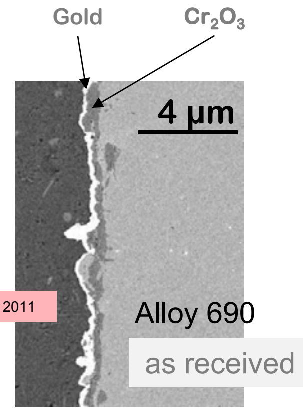


From C. Cabet & al.

PASSIVE ALLOYS IN SUPERCRITICAL WATER

316L stainless steel exposed 335h at 600°C, 25 MPa in ultra pure water with H_2





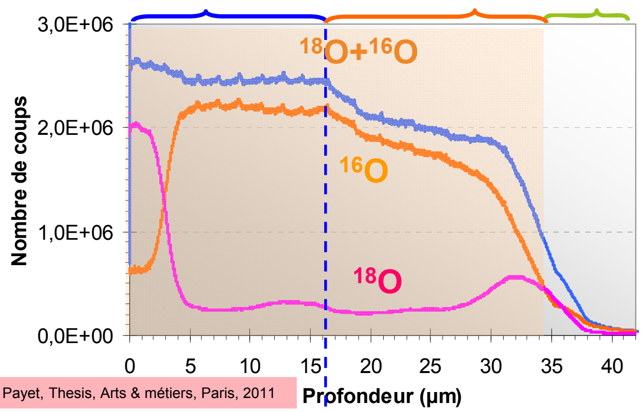
Alloy 690, 840h

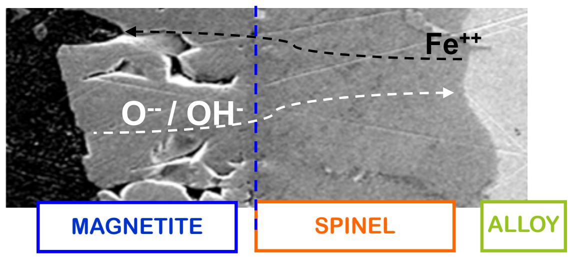
- **Importance of the surface treatments on 316L stainless steel**
  - High corrosion rates with duplex oxide layer on polished surfaces
  - Formation of a protective chromium oxide layer on hardened or cold rolled surfaces linked to the preferential diffusion of chromium via internal defects due to the hardening.
- **Good behavior of 690 nickel base alloy (higher chromium content)**

SUPERCRITICAL WATER

Mechanism of the formation of the double layer observed in SCW on stainless steels: use of tracers, ^{18}O

- First oxidation
  760h, 600°C, 25 MPa, $H_2{}^{16}O$
- Second oxidation
  305h, $H_2{}^{18}O$, idem
- SIMS analyses to locate ^{18}O which is found at two locations
  - Magnetite/SCW
  - Spinel/alloy
- Growth of the oxide layers at the two interfaces
  - Magnetite/SCW
  - Spinel/alloy
  - Modelling





DE LA RECHERCHE À L'INDUSTRIE

cea den

CONTENT

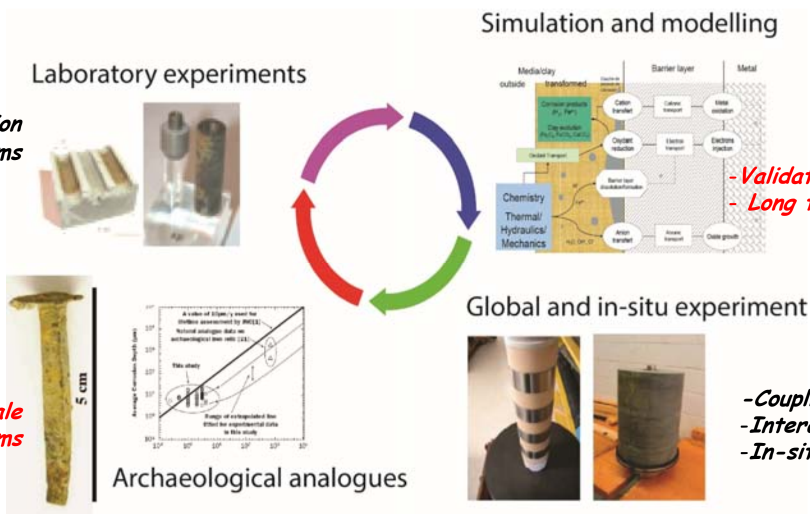
DE LA RECHERCHE À L'INDUSTRIE

cea den

LONG TERM CORROSION

How to predict corrosion over millennia ?

- data for conception
- mechanisms



- Validation of mechanisms
- Long term extrapolation

- Validation of time scale
- Mechanisms

- Coupling
- Interactions
- In-situ

- Communication
- Technology
- Science

D. Féron & al., Corrosion (2009) 65-3, 213-223
P. Dillmann & al., CEST (2014) 49-6, 567-576

LONG TERM CORROSION - MODELING

Corrosion modeling of an iron based alloy in passive conditions

Arcorr experiments

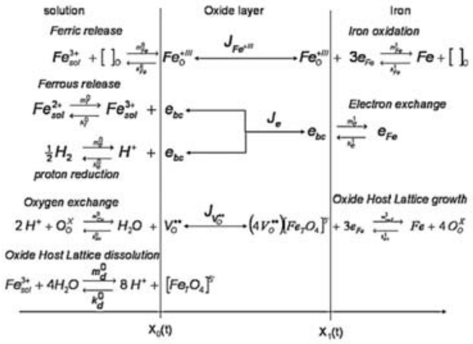


Fig. 3. Flow chart for electrons, octahedral cations and oxygen vacancies. Kröger–Vink notation is used. $[\ ]_O$ corresponds to a free octahedral site.

In situ experiments (Mont Terri and Bure underground laboratories)

C. Bataillon & al. , Elect. Acta 55 (2010) 4451-4467

- **Corrosion modeling based on Fick and Poisson equations with moving interfaces (Diffusion Poisson Coupling Model - DPCM)**
- **Electrochemical experiments for data acquisition and verification**
- **Coupling with geochemical models**
- **Clay and concrete**

LONG TERM CORROSION - MODELING

Corrosion modeling of an iron based alloy in passive conditions
Example of obtained results

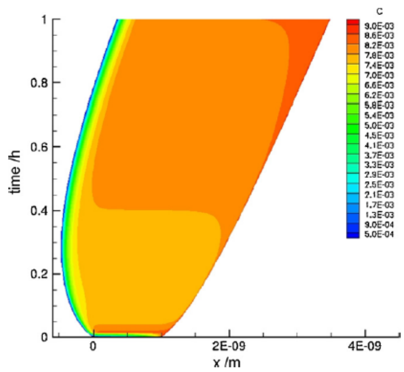
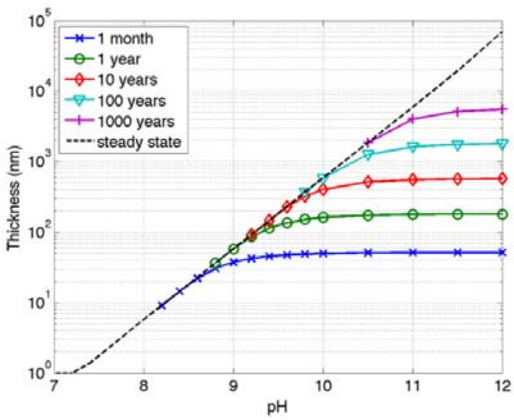


Fig. 36. Evolution of the location of the outer and inner interfaces with time for V= 0.05 V/SHE. The concentration of oxygen vacancies is indicated by the color on the right band. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

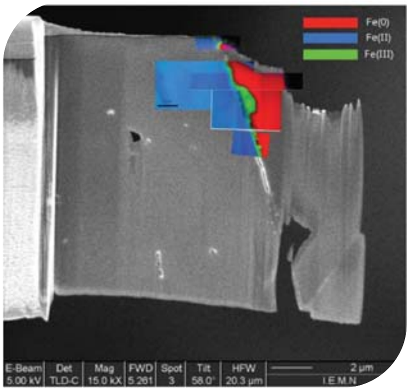


C. Bataillon & al. , Elect. Acta 55 (2010) 4451-4467

C. Bataillon & al. , J. Comput. Physics 231 (2012) 6213-6231

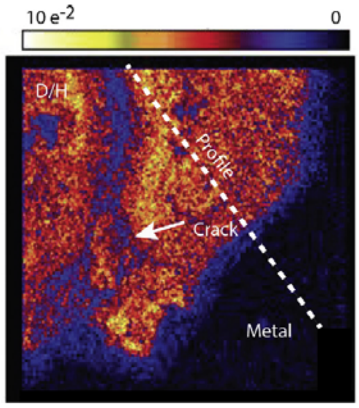
This model is under implantation in the nuclear waste simulations codes

USE OF ARCHEOLOGICAL ARTEFACTS



A. Michelin & al., JAAS (2012)
Michelin et al., J. Analytical Atomic Spectrometry, 2013
Leon et al., Corrosion Science (2014)

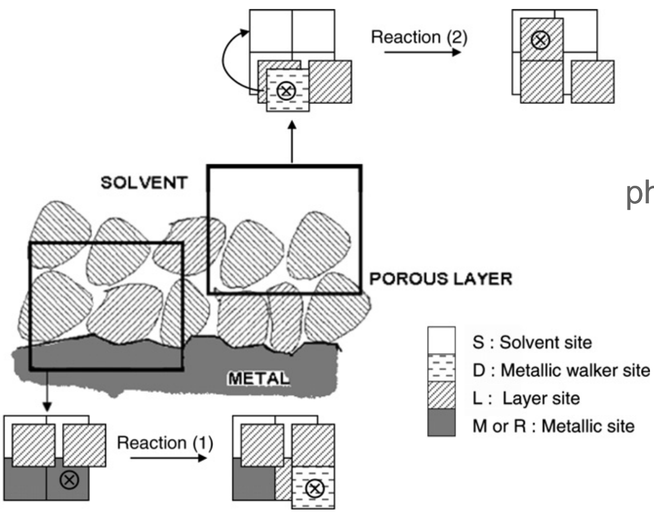
D/H ratio map obtained at the metal/corrosion product interface



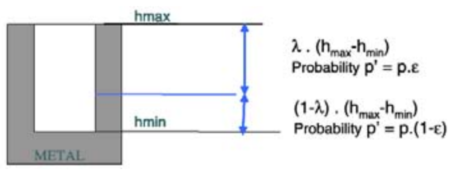
- Corrosion products on a 450 year-old archaeological iron nail in anoxic environment were investigated at the nanometer level using STXM
- **Interfacial layer of 100nm to few µm at the interface metal/oxide interface (magnetite + maghemite, low porosity)**
- Support the hypothesis of a nanolayer controlling the corrosion process (DPCM, Point Defect Model and associated models)

STOCHASTIC MODELING & CORROSION

Use of cellular automata to model morphological evolutions during corrosion



Aqueous corrosion is a stochastic phenomena regarding the occurrence of anodic and cathodic reactions

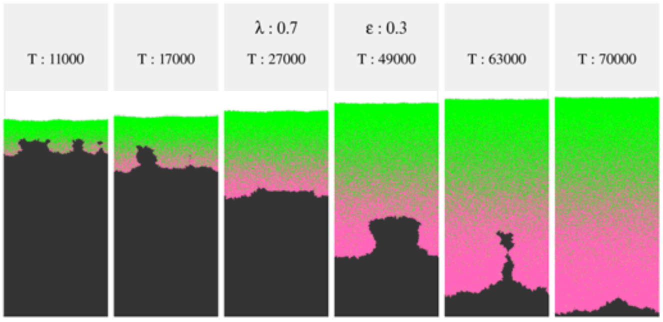


Reaction 1: formation of the oxide layer
Réaction 2: dissolution of the oxide

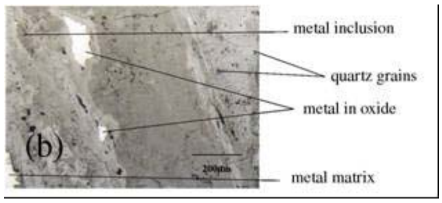
Probability of reaction 1 is function of the corrosion depth

D. di Caprio & al.,

Use of cellular automata to model corrosion phenomena



Archeological analogue with the presence of metallic inclusions inside the oxide layer



Continuous evolution of the interface morphology from uniform corrosion to more localized corrosion and creation of metal inclusions as observed on archeological analogues λ = 0.70 and ε = 0.30

D. di Caprio & al., Corrosion Science 53 (2011) 418–425

CONTENT

- ❑ Introduction: CEA Corrosion Unit
- ❑ Gen 2&3 (Pressurized Water Reactor – PWR)
- ❑ Gen 4
- ❑ Nuclear waste storage
- ❑ **Decommissioning**
- ❑ Conclusion: modelling

NEW CHALLENGE: DECOMMISSIONING

Generic activities

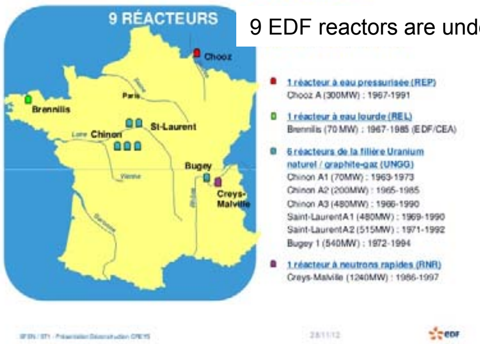
- **Atmospheric corrosion (from mechanisms to corrosion code)**
- Chloride pitting on passive alloys

Specific programs

- Graphite
- Corrosion in supercritical fluids (**SCWO** and $SCCO_2$)
- Mg alloys corrosion in concrete or geo-polymer matrix

Expertise & consulting

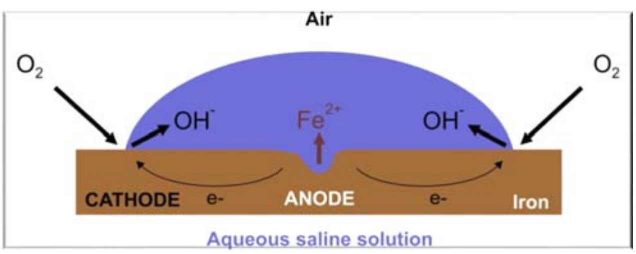
- Transport
- Interim storage



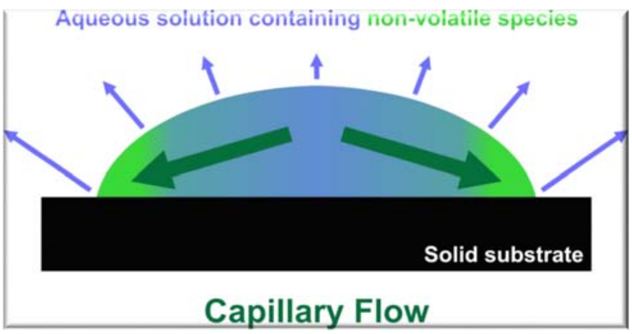
9 EDF reactors are under decommissioning

Specificity: 6 UNGG reactors (graphite moderator, carbon dioxide, natural uranium)

ATMOSPHERIC CORROSION / BASICS



The Evans droplet model (static conditions)



Capillary flow towards the three-phase contact line

« Coffee-ring » effect

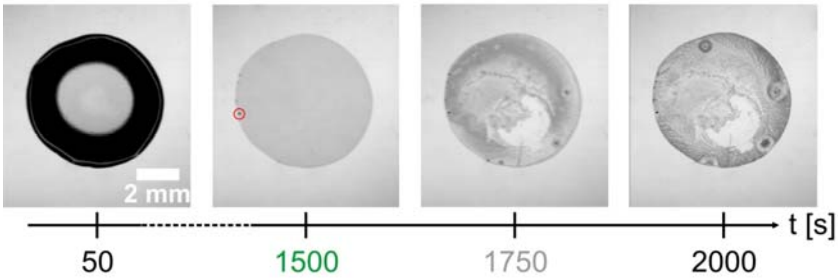
R. D. Deegan. *Nature*, **1997**, 389, 827-829
H. Hu. *J. Phys. Chem.*, **2002**, 106, 1334-1344

ATMOSPHERIC CORROSION / BASICS

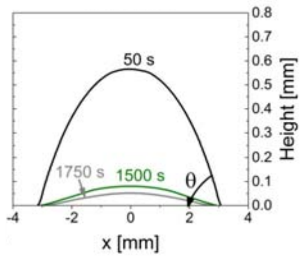
Corrosion under Evaporating Salty Sessile Droplets

Relative Humidity: **RH = 40%** (T = 23°C)
Gaseous phase: **Air**
Initial volume: **V_0 = 10 µl**
Salt initial concentration: **10^{-3} M NaCl**
Substrate: **Iron**

Top view



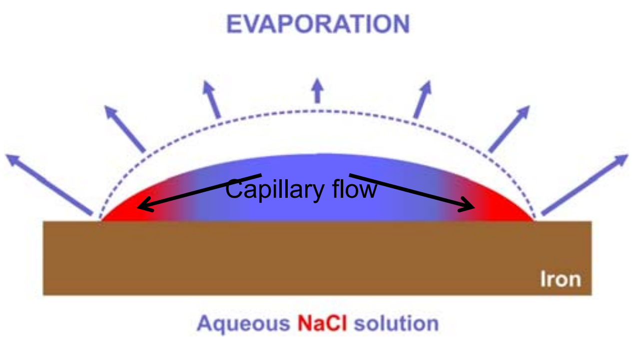
Side view

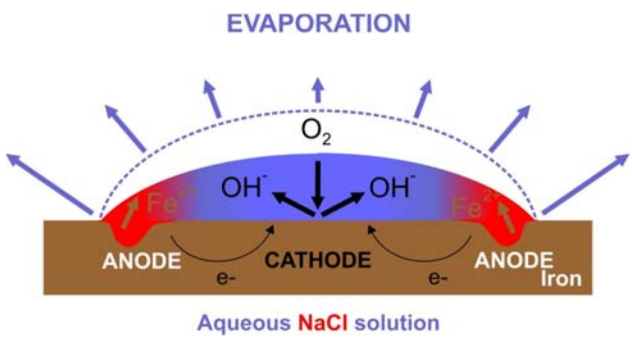


Pitting corrosion starting **near the contact line**

V. Soulié, thése Université de Montpellier, 2014

ATMOSPHERIC CORROSION / BASICS





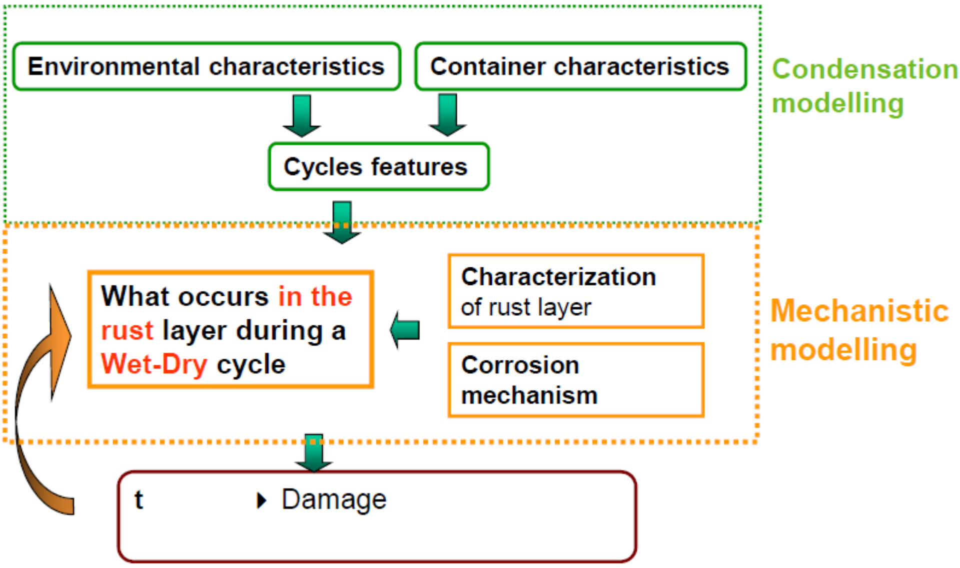
- ❑ Evaporation of pinned salty sessile droplets causes peripheral salt enrichment
- ❑ Local chloride enrichment decreases oxygen solubilty and promotes the initiation of corrosion

Inversion of the classical Evans droplet scenario

V. Soulié, thése Université de Montpellier, 2014

ATMOSPHERIC CORROSION / MODELLING

- « Calculations » based on ISO standards (9223 & 9224)
- Mechanistic modelling



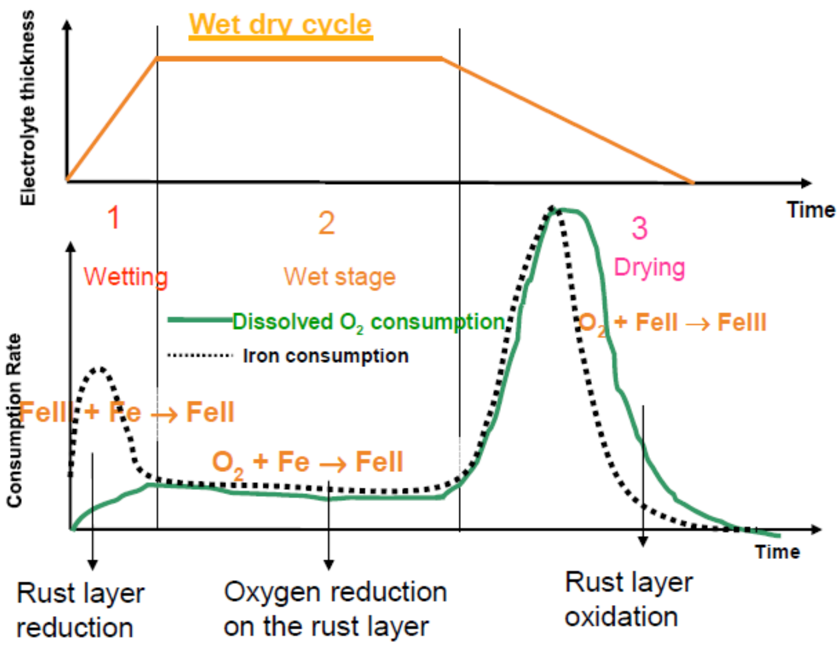
ATMOSPHERIC CORROSION / MODELLING

Corrosion mechanism during a wet dry cycle (Based on Strattman works)

1 Iron is consumed but not O_2

2 Both iron and O_2 are consumed

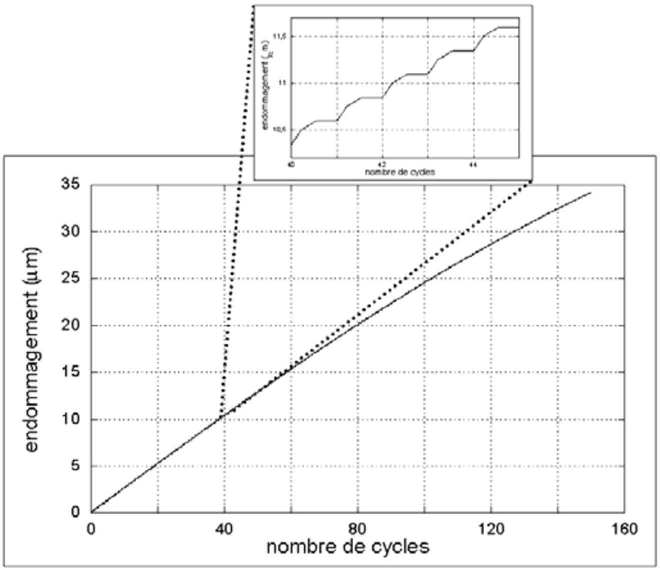
3 O_2 consumption is longer than iron consumption



E. BURGER, & AL. CORROSION SCIENCE, V. 53(6), 2011, 2122-2130

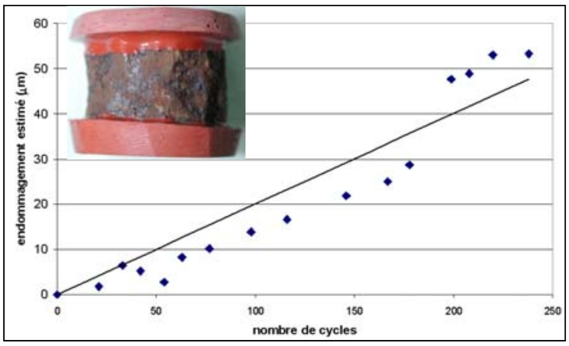
ATMOSPHERIC CORROSION / MODELLING

Verification of the atmospheric mechanistic modelling



calculation of n wet dry cycles

ε=3%, S_a=10 $m^2.g^{-1}$ L_0=150 μm



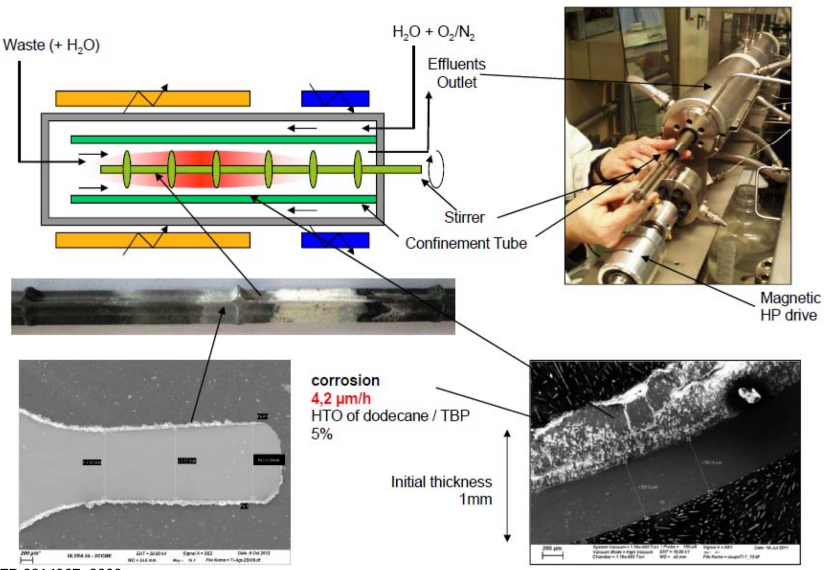
Experimental data:
Ageing in climatic chamber

E. BURGER & AL. CORROSION SCIENCE, V. 53(6), 2011, 2122-2130

SUPERCRITICAL WATER OXIDATION

ATALANTE / DELOS
DESTRUCTION OF CONTAMINATED ORGANIC LIQUID WASTES

- Treatment of spent fuel contaminated organic liquids
- C.H.O.N., **TBP/alcane,** amines, aromatics…



Joussot-Dubien C., Turc H.A., Didier, G., Brevet FR 2814967, 2000
S. Sararde, 11th International Symposium on Supercritical Fluids, October 11-15, 2015, Seoul, Korea

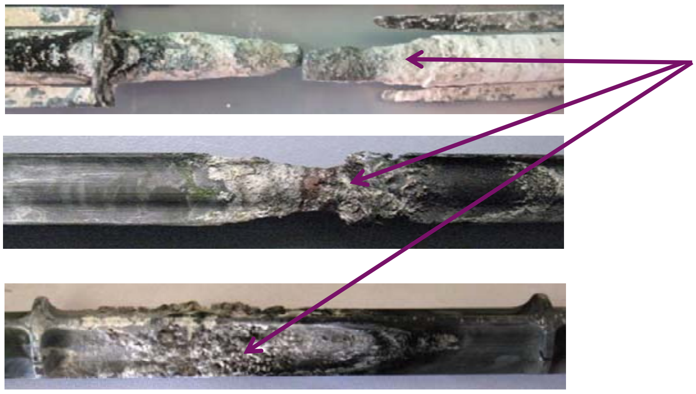
SUPERCRITICAL WATER OXIDATION

Combustion of dodecane/tributylphosphate/dichloromethane

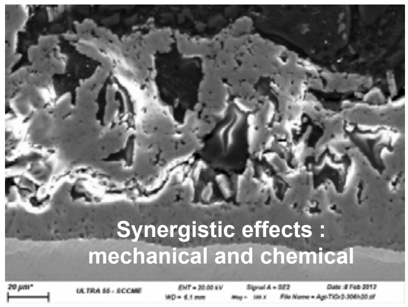
Material : Ti Grade 2

Welding design

Massive design



TiP_2O_7, $Ti(OH)PO_4$



Final Scale up **DAMAGE MANAGEMENT & FINAL PROCESS**

100 h → **300 h** → **1000 h**

Corrosion < 5 μm/h

Corrosion < 5 μm/h
Mechanical Strength

Industrial Conditions
6 months Batch
1 hour maintenance

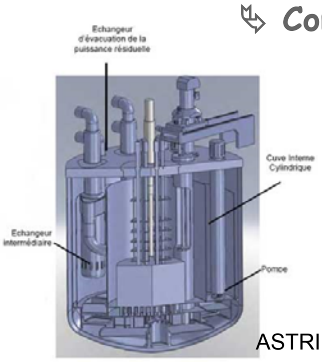
Joussot-Dubien C., Turc H.A., Didier, G., Brevet FR 2814967, 2000
S. Sararde, 11th International Symposium on Supercritical Fluids, October 11-15, 2015, Seoul, Korea

CONCLUSIVE COMMENTS

CORROSION CHALLENGES

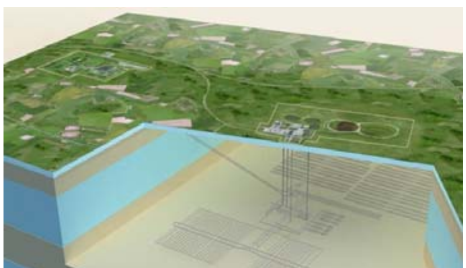
- Extension of life time of NPPs
  life time extension (FAC & SCC)
- Nuclear waste disposals
  Long term prediction (methodology)
- Generation 4 & fusion
  high temperatures & aggressive media
- Decommission

Source : EDF



ASTRID, CEA

- Common approaches & processes
  - experimental (use of tracers)
  - modelling



ANDRA

Major challenges linked with corrosion behaviour

DE LA RECHERCHE À L'INDUSTRIE

cea den

CONCLUSIVE COMMENTS

instn Institut national des sciences & techniques nucléaires

Materials Simulation & Engineering

Winter School
" Modelling of Corrosion "
INSTN CEA Saclay, December 10-14, 2012

Spring School
" Modelling of corrosion for Nuclear Reactors "
INSTN CEA Saclay, March 31-April 4, 2014

Fall School
" Modelling of Corrosion "
INSTN CEA Saclay, October 26-30, 2015

"School for Advanced Thermodynamic Assessments"
Summer school

June 23-27, 2014
Centre Port-Royal, France

July 6 —10, 2015
Centre Port-Royal, France

HTCorrosion Toulouse 2013 Spring School

HTCorrosion Biarritz 2014 2nd Spring School

Thank you for your attention

FROM RESEARCH TO INDUSTRY

French Alternative Energies and Atomic Energy Commission

Alternative Energies and Atomic Energy Commission
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