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# Corrosion in nuclear waste geological storages how to predict corrosion for millenniums ?

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D. Feron. Corrosion in nuclear waste geological storages how to predict corrosion for millenniums ?. Cycle de conferences donnees sur invitation de l'IMR CAS, Nov 2016, Shenyang, China. cea-02437059

**HAL Id: cea-02437059**

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# CORROSION IN NUCLEAR WASTE GEOLOGICAL STORAGES: HOW TO PREDICT CORROSION OVER MILLENNIUMS?

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

### Overviews of nuclear waste disposal in France

### How to predict corrosion over millennia?

- Laboratory tests
- Modeling
- Archeological artefacts
- Integrated experiments

# BACKGROUND

# NUCLEAR WASTE MANAGEMENT

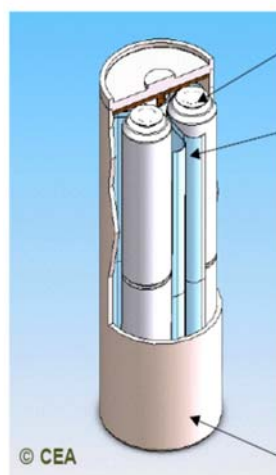
## NUCLEAR WASTE

### VITRIFIED WASTE CONTAINERS



Standard container for vitrified waste (CSD-V)

Illustration of planned container for vitrified High Level Radioactive Waste for long term interim storage and clay disposal



6 Stainless steel canisters on two levels

3 Carbon steel spacers

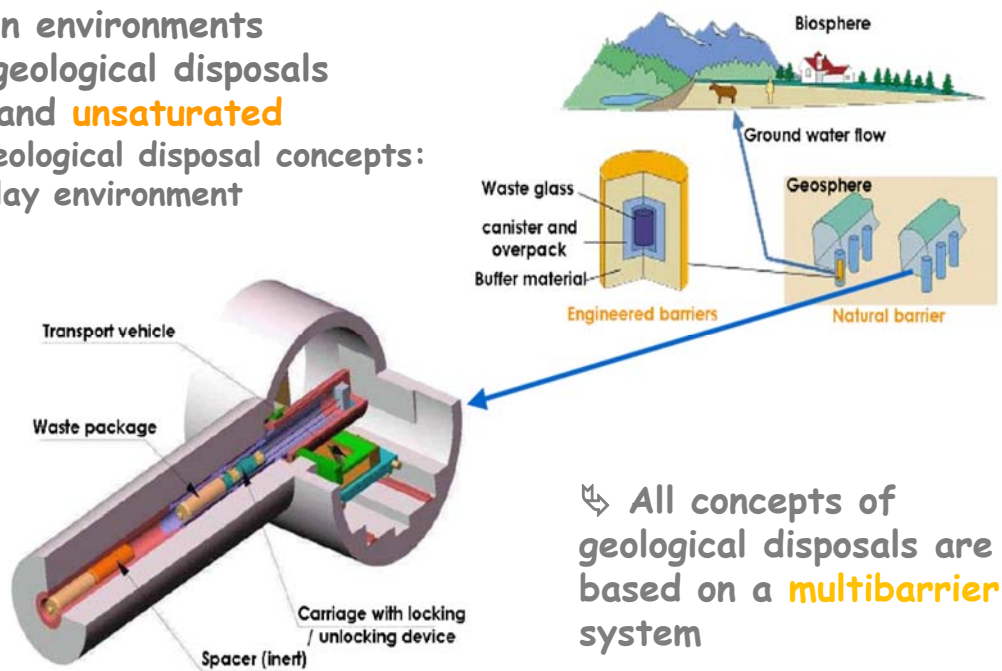
The containers are made of six stainless steel canisters containing the vitrified waste and placed into an overpack made of cast iron, with carbon steel spacers

Cast iron overpack

# UNDERGROUND DISPOSAL

↪ Two main environments regarding geological disposals **saturated** and **unsaturated**

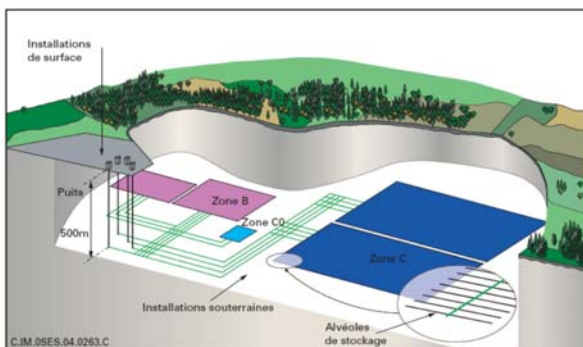
↪ French geological disposal concepts: saturated clay environment



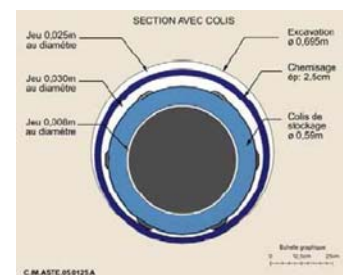
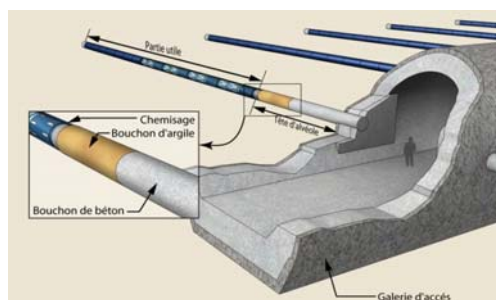
↪ All concepts of geological disposals are based on a **multibarrier** system

# UNDERGROUND DISPOSAL

## Background of the French nuclear waste disposal



- 1991: The French government decided to plan research for nuclear waste management
- 2006: Choice of a clay environment for deep geological experimental laboratory
- 2016: Licensing authorization (start of the process)



## UNDERGROUND DISPOSAL

↳ 3 periods: unsaturated and aerated conditions (over decades-exploitation phase), mixed period (over decades), and saturated & anoxic period (over milleniums)

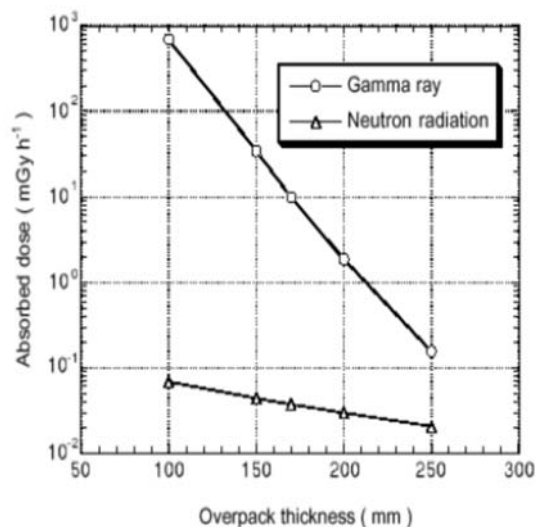
↳ The corrosion resistance of the container material over centuries (long term interim storages) and millenniums (geological waste disposal) is one of the greatest scientific and technical challenges

↳ The reliability and the viability of integrity predictions in HLNW storages and disposals are of paramount importance for public acceptance

- ◇ Local Committees
- ◇ National Commissions
- ◇ International organisations OCDE/NEA, IAEA

## UNDERGROUND DISPOSAL

### Radiolysis effect



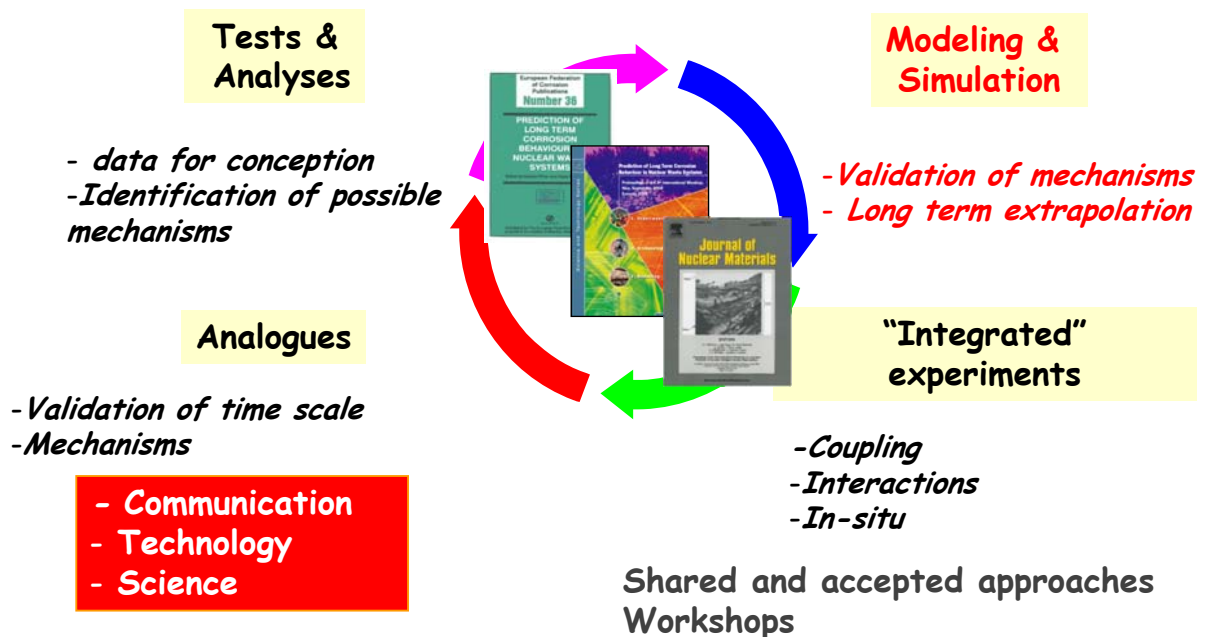
↳ Is function of the container thickness

↳ With corrosion allowance materials (copper or carbon steel), the overparck will be quite thick

# UNDERGROUND REPOSITORY

## HOW TO PREDICT CORROSION FOR MILLENNIA ?

### How to predict corrosion over millennia ?



## UNDERGROUND REPOSITORY

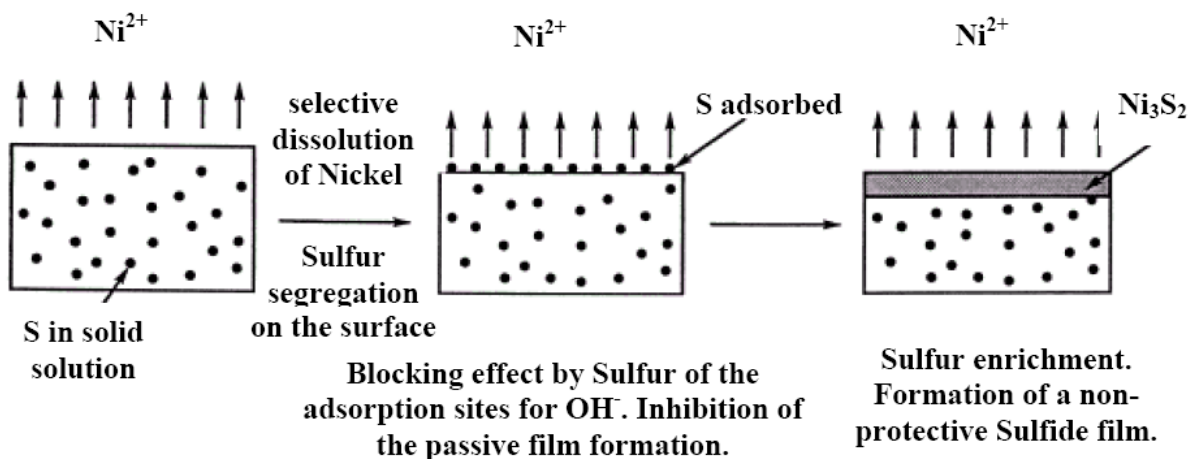
## HOW TO PREDICT CORROSION FOR MILLENNIA ?

## LABORATORY TESTS & ANALYSIS

- passive alloys are not the first choice in France
- carbon steels data

## LABORATORY TESTS

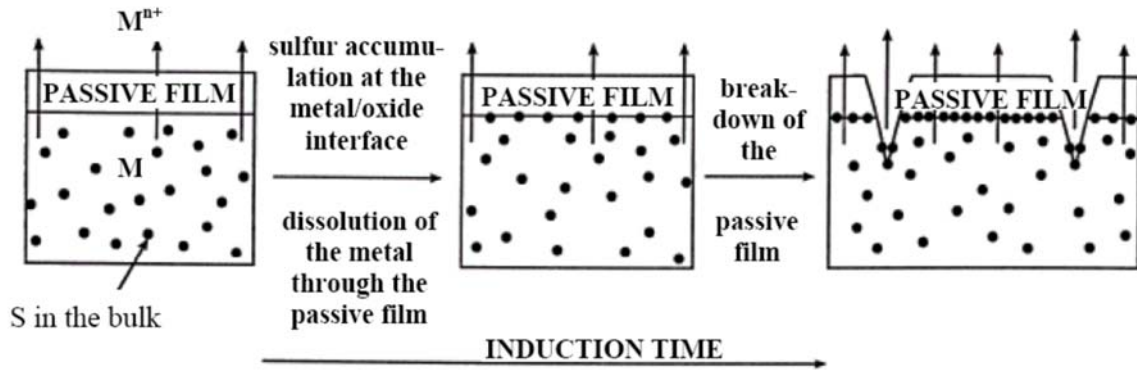
### Long term behaviour of passive Ni alloys Anodic segregation of sulphur at the alloy interface





# LABORATORY TESTS

## Anodic segregation of sulphur at the Ni alloy/passive film interface leading to passivity breakdown



$$\tau = (\Theta_{s, \max}^{interf} nF)/(iMS), \quad \Theta_{s, \max}^{interf} = \frac{MS}{nF} \int_0^{\tau} i dt.$$

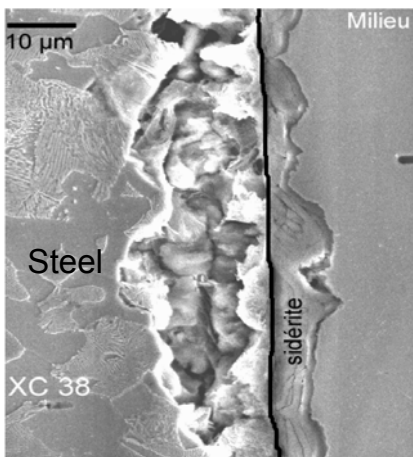
With 5 ppm of S in the alloy, and a passive current of 1 nA.cm<sup>-2</sup> (0.01 μm/an)  $\tau$  is predicted to be ~900 years

[Suppl.](#)

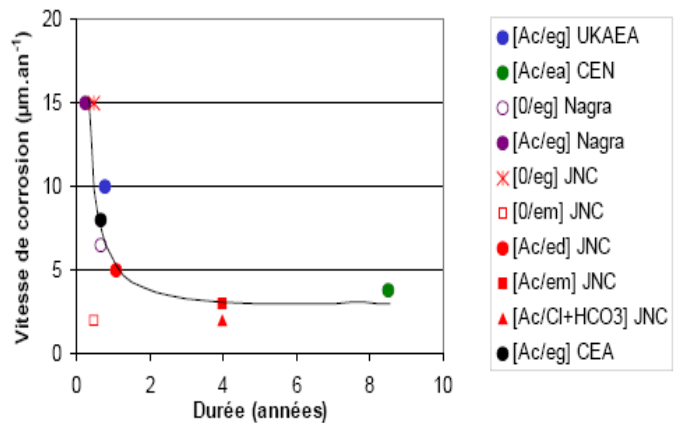
*P. Marcus & Co., Corrosion Science 24(1984)259, 29(1989)455, 31 (1990) 377*

# LABORATORY TESTS

## Evaluation of uniform corrosion rates of carbon steel under anaerobic conditions at 80°C-85°C with various water chemistries



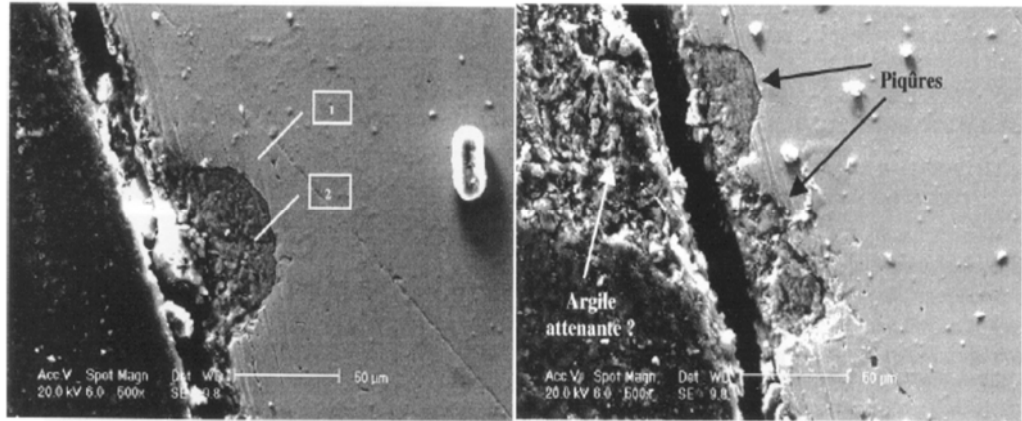
Carbon steel (micrography) in clay environment



G : granite ; Ac : argile compacte ; 0 : immersion  
 ed : eau distillée ; eg : eau granitique ; em : eau de mer ; ea : eau argileuse  
 From J.M. Gras, *Référentiel Matériaux*, ANDRA, 2005



## LABORATORY TESTS



CEA results, Référentiel Matériaux, ANDRA, 2005

*Pitting observed on carbon steel after 8 months in saturated clay*

$$P = \text{Pitting factor} = D/X$$

*D = maximum pit depth at t*

*X = Mean uniform corrosion depth at t*

**UNDERGROUND REPOSITORY**

**HOW TO PREDICT CORROSION FOR  
MILLENNIA ?**

**MODELLING**

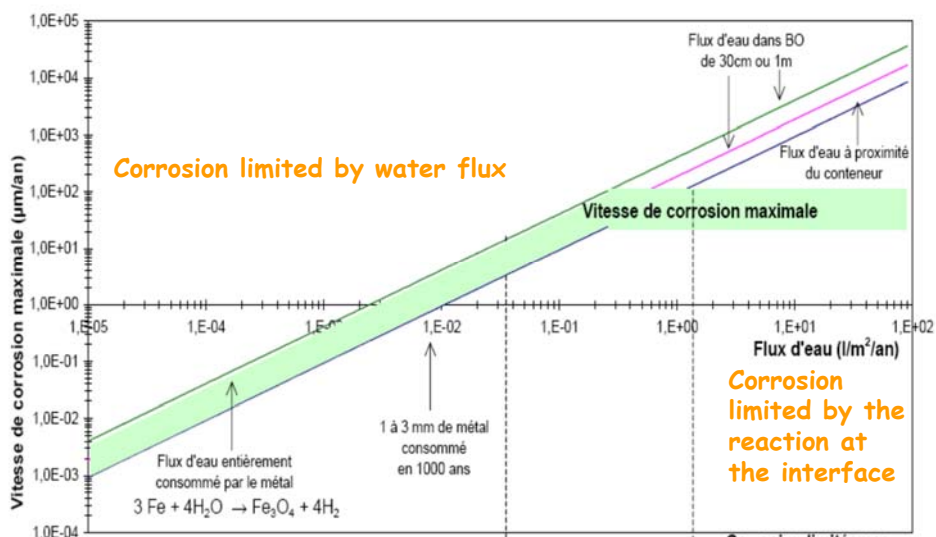
## MODELLING

- Empiricism (semi-empirical models)
  - ✓ (Semi-)empirical modelling is based on experimental data or service life data
  - ✓ It is used for obtaining initial estimates
  - ✓ It has the disadvantage of having to know the answer "in advance"
- Determinism (mechanistically based models)
  - ✓ it is based on physics, requires viable physical model
  - ✓ the greatest challenge is to decide what processes should be included
  - ✓ continuously improved via the knowledge evolution
- Stochastic taking into account the stochastic nature of corrosion phenomena

↻ In complementary, rather than supplementary manner  
 ↻ The validation of these models is an absolute necessity:  
 archaeological analogues

## MODELLING - 1

## First calculations in clay environment: diffusion of water



From D. Crusset, Référentiel Matériaux, ANDRA, 2005

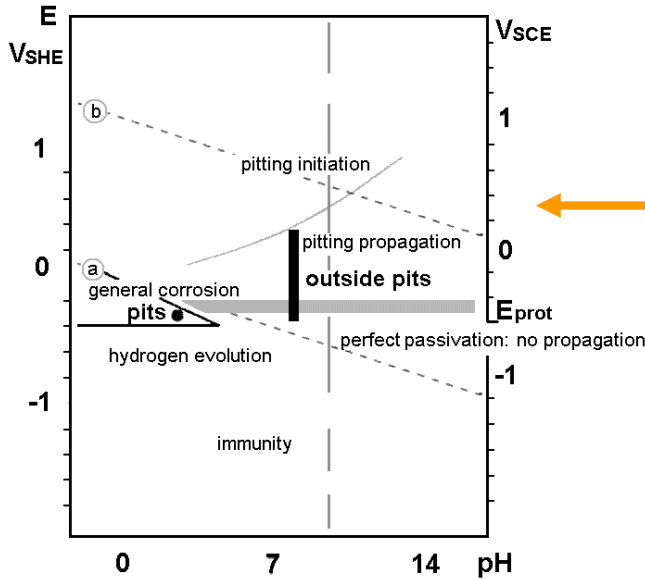
Uniform corrosion rate of carbon steel in clay (anaerobic conditions) limited by the water flux or by the interface reaction

# MODELLING - 2

## Thermodynamics / Critical crevice potential

Below  $E_{cc}$ , crevice corrosion does not occur

- ✓ Thermodynamic (absolute) value ?
- ✓ Data depending on test device ?



Conditions inside and outside pits of carbon steels with the protection potential range and the domain for perfect passivation

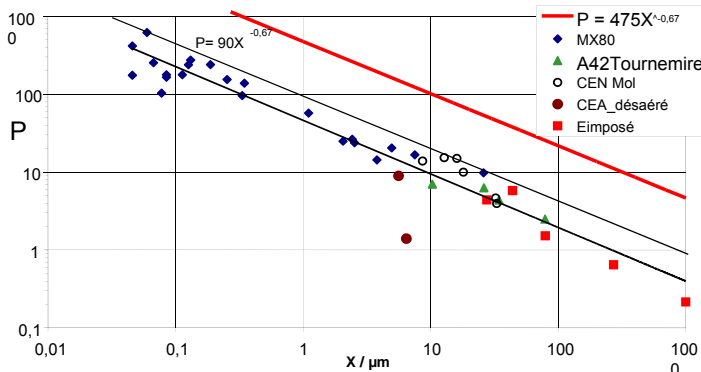
From A. Pourbaix., Cadarache Workshop 2001

# MODELLING - 3

$P = \text{Pitting factor} = D/X$

$D = \text{maximum pit depth at } t$

$X = \text{Mean uniform corrosion depth at } t$

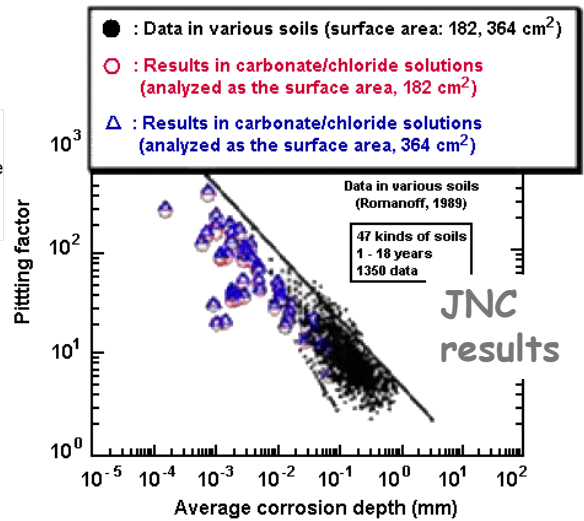


From F. Focf, Référentiel Matériaux, ANDRA, 2005

$P = \text{Pitting factor}$

(max. pitting depth / mean corrosion depth)

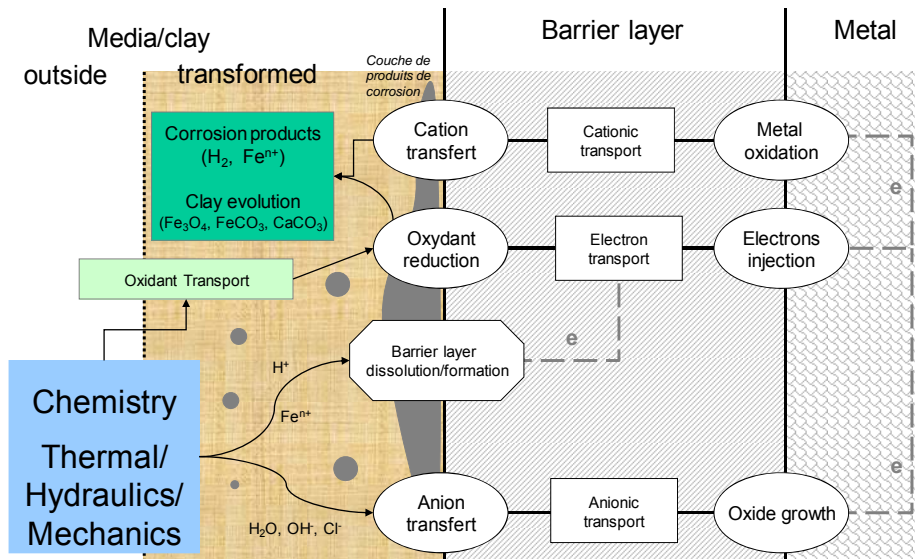
$X = \text{Mean uniform corrosion depth}$



# MODELLING - 4

The Point Defect Model is applied and describes:

- ✓ the evolution of oxide films on carbon steel in clay and concrete environments
- ✓ the growth and breakdown of passive films of high alloyed materials in saturated brine



From C. Bataillon & al., Référentiel Matériaux, ANDRA, 2005  
D. Féron

page 21

Berkeley April 2015

# MODELLING - 4

## Corrosion modeling of an iron based alloy in passive conditions

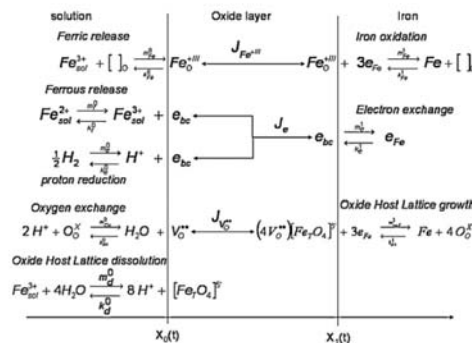


Fig. 3. Flow chart for electrons, octahedral cations and oxygen vacancies. Kröger-Vink notation is used. [ ]<sub>o</sub> corresponds to a free octahedral site.

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

# MODELLING - 4

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

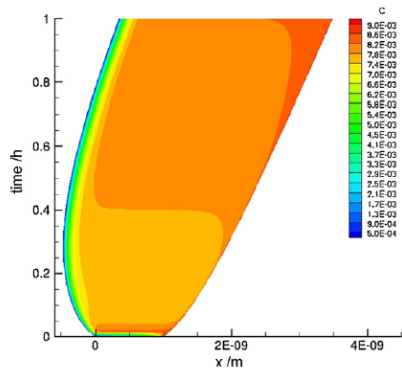
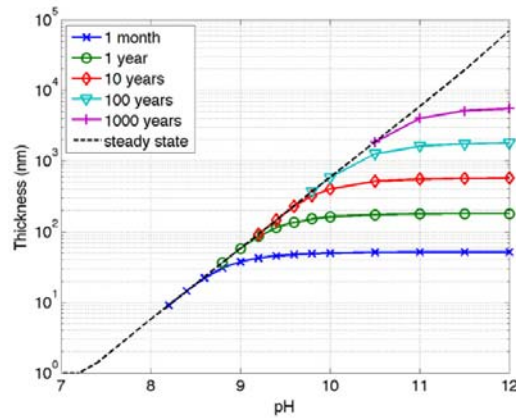


Fig. 36. Evolution of the location of the outer and inner interfaces with time for  $V=0.05V/SHE$ . The concentration of oxygen vacancies is indicated by the color on the right band. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the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



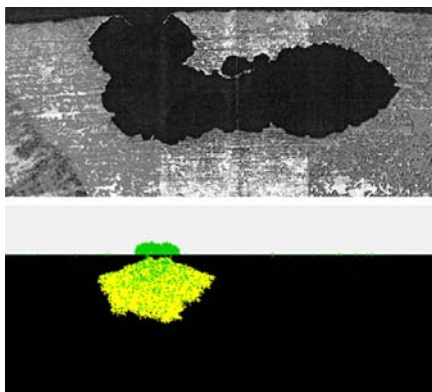
C. Bataillon & al. , *Elect. Acta* 55 (2010) 4451-4467

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

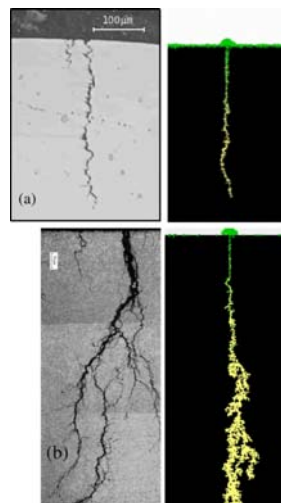
This model is under implantation in the nuclear waste simulations codes

# MODELLING - 5

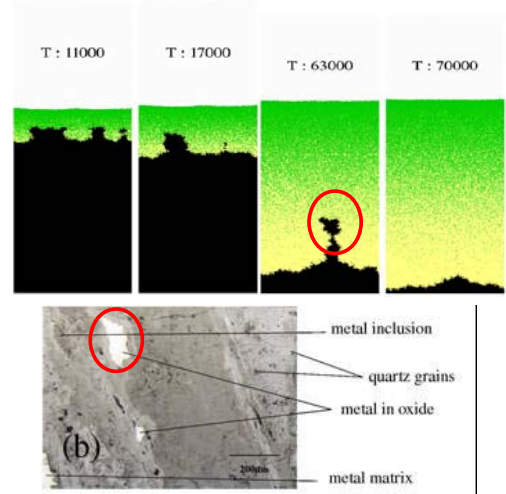
## Use of cellular automata to model corrosion phenomena Same description / difference: statistic of occurring events



Localised corrosion  
 $\lambda = 0.3$  and  $\epsilon = 0.005$



Stress corrosion cracking  
(a)  $\lambda = 0.99$  and  $\epsilon = 0.01$ ,  
(b)  $\lambda = 0.978$  and  $\epsilon = 0.001$ .



Evolution of the interface morphology (metal inclusions)  
 $\lambda = 0.70$  and  $\epsilon = 0.30$

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



## UNDERGROUND REPOSITORY

## HOW TO PREDICT CORROSION FOR MILLENNIA ?

## ARCHEOLOGICAL ARTIFACTS / ANALOGUES

- corrosion rates
- influence of the environment
- influence of the metal
- corrosion mechanisms
- modeling validation

## ARCHEOLOGICAL ARTIFACTS



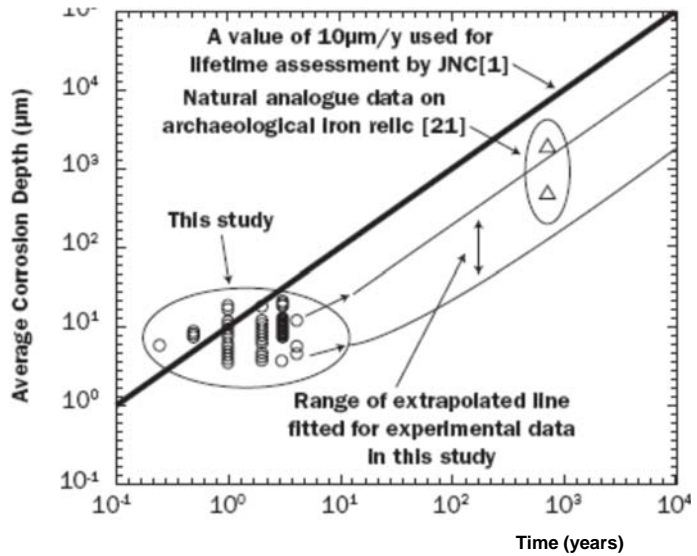
Roman nail found at the Adrian Wall (1900 years old, 35 cm long), from Miller W & Co. 1994

- Use of archaeological analogues
  - ✓ to demonstrate
  - ✓ to provide a database
- Sufficient care has to be taken
  - ✓ many old metallic materials have corroded away
  - ✓ differences between old and new materials
  - ✓ poor knowledge of exposure conditions
- Illustrations:
  - ✓ Corrosion rates (but take care!)
  - ✓ Importance of the corrosion product layer (and not only the corrosion rate)

# ARCHEOLOGICAL ANALOGUES - 1

## Uniform corrosion

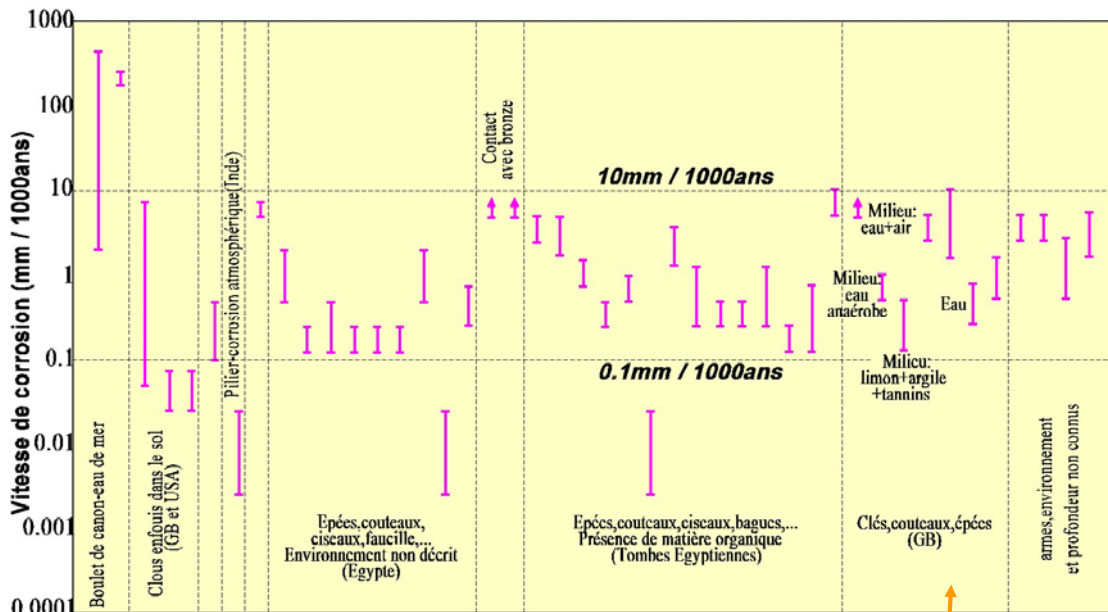
Evaluation of long term evolution of the average corrosion depth of carbon steel in contact with bentonite under anaerobic conditions based on experimental data and a comparison with lifetime assessment and with natural analogue data



From Taniguchia & col., Nice workshop, 2004

# ARCHEOLOGICAL ANALOGUES - 1

## Corrosion rates



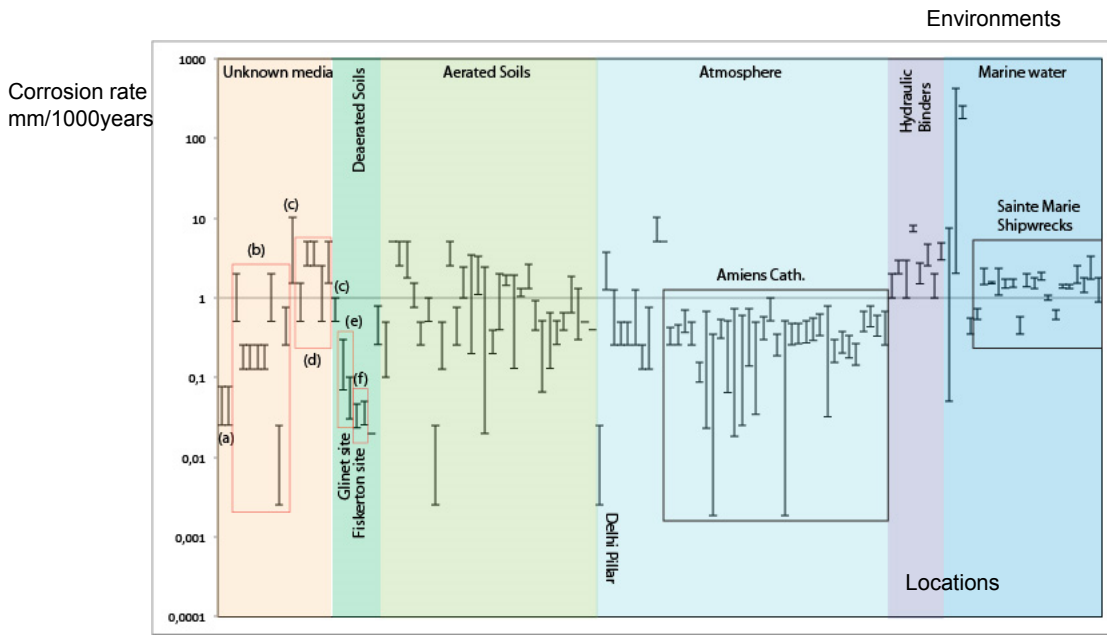
From David, Cadarache w., 2001

Swords, knives, scissors, from Ancient Egypt

UK (Roman period)



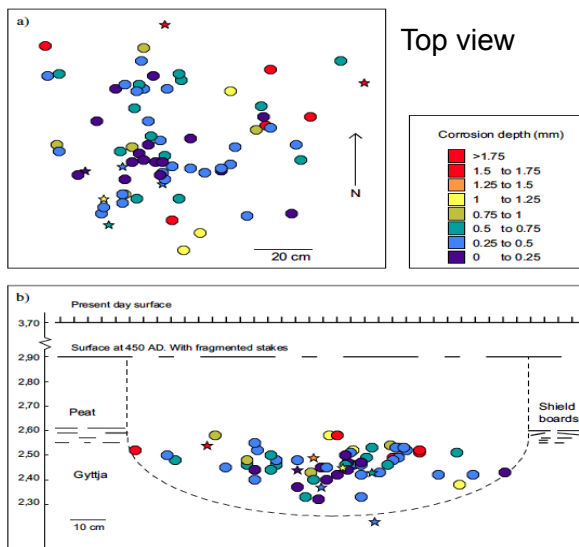
# ARCHEOLOGICAL ANALOGUES - 1



Mean corrosion rates observed on artifacts exposed more than a century in various environments (from P. Dillmann)

# ARCHEOLOGICAL ANALOGUES – 2

**Influence of the local environment:**  
highest corrosion rates for objects close to the surface



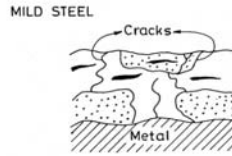
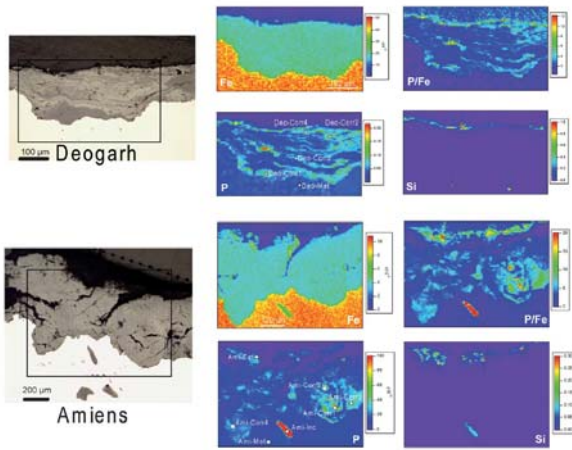
Nydam Mose site (Denmark), from H. Matthiesen & al., 114-127, 2<sup>nd</sup> international workshop, Nice 2004 – proceedings edited by Andra

Section view

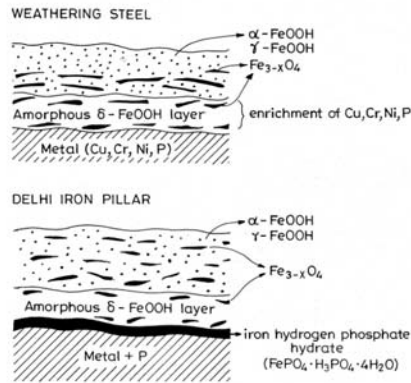
- Without oxygen, corrosion rates are lower than 10  $\mu\text{m}/\text{year}$  (and often lower than 1  $\mu\text{m}/\text{year}$ )
- In aerated conditions, large variations of the corrosion rates are observed (from few  $\mu\text{m}$  to several hundreds  $\mu\text{m}$ )

# ARCHEOLOGICAL ANALOGUES - 3

Monnier J. & al. Anal. At. Spectrom., 2011, 26, 885



Delhi iron pillar from R. Balasubramaniam & al. in EFC 36, published by Maney (2002), pp 261-280 (1st workshop) & Corrosion science, 42, 2000, 2103-20129

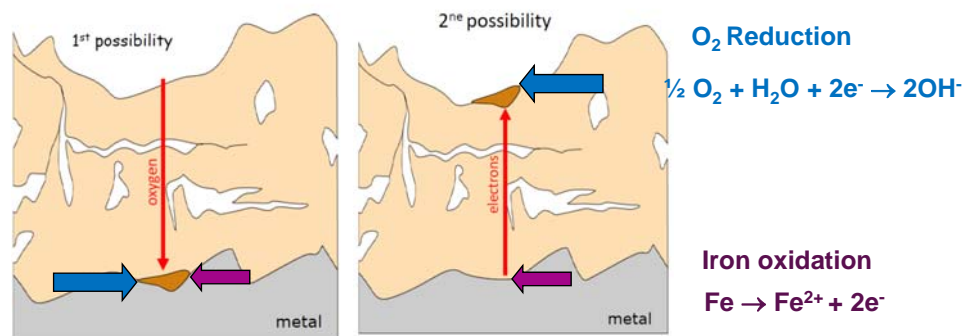


**Importance of the metallurgy (minor elements)**  
 Role of phosphorous found on the votive columns of India from the 6th century and on other artifacts

# ARCHEOLOGICAL ANALOGUES - 4

## Mechanisms

Localization of the cathodic reaction in aerated conditions (oxygen reduction) : use of tracers <sup>18</sup>O et <sup>2</sup>H



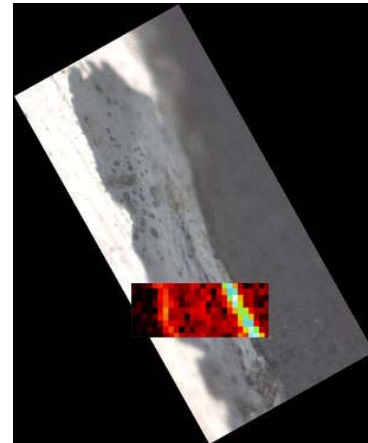
## Corrosion mechanisms: localization of the cathodic reaction

Use of  $^{18}\text{O}_2$  during reexposure of the specimen to atmospheric corrosion

Rutherford backscattering spectroscopy (RBS) and nuclear reaction analysis (NRA)



Isolating layer (goethite): reaction at the interface metal/oxide



Conductive oxide layer: external interface

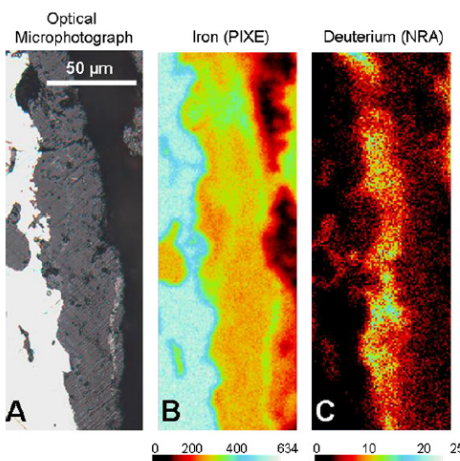
E. Burger & al., J. Mater. Res., Vol. 26, No. 24, Dec 28, 2011  
D. Féron page 33

Berkeley April 2015

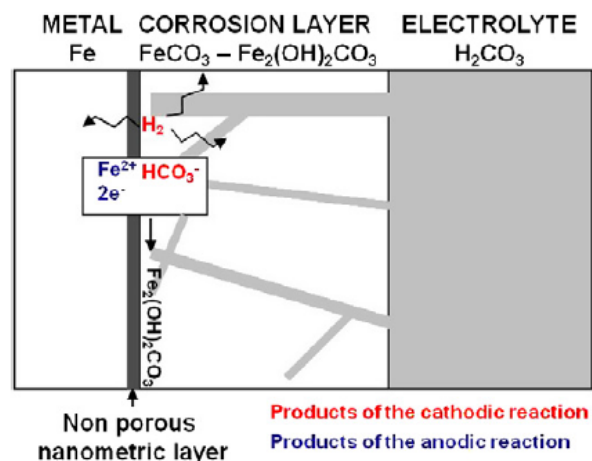
## Localization of the cathodic reaction in anoxic conditions

Use of  $\text{D}_2\text{O}$  during re-exposure of an artefact from the Glinet site to aqueous corrosion

Rutherford backscattering spectroscopy (RBS) and nuclear reaction analysis (NRA)

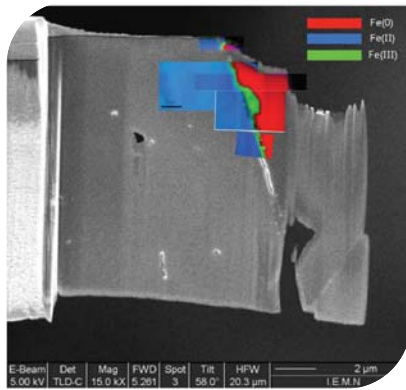


Deuterium in the oxide layer, near the interface metal/oxide



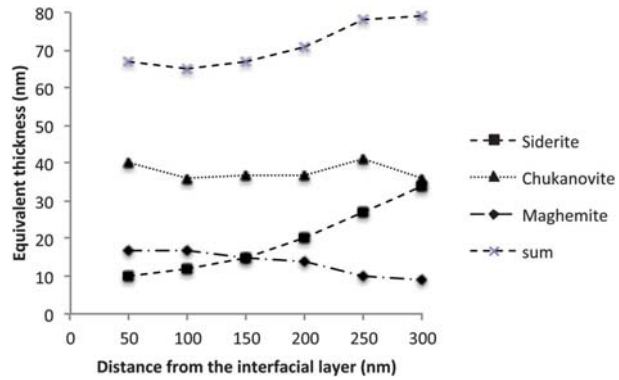
M. Saheb & al., JNM, 423 (2012) 61–66

## ARCHEOLOGICAL ANALOGUES - 5



From A. Michelin & al., JAAS, 2012

Equivalent thicknesses of the different phases obtained from the fit of the extracted spectra.



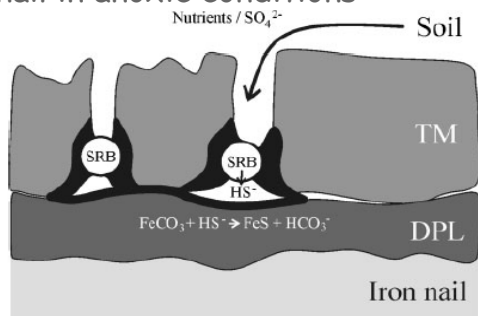
### Support for modelling

- Corrosion products of a 450 year old archaeological iron nail in anoxic environment were investigated at the nanometer level using STXM
- **Interfacial layer of about 100 nm at the interface metal/oxide**
- Support the hypothesis of a nanolayer controlling the corrosion process (Point Defect Model and associated models)

## ARCHEOLOGICAL ANALOGUES - 6

In many archeological sites, SRBs are found and/or corrosion products with  $S^{2-}$  are observed in the corrosion product layer

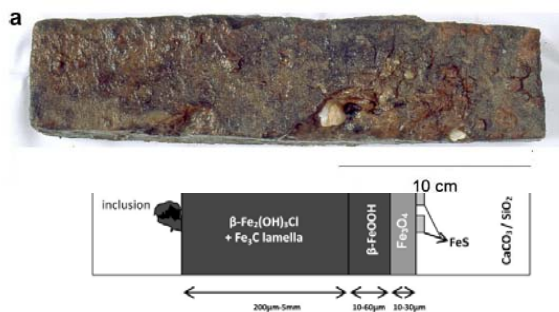
Observations of a 16<sup>th</sup> century nail in anoxic conditions



7 Schematic representation of influence of SRB on corrosion system formed by archaeological nails in anoxic soils (TM, transformed medium; DPL, dense products layer)

C. Remazeilles & al., CEST, 2010 VOL 45 NO 5, 388-394

Roman ingot (2000 years old)



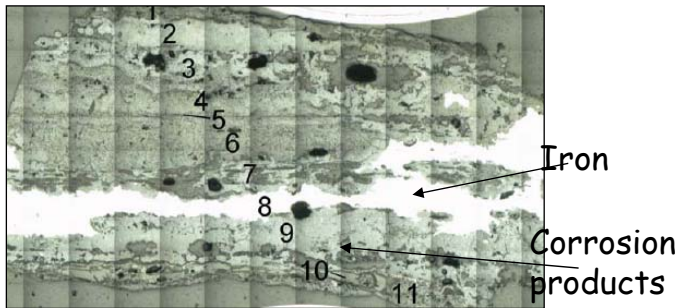
C. Remazeilles et al., Corrosion Science 51 (2009) 2932-2941

Even with SRBs, low corrosion rates are observed

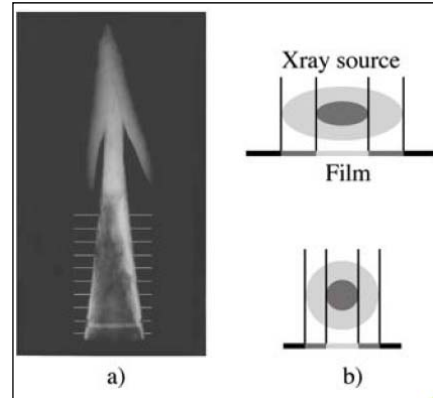


# ARCHEOLOGICAL ANALOGUES - 6

(Nydam site in Denmark - anoxic conditions with sulphides)



H. Matthiesen, Proceedings of the Second International workshop, Nice, 2004 - published by ANDRA (ISBN 2-95101108-6-9, p.114)



	Min.	Max.	Mean	95% CI of Mean	n
pH	5.99	7.02	6.50	6.47 to 6.54	140
Sulphate (mg SO <sub>4</sub> /L)	<10	200	21	16 to 27	101
Sulphide (mg S(-II)/L)	<0.03	2.22	0.18	0.12 to 0.23	116

Measurements on 151 lances have demonstrated corrosion depths as low as 50 μm (average of 20 measurements on a lance). With 1700 years of age this corresponds to an average corrosion rate of 0.03 μm/year (or even lower,

**Even with sulphur environments and bacteria, very low corrosion rates**

**UNDERGROUND REPOSITORY**

**HOW TO PREDICT CORROSION FOR MILLENNIA ?**

**INTEGRATED EXPERIMENTS**

# INTEGRATED EXPERIMENTS

Six years in bentonite



Nothing on stainless steels & titanium alloys  
0.1  $\mu\text{m}/\text{year}$  on mild steels  
0.7-0.8  $\mu\text{m}/\text{year}$  on copper alloys

But on one sensor ...

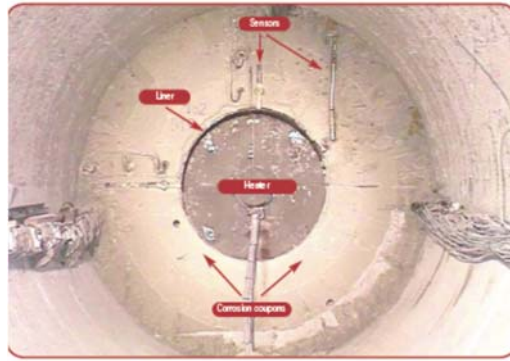


Fig. 4 Sensor in block of bentonite

V. Madina & Co., Corrosion of several components of the *in situ* test performed in a deep geological granite disposal site, Proceedings of the Second International workshop, Nice, 2004 - published by ANDRA (ISBN 2-95101108-6-9, p.61)

# INTEGRATED EXPERIMENTS



Fig. 7 Transversal section of sensor

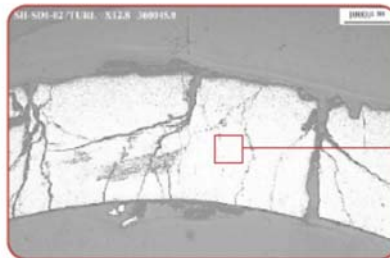


Fig. 8 SCC in transversal section of sensor



Fig. 9 Detail of Fig. 8

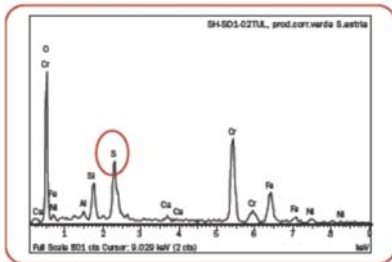


Fig. 6 EDS spectrum of corrosion products on sensor

Microbe group	c.f.u./g count of sample	
	Bentonite ref. "Sensors"	Bentonite ref. "coupons"
Anaerobic bacteria	0	0
Aerobic bacteria	4.23 x 10 <sup>6</sup> (*)	0
Sulphate-reducing bacteria (SRB)	3.77 x 10 <sup>6</sup>	0
Iron-oxidizing bacteria	0	0
Sulphur-oxidizing bacteria	0	0

Table-1 Microbiological characterization of two samples of bentonite  
(\*) The whole count consisted of large c.f.u.: Colony forming units.

Following the authors, this corrosion mainly due to water ingress & SRB

In addition, simultaneous presence of SRB and aerobic bacteria leads to the worse conditions for passive alloys, as seen for seawater applications

V. Madina & Co., Corrosion of several components of the *in situ* test performed in a deep geological granite disposal site, Proceedings of the Second International workshop, Nice, 2004 - published by ANDRA (ISBN 2-95101108-6-9), p.61

# CORROSION AND THE FRENCH CONCEPT OF THE UNDERGROUND DISPOSAL FOR HIGH RADIOACTIVE NUCLEAR WASTES

## FINAL COMMENTS

## FINAL COMMENTS

### Life time prediction over millenna

#### Experimentation & analysis

- Preliminary data for design
- Identification of possible mechanisms

#### Historical & archaeological artifacts

- Validation of time constants
- Validation of mechanisms

#### Simulation

- Validation of mechanisms
- Extrapolation to long term

#### Integrated experiments

- Coupling of mechanisms
- Interactions
- In-situ





<http://www.cigeo.com/>

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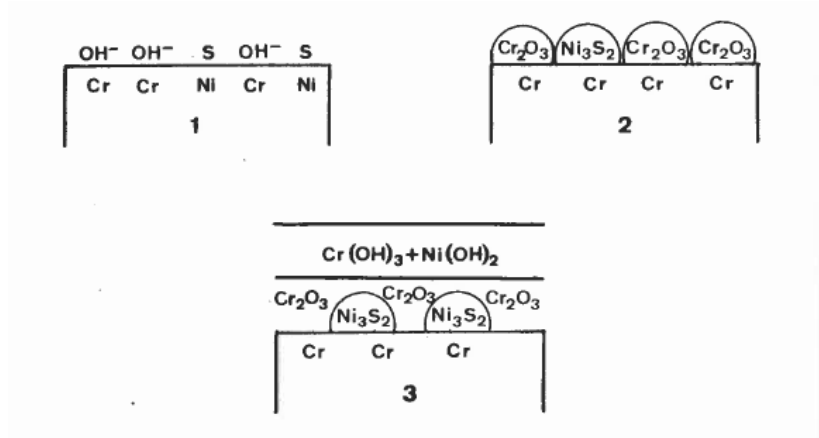
Etablissement public à caractère industriel et commercial | RCS Paris B 775 685 019

Direction de l'Energie Nucléaire  
Département de physico-Chimie  
Service de la corrosion et du  
comportement des matériaux dans leur  
environnement



## SUPPLEMENTARY OVERHEADS

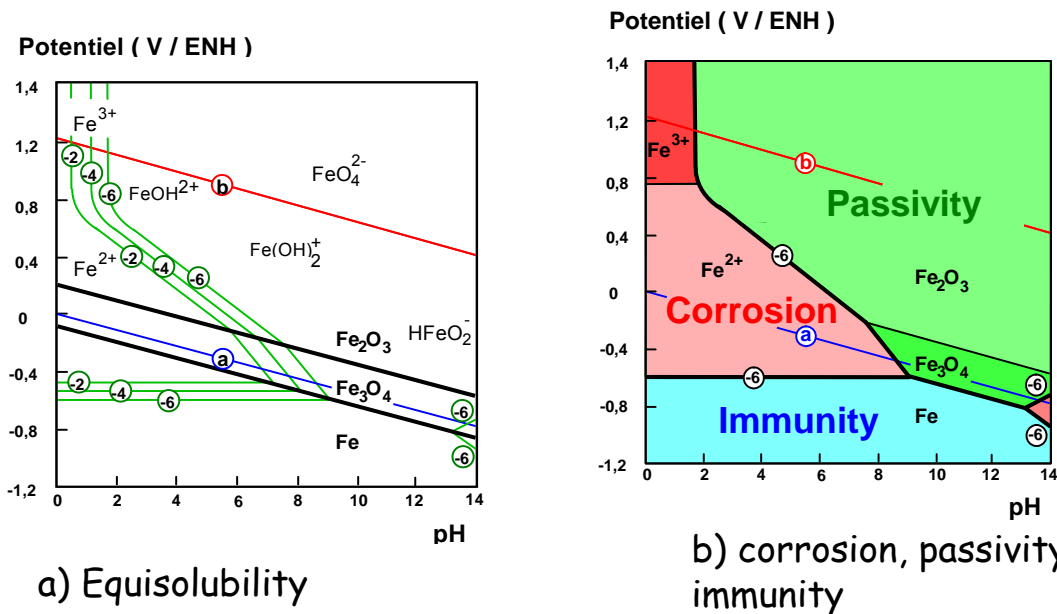
## Antagonistic roles of chromium and sulphur on passivation



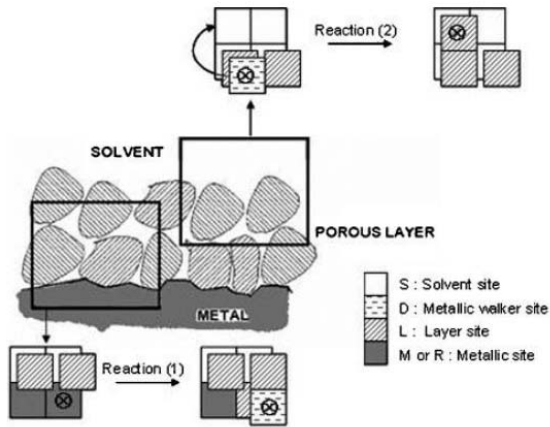
Ni-21Cr-8Fe at.% with 0,009 at.% of S

**Chromium strongly counteracts the detrimental effect of sulphur**

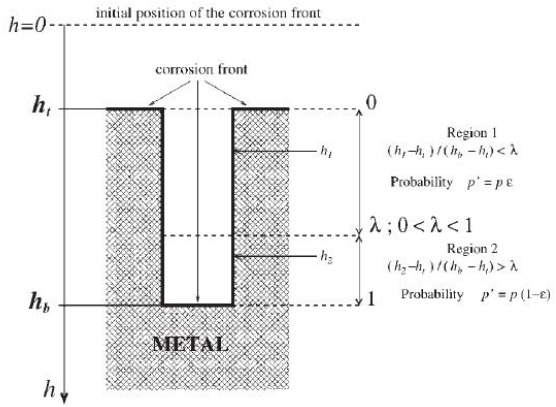
## Pourbaix diagram for Iron



Bases of the modeling: probabilities of reactions



1 Simple scheme of forming layer with clusters and solution representation of reactions (1) and (2)



2 Definition of  $\lambda$  and  $\varepsilon$ :  $\lambda$  defines extension of top region where probability of corrosion is  $p\varepsilon$ ; in remaining bottom area, probability of corrosion is  $p(1-\varepsilon)$