

DE LA RECHERCHE À L'INDUSTRIE

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Reinforced Concrete structures  
degradation issues:  
Impact of Chlorides and of Thermal  
loadings on Corrosion development

Valérie L'Hostis\*, Patrick Le Bescop\*,  
Benoit Bary\*, Raoul François\*\*

\* Den-Service d'Etude du Comportement des Radionucléides (SECR), CEA,  
Université Paris-Saclay, F 91191, Gif-sur-Yvette, France; valerie.lhostis@cea.fr

\*\* Université de Toulouse, INSA, UPS, Laboratoire Matériaux et Durabilité des  
Constructions, F-31077 Toulouse, France.

## General aspects of corrosion in concrete structures

- Cement chemistry
- Passivity of steel embedded in concrete
- Chloride chemical interaction with concrete
- Thermal loadings effects on concrete

## Application to Fukushima Daiichi conditions

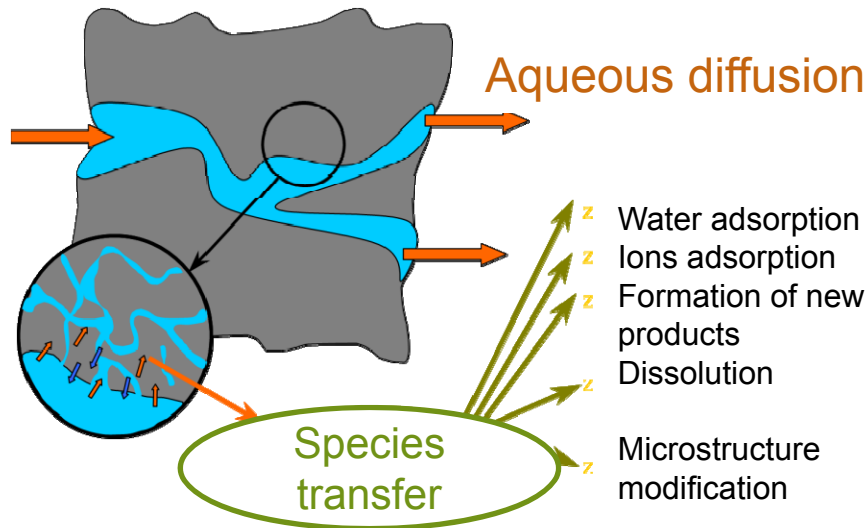
- Scenario 1 : Chloride interaction
- Scenario 2 : Thermal loading

## Concluding remarks

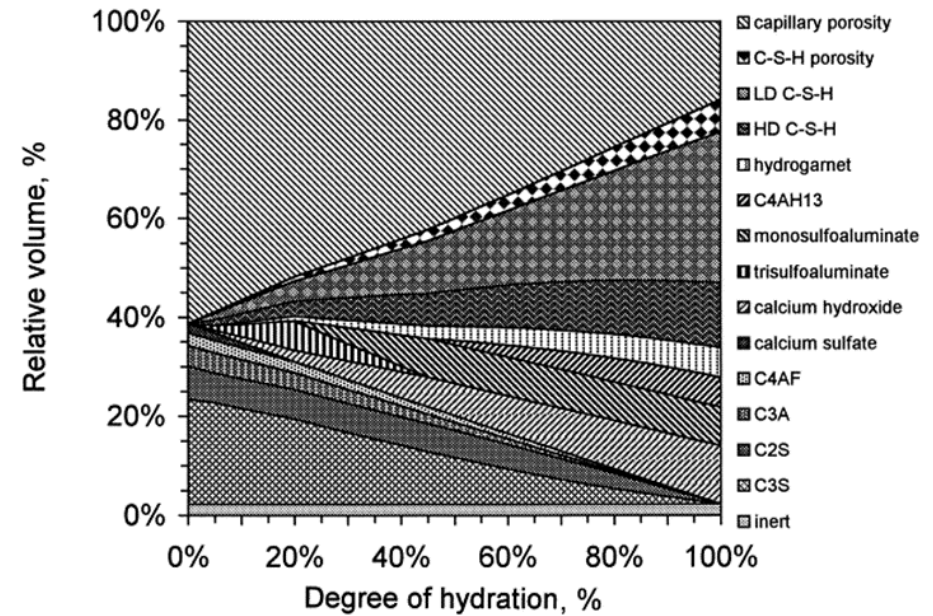
# CEMENT CHEMISTRY



Concrete is a porous material



... Chemistry of its interstitial solution is fixed by minerals

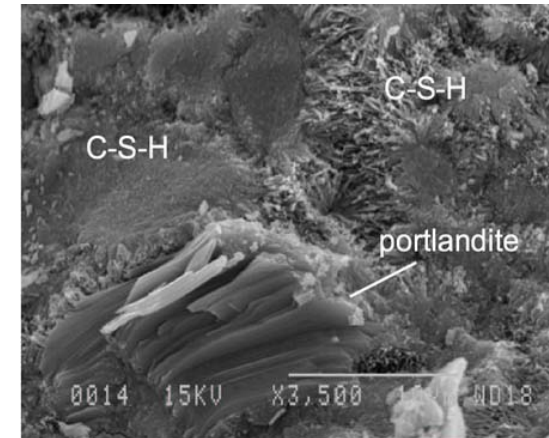


*P. D. Tennis and H. M. Jennings, Cem. Concr. Res., vol. 30, pp. 855-863, 2000.*

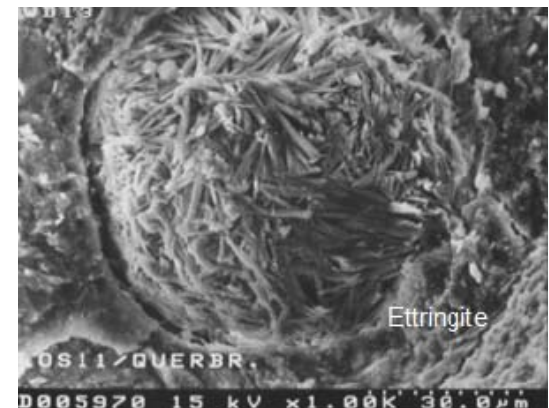
pH of concrete pore solution is around 13

Phase	Mineral	Formula
	Portlandite	$Ca(OH)_2$
C-S-H	Jennite Tobermorite	$Ca_{1.67}(SiO_2)(OH)_{3.33}(H_2O)$ $Ca_{0.83}(SiO_2)(OH)_{1.67}(0.5H_2O)$
phase AFm	Monosulfoaluminate Monocarboaluminate Hemicarboaluminate	$Ca_4Al_2(SO_4)(OH)_{12.6}H_2O$ $Ca_4Al_2(CO_3)(OH)_{12.5}H_2O$ $Ca_4Al_2(CO_3)_{0.5}(OH)_{13}(5.5H_2O)$
phase AFt	Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12.26}H_2O$
phase Hydrogrossular	Hydrogarnet KatoiteSi Siliceous hydrogarnet	$Ca_3Al_2(OH)_{12}$ $Ca_3Al_2(SiO_4)(OH)_8$ $Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8}$

**Mineral phases are fixing pH value as well as chemical reactivity of cement**

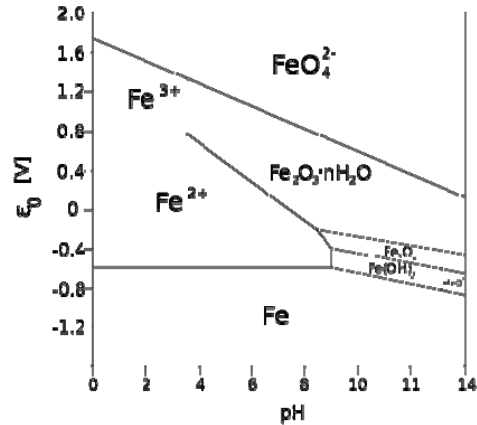


V. Baroghel-Bouny, "PhD, 1994.

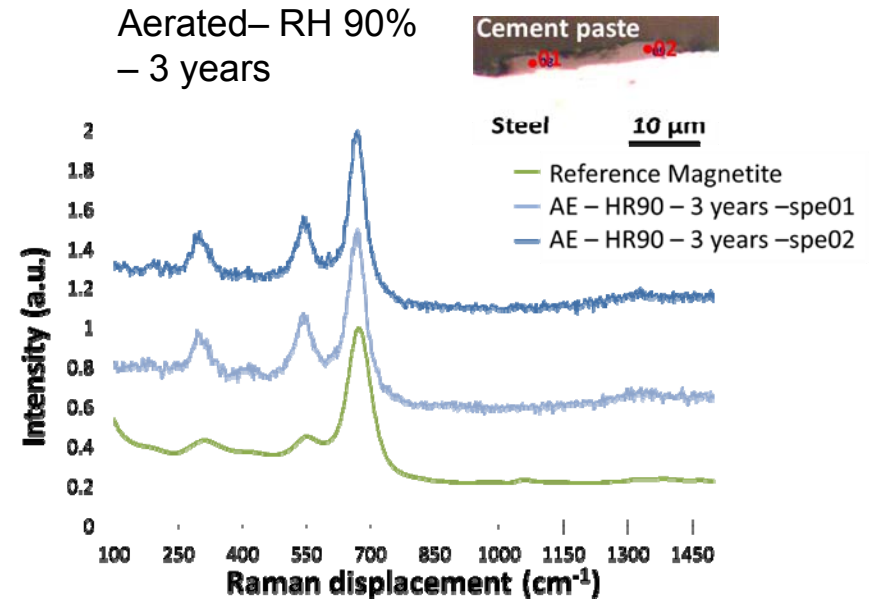
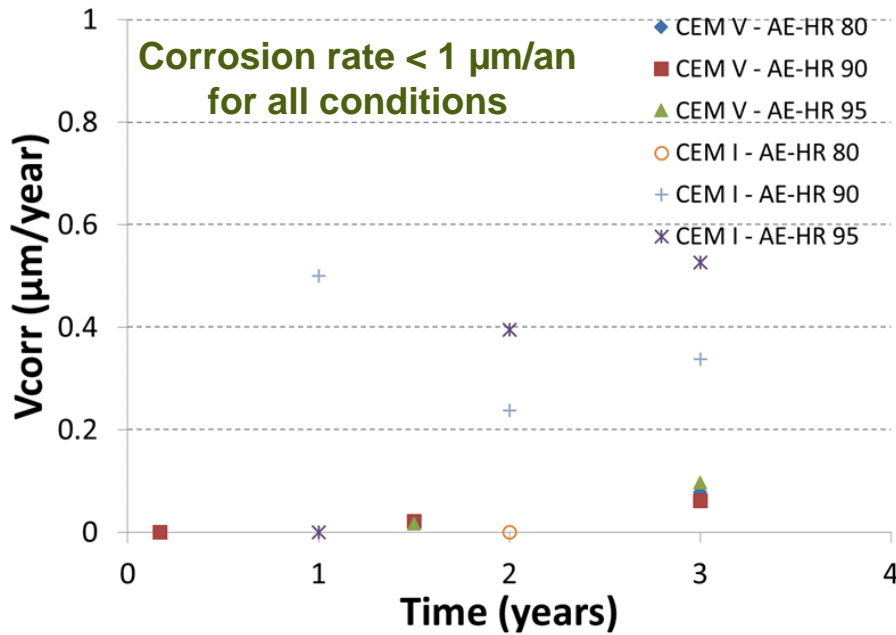
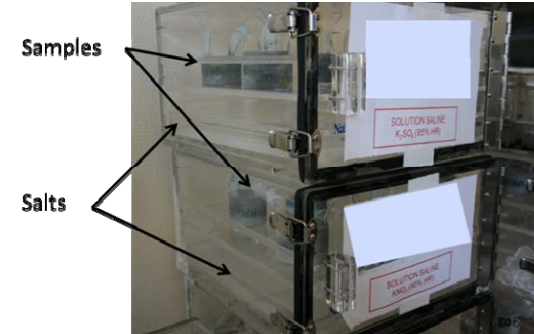


J. Stark and K. Bollmann, Nord. Concr. Res., vol. 23, pp. 4–28, 2000.

# **PASSIVITY OF STEEL EMBEDDED IN CONCRETE**



**Evidenced of passivity in cementitious material**



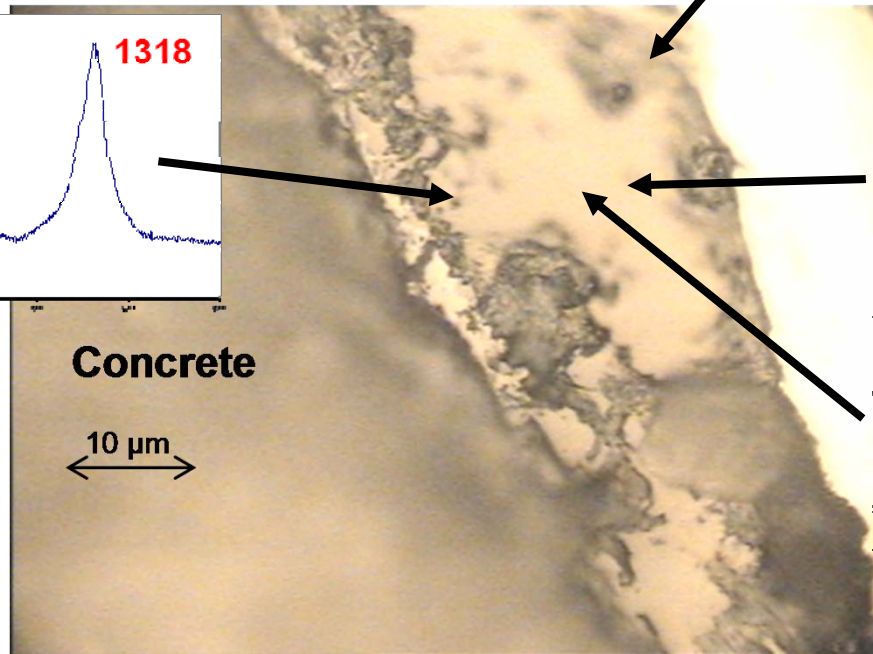
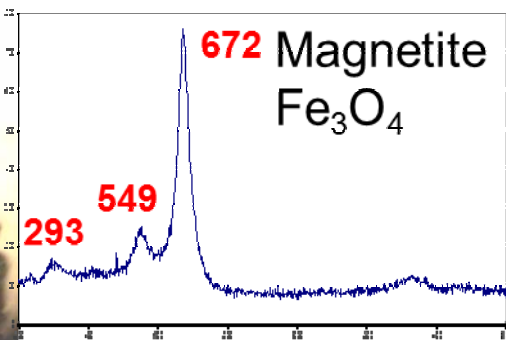
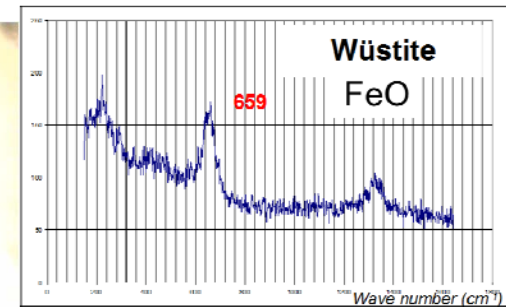
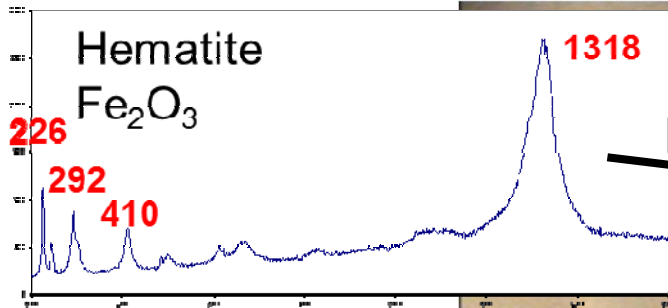
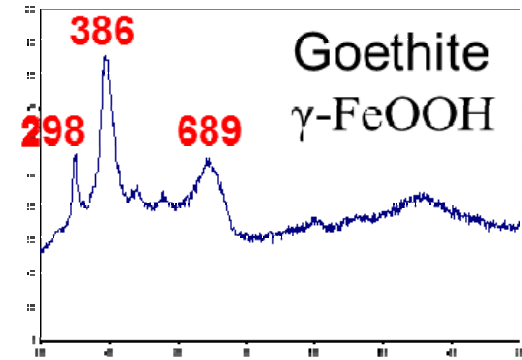
**Stable corrosion product layer in term of composition (magnetite) and thickness (few μm)**

L. Chomat, V. L'Hostis, E. Amblard, L. Bellot-Gurlet, *Corrosion Engineering, Science and Technology*, 49 (6) pp. 467-472 (2014).



Bresil House (Paris International University)  
50 years old

Evidenced of passivity even after few tens of years



V. L'Hostis, D. Neff, L. Bellot-Gurlet, P. Dillmann,  
*Materials and Corrosion*, Vol. 60, n°2, pp. 93-98, 2009

Corrosion product layer  
thickness 10-50 μm (mill scale)



# **CHLORIDE CHEMICAL INTERACTION WITH CONCRETE**

Phase	Mineral	Formula
	Portlandite	$Ca(OH)_2$
C-S-H	Jennite Tobermorite	$Ca_{1.67}(SiO_2)(OH)_{3.33}(H_2O)$ $Ca_{0.83}(SiO_2)(OH)_{1.67}(0.5H_2O)$
phase AFm	Monosulfoaluminate Monocarboaluminate Hemicarboaluminate	$Ca_4Al_2(SO_4)(OH)_{12} \cdot 6H_2O$ $Ca_4Al_2(CO_3)(OH)_{12} \cdot 5H_2O$ $Ca_4Al_2(CO_3)_{0.5}(OH)_{13} \cdot (5.5H_2O)$
phase AFt	Ettringite Tricarboaluminate	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$ $Ca_6Al_2(CO_3)_3(OH)_{12} \cdot 26H_2O$
phase Hydrogrossular	Hydrogarnet KatoiteSi Siliceous hydrogarnet	$Ca_3Al_2(OH)_{12}$ $Ca_3Al_2(SiO_4)(OH)_8$ $Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8}$

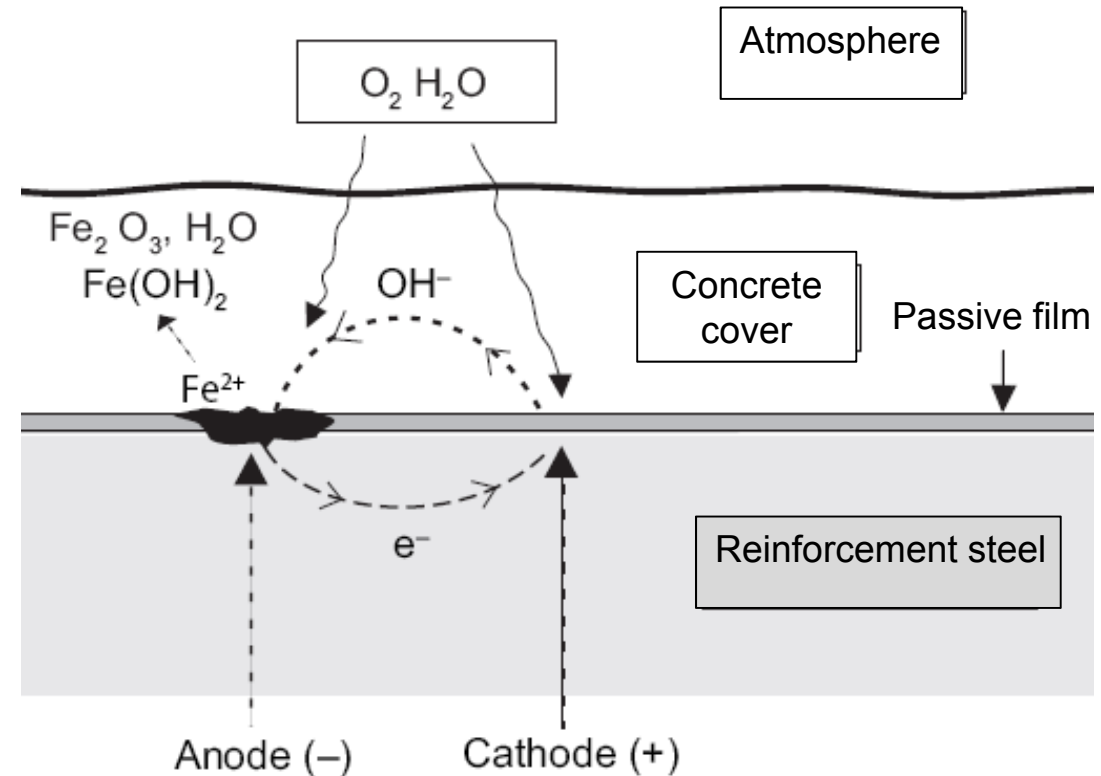
**Friedel salt** (chloroaluminate):  $Ca_4Al_2Cl_{1.95}(OH)_{12.05} \cdot 4H_2O$   
 comes from  $4Ca^{2+} + 2AlO_2^- + 1.95Cl^- + 4.05OH^- + 8H_2O$

**Kuzel salt:**  $Ca_4Al_2(SO_4)_{0.5}Cl(OH)_{12} \cdot 6H_2O$   
 comes from  $4Ca^{2+} + 2AlO_2^- + Cl^- + 0.5SO_4^{2-} + 4OH^- + 10H_2O$

Chloride ions can also adsorbed on C-S-H minerals

Chloride content  
 = Equilibrium  
 between solid  
 phase and  
 aqueous  
 concentration  
 → **Total, fixed  
 and free chloride**

**Corrosion mechanism**  
**Anodic and cathodic**  
**reactions are delocalized**



- Local cells where  $[Cl^-]/[OH^-] >$  threshold (value controversial in the literature  $\approx 0,6$ )
- Formation of **ferrous-chloride ( $FeCl_2$ )** and **green rust** as precursor corrosion products
- Dissolution of reinforcement bars

## Green rust formation

Steel dissolution

Green rust



## Consequences on rebar

**Steel section losses**



**Green rust is oxidized in aerated media**

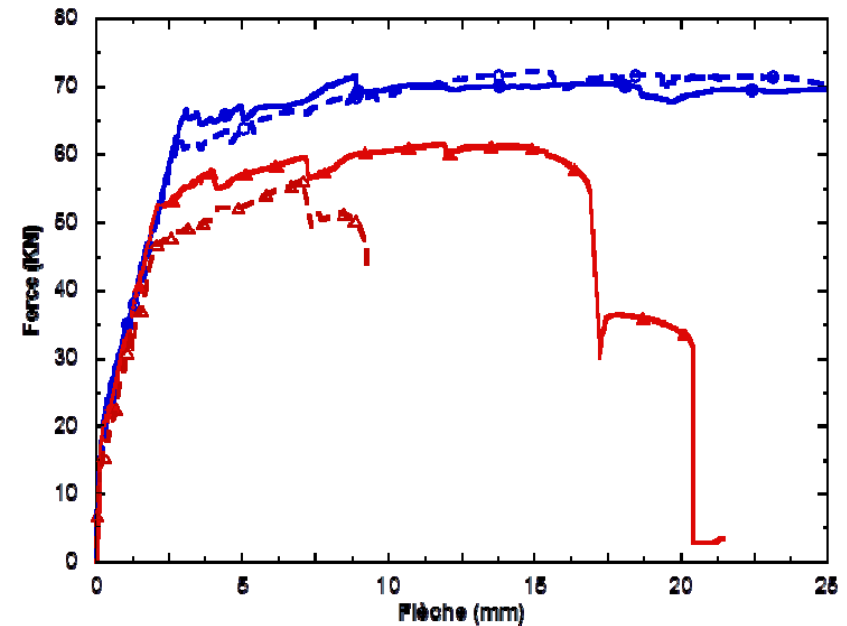


**Visible sign :  
Cracks associated with rust spots**



O. Poupard, V. L'Hostis, S. Catinaud, I. Petre-Lazar, Cement and Concrete Research, Vol. 36, pp. 504-520 (2006).

**Mechanical consequence : Loss of  
loading capacity of the structure**



**Beams without corrosion**  
**Beams with 11% steel section loss**

Q.T. Nguyen, A. Millard, S. Caré, V. L'Hostis, Y. Berthaud, Journal de Physique IV, Vol. 136, pp. 109-122, 2006.

# **THERMAL LOADINGS EFFECTS ON CONCRETE**

## Assumptions for the T-H-M model from [B. Bary et al.]

- The gaseous phase is supposed to be only composed of vapor (dry air neglected & only 1 mass conservation equation) → Mass balance equation is:

$$A \frac{\partial p_l}{\partial t} + B \frac{\partial \varepsilon}{\partial t} + C \frac{\partial T}{\partial t} = \nabla \cdot \nabla (p_l) + \dot{d}$$

Water pressure local variation, volumetric deformations, thermic dilatation

Water transfer gradient, water due to deshydration

- Heat equation:

$$c(S_l, d) \frac{\partial T}{\partial t} + \nabla \cdot (q) = -L_{l \rightarrow v}(T) \mu_{l \rightarrow v} - L_{s \rightarrow l} \dot{d}$$

heat flux (Fourier)

vaporization

dehydration of solid phases

- Behavior law

$$\sigma = 2\mu \mathbf{J} : \varepsilon + k \mathbf{L} : \varepsilon - b I p_l - 3\alpha k \theta \mathbf{I}$$

Stress

Deformation, hydric contribution (Biot), thermal contribution

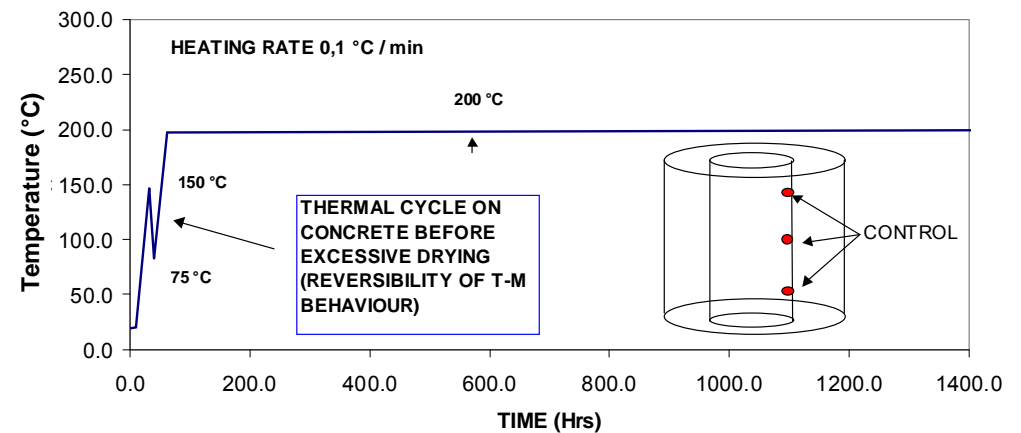
Partially saturated material: mechanical effect of gas pressure neglected

## MAQBETH mock-up (cylinder heated by internal resistance)

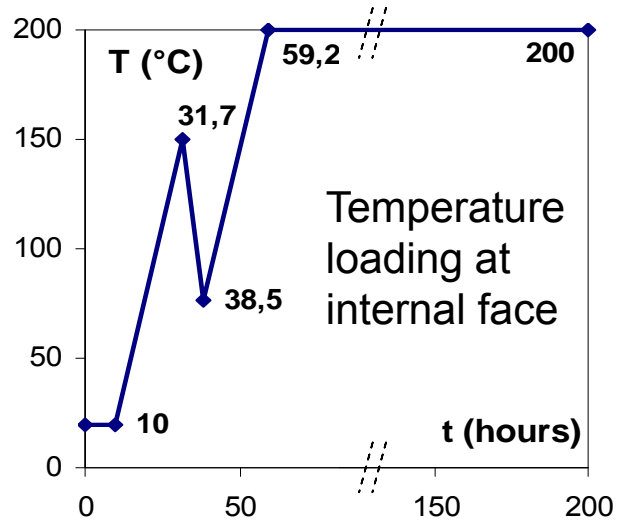


Heating until 200°C lead to concrete drying and cracking

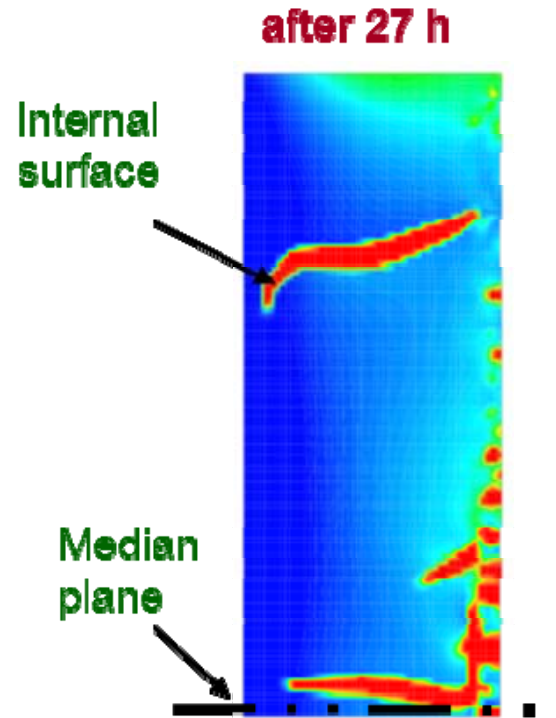
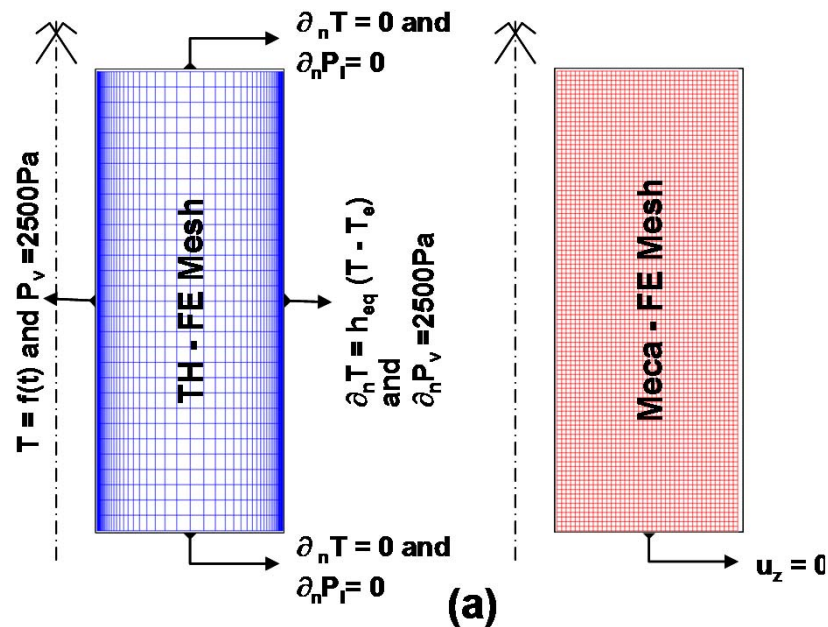
HEATING PROGRAMM







## Finite elements modelling



**Main cracks appears in the cold face**

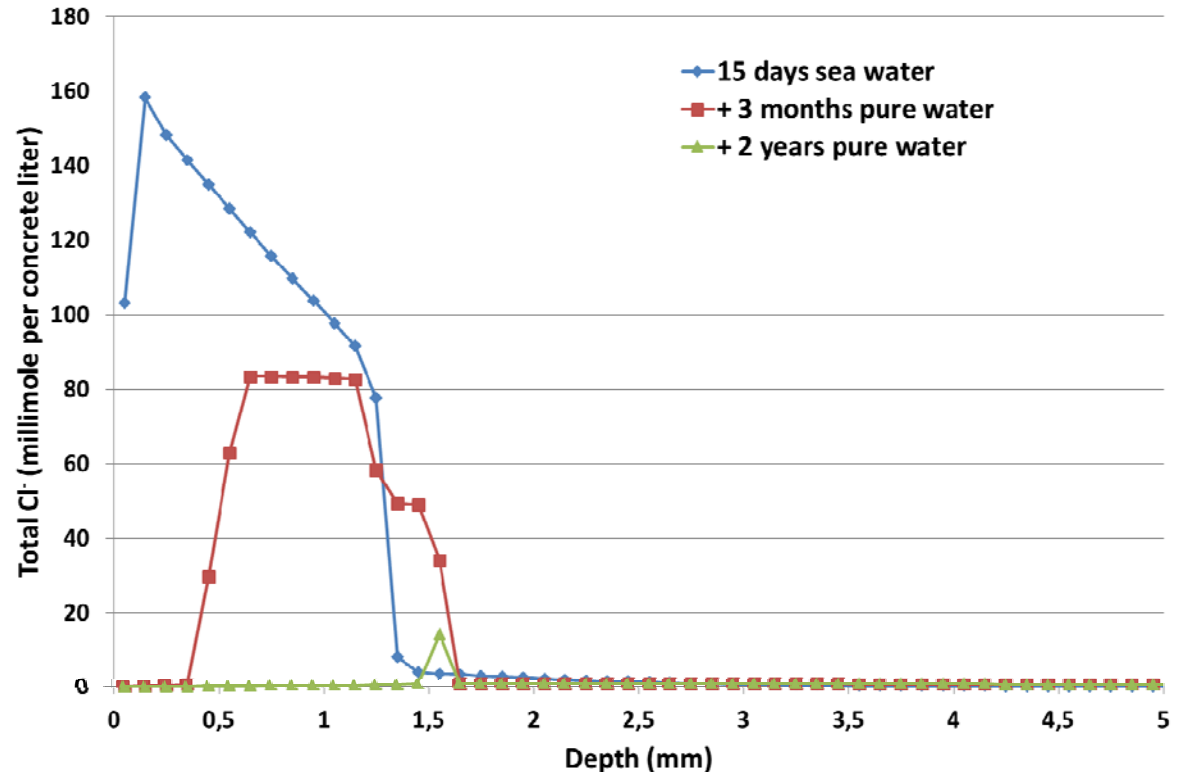
Bary B, et al., Engineering Structures, 36 (2012) 302–315

# **APPLICATION TO FUKUSHIMA DAIICHI CONDITIONS**

Reinforced concrete structures of Fukushima Daiichi NPP have been submitted temporarily to specific environmental conditions such as chloride ingress (from seawater) and thermal loading (up to 200°C).

- Scenario 1 : effect of chloride ingress (without temperature consideration)
- Scenario 2 : taking into account the thermal loading on concrete behaviour

- Coupled chemistry-transport software (Hytec)
- CEM V type concrete (Portlandite, Jennite, Ettringite and Monosulfate)
- 15% porosity
- Effective diffusion coefficient:  $5 \cdot 10^{-13} \text{ m}^2/\text{s}$
- From  $t=0$  to  $t = 15$  days : NaCl solution at 0.55 mole/L; pH =7
- From  $t=15$  to  $t= 745$  days : pure water pH=7



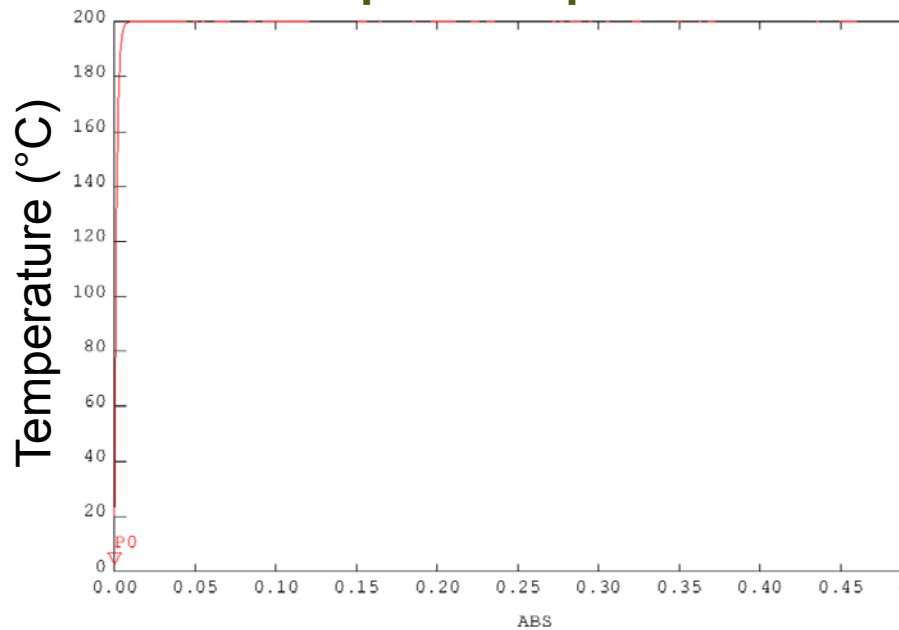
- Chloride penetrates into concrete up to several millimeters during the 15 days in contact with seawater. As soon as pure water replaces seawater, chloride species are leached out from the material.
- After 2 years, almost all chloride species disappeared from concrete cover.

**Reinforcement bars located few centimeters inside concrete should not developed chloride-induced-corrosion.**

## Simplified illustrative TM simulation

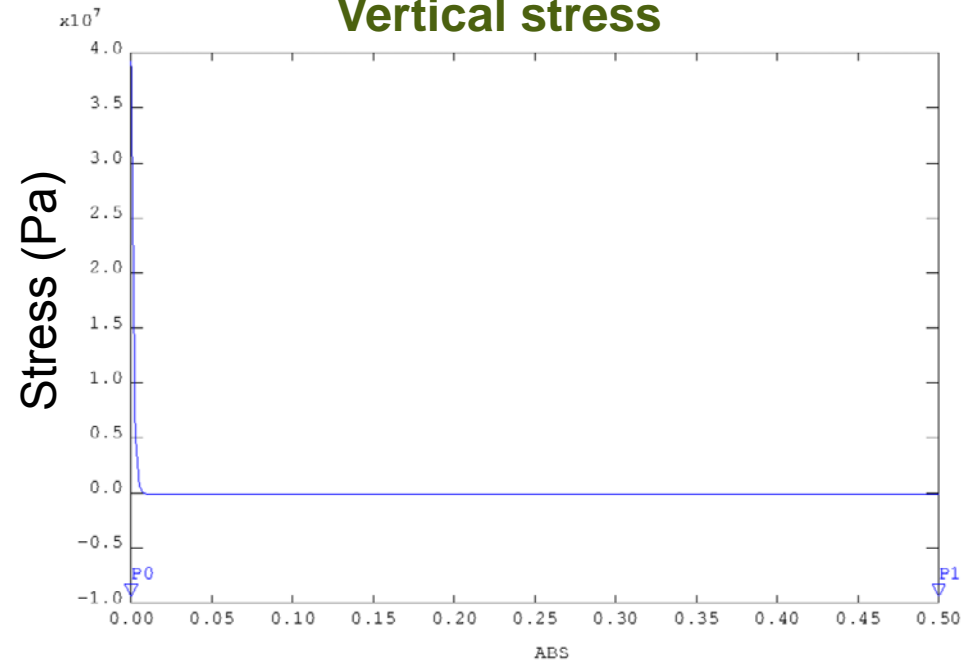
- Wall 1 m thickness, 10 m high
- Homogeneous concrete (no reinforcements), supposed to behave elastically
- Initial temperature of 200°C, subjected to the exposure of water at 20°C on both surfaces
- Young modulus = 35 GPa, Poisson ratio = 0.2
- Heat capacity = 900 kJ/kg/K, thermal conductivity = 2 W/m<sup>2</sup>/K

**Temperature profiles**



Time: 1.65281E+00 s

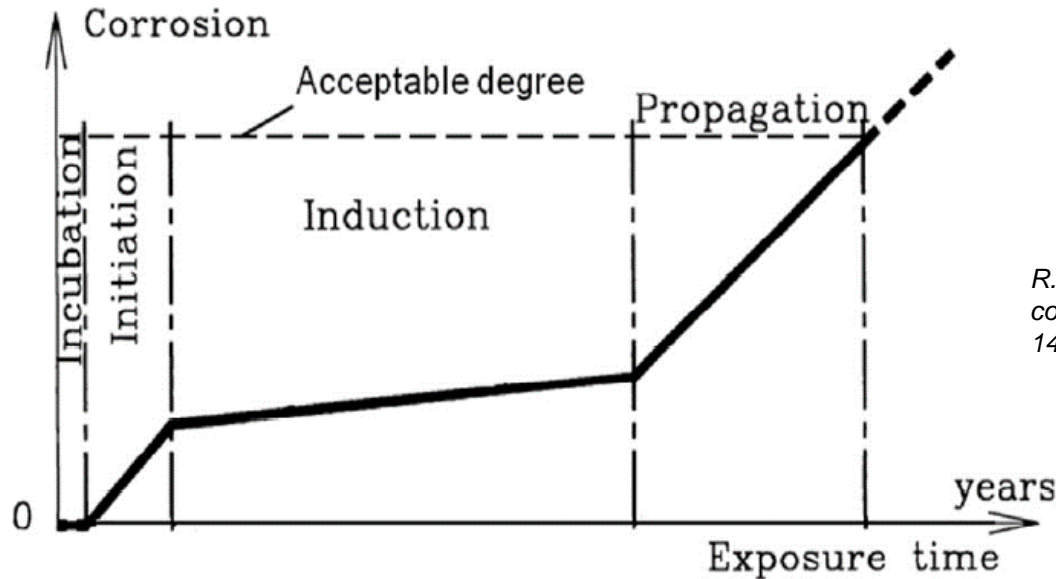
**Vertical stress**



Time: 1.65281E+00 s

**Maximum tensile stress up to about 40 Mpa → Cracking!**

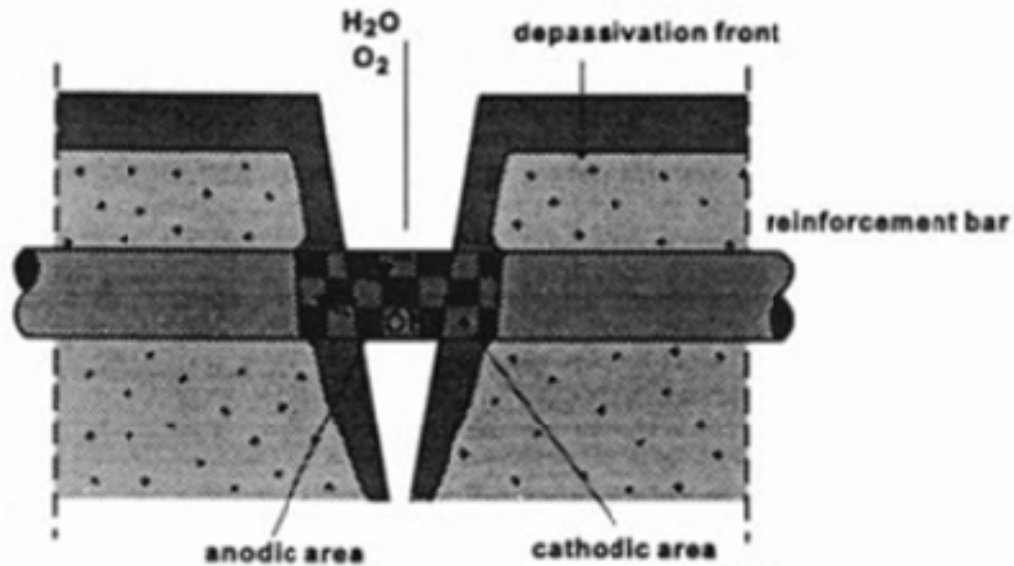
# **CORROSION IN CRACKED CONCRETE**



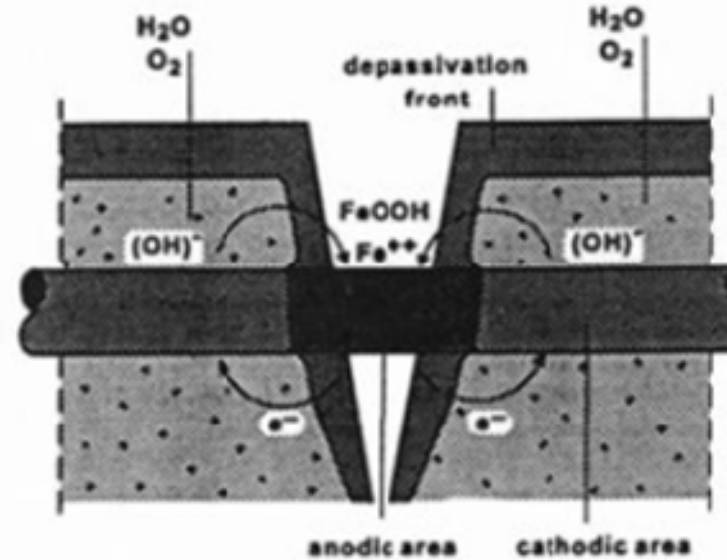
*R. François and G. Arliguie, "Durability of loaded reinforced concrete in chloride environment," ACI Spec. Publ., vol. 145, pp. 573–596, 1994.*

- 1/ and 2/ Chloride penetrates through the crack (initiation period).
- 2/ Corrosion rate reduced (induction period) : corrosion products fill the crack. Corrosion products continue to develop along the steel/concrete interface → new corrosion cracks.
- 3/ If corrosion crack appear, the propagation phase begins. Increase in the corrosion rate. Corrosion cracks interconnect between them progressively and increase in width also.
- In the structure, some zones will be in the induction phase while others can be in the propagation phase.

*Micro-cell corrosion*



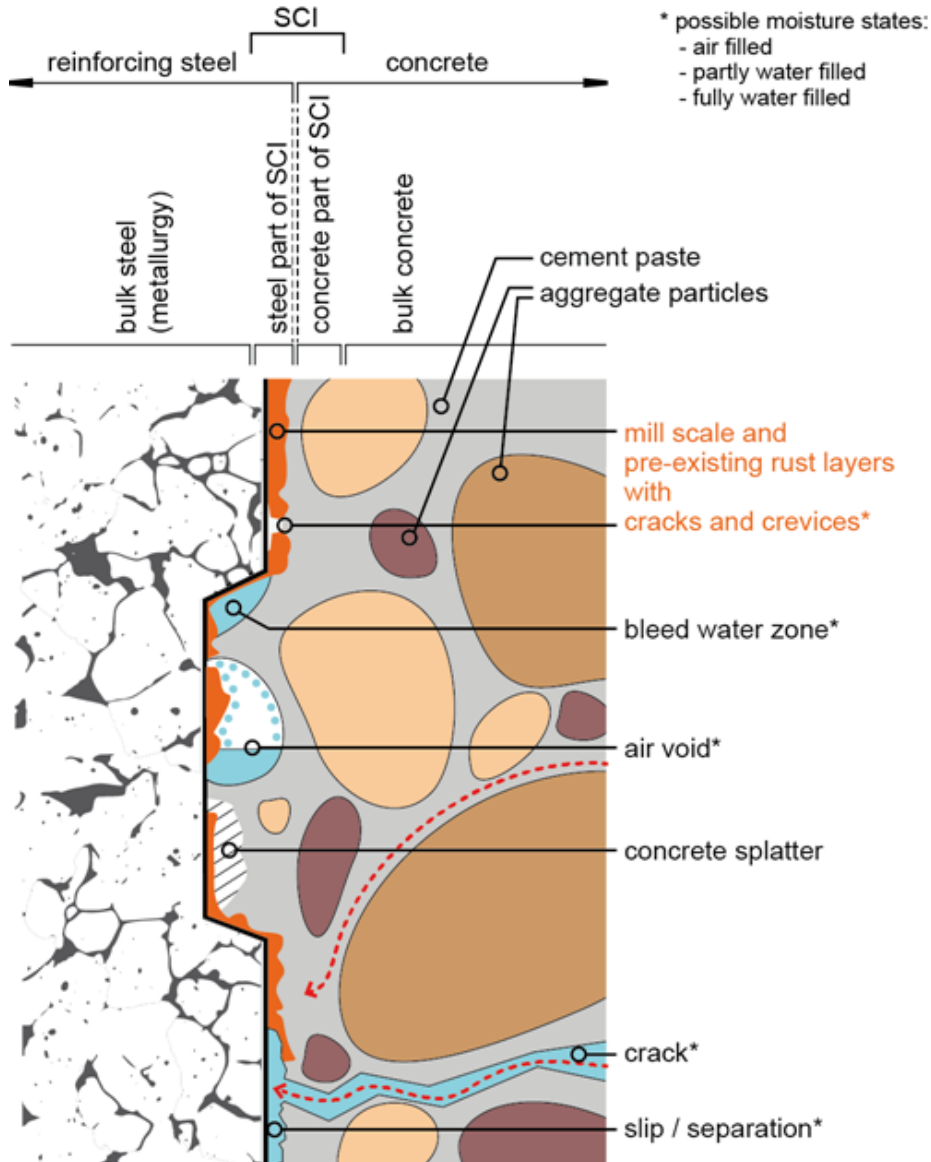
*Macro-cell corrosion*



- Micro-cell corrosion : anodic and cathodic reactions = in the adjacent sub-areas on the cracked zone (oxygen is supplied through the crack).
- Macro-cell corrosion : anodic dissolution = in the cracked area / cathodic reaction at the passive reinforcement being in non-cracked concrete (oxygen penetrates through un-cracked zone of concrete)



# CORROSION IN CRACKED CONCRETE



Field and laboratory experiments show that the quality of steel/concrete interface is the main parameter that has to be considered, more than chloride threshold and crack width as it is commonly specified in codes.

*Schematic illustration of various "defects" that may or not be present locally at the steel-concrete interface. The red dotted lines indicate preferential routes of entry for chlorides; the blue dots represent adsorbed water (for large pores only), according to Angst et al., 2017. [ANG 17a]*

## **CONCLUDING REMARKS**

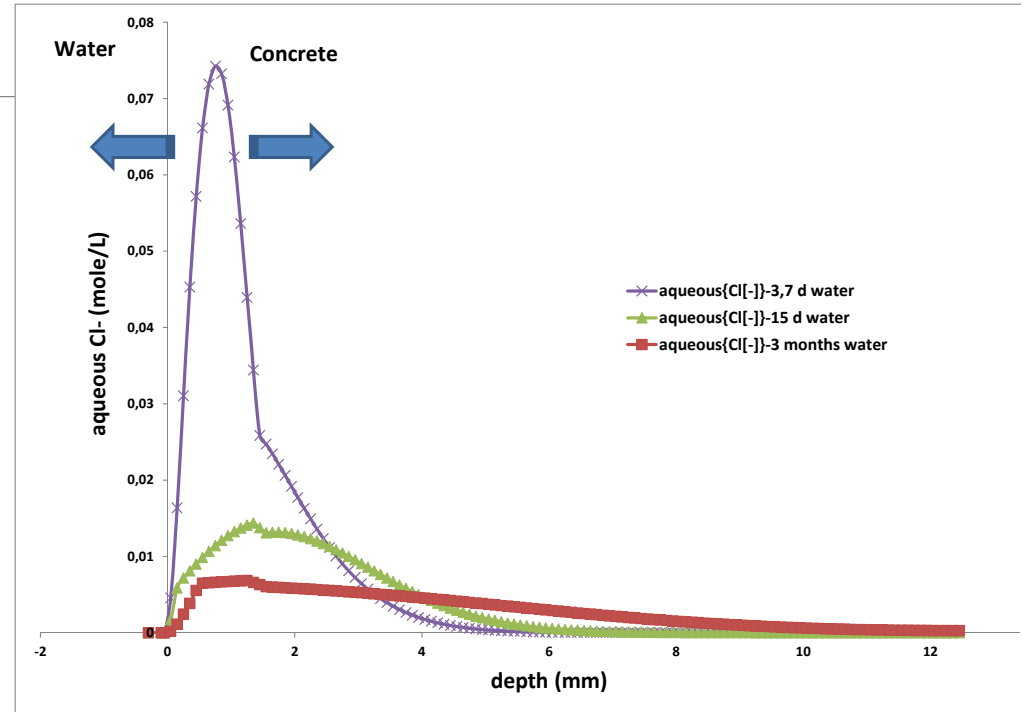
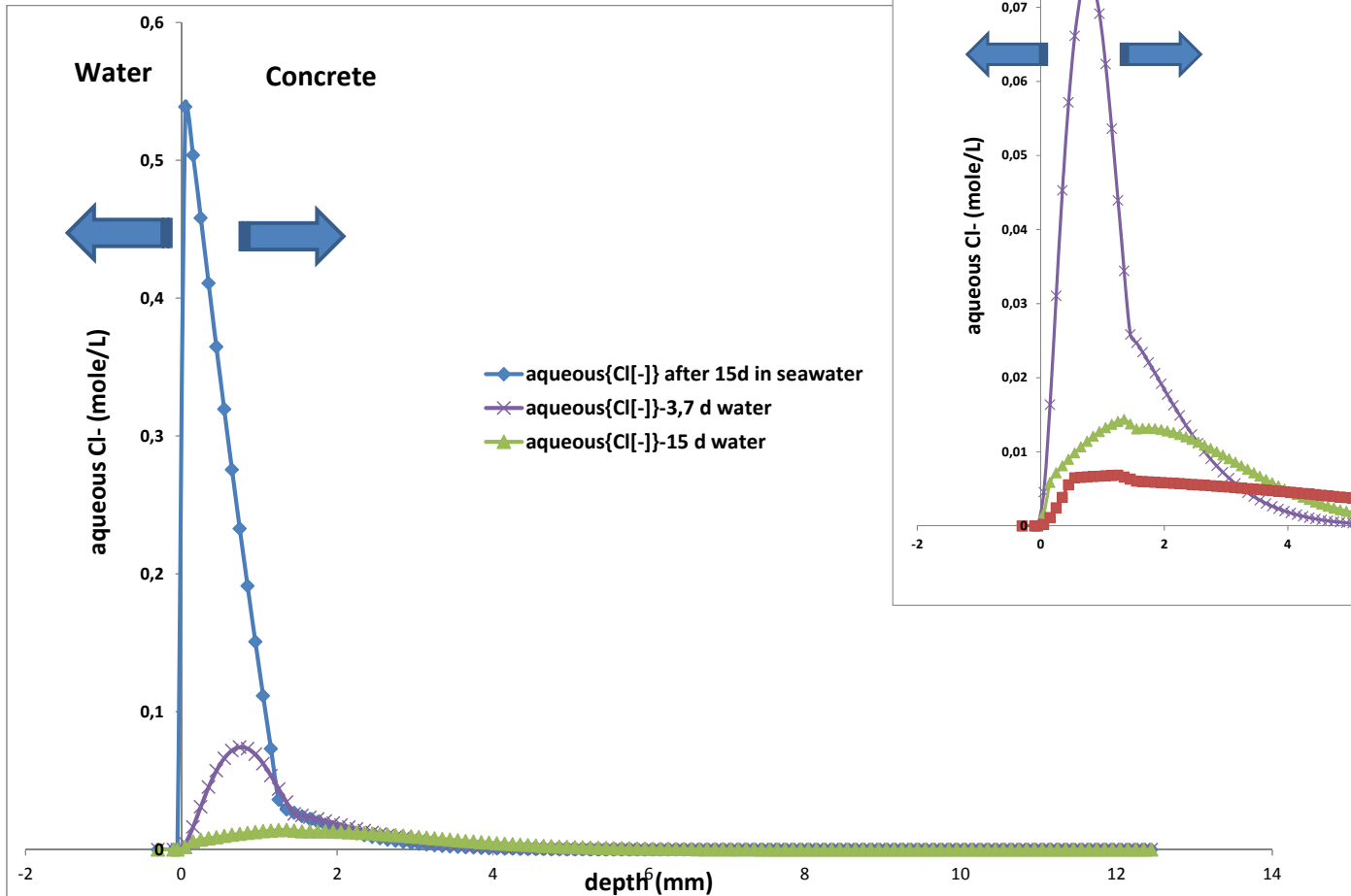
- Passivity of steel embedded in concrete is demonstrated even after tens of years
- Chloride from seawater used for cooling structures did not lead to active corrosion initiation
- Thermal loadings due to nuclear accident and cooling by cold water should have lead to concrete cracking
- Corrosion process that has to be considered is corrosion in cracked concrete
- In this condition, the main parameter that has to be taken into account is the quality of steel/concrete interface in massive structure (top bar effect)

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Reinforced Concrete structures degradation issues: impact of Chlorides and of Thermal loadings on Corrosion development 28th November 2017, Fukushima  
Research Conference – CORR 2017

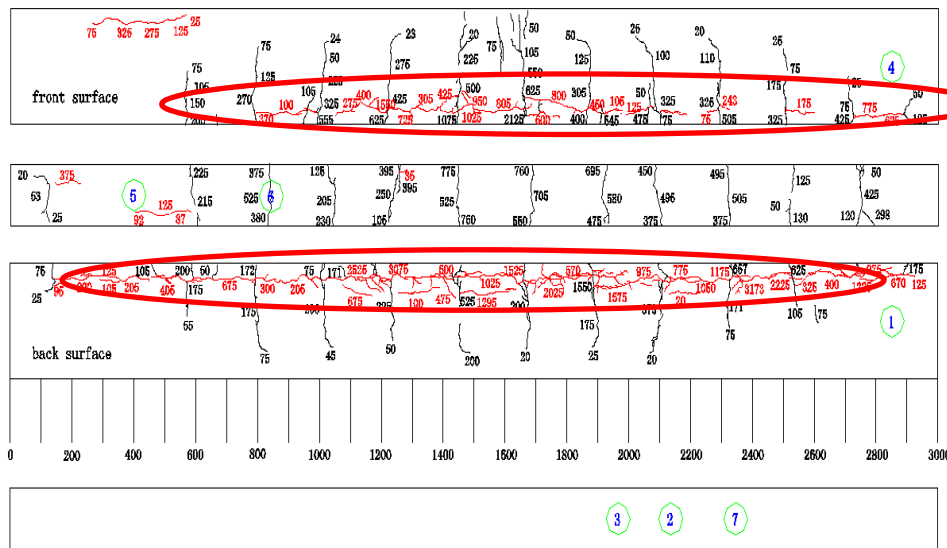
Valérie L'Hostis\*, Patrick Le Bescop\*, Benoit Bary\*, Raoul François\*\*

# AQUEOUS CHLORIDE PROFILES



Pre-cracks + Interface defects >>> Pre-cracks without Interface defects

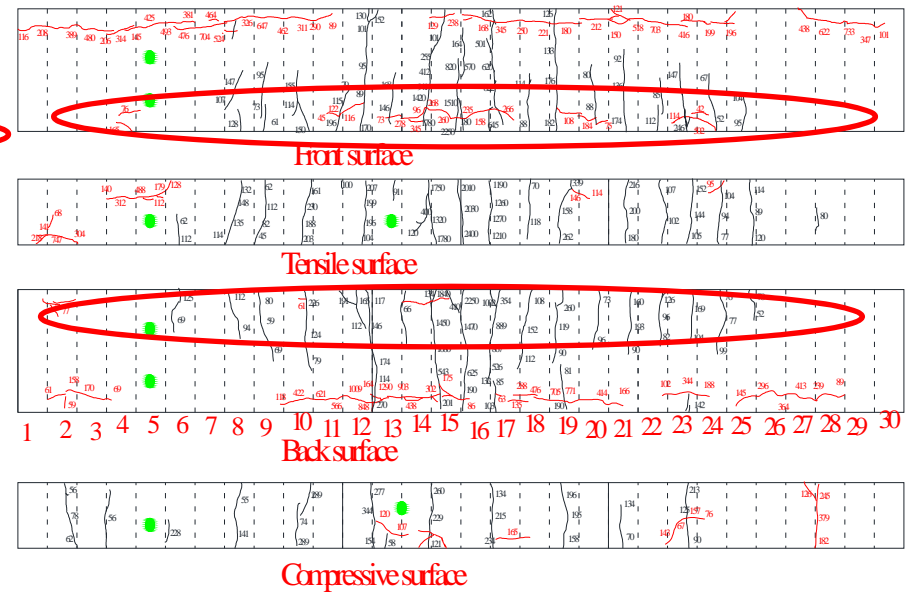
Beam exposed 51 months in saline chamber



the beam of C3

bottom bars with casting defects

Beam exposed 29 months in saline chamber



bottom bars without casting defects