Presented at the COMSOL Conference 2009 Milan

Modelling of the Hydrogen Diffusion in Martensitic Steels in contact with H_2SO_4 Media

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CNRS 3097

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Overview

- 1. Context of the study
- 2. The electrochemical permeation test : Theory
- 3. The electrochemical permeation test : Simulation
- 4. Results
- 5. Conclusions & Perspectives

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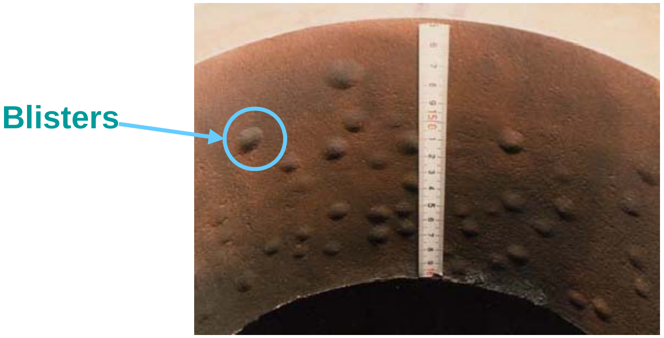
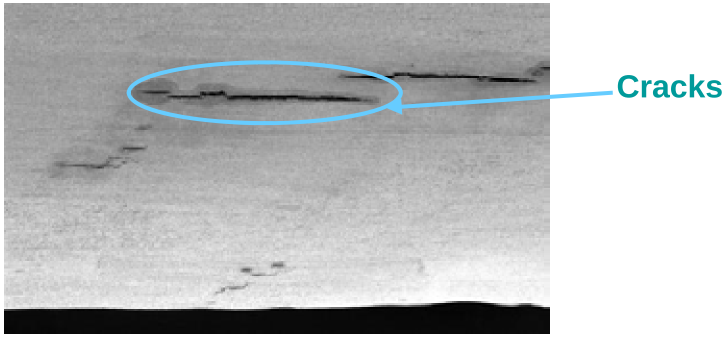
Context

- Hydrogen Embrittlement (HE) ⟶ premature failure of structures





- Hydrogen transport (Diffusion) is one of the important parameter of HE

- Studies about hydrogen diffusion in steels are often implemented using permeation tests.

- **Hypothesis:** the conditions of diffusion are established beneath the entry side, where the concentration of hydrogen C_0 is supposed to be constant.

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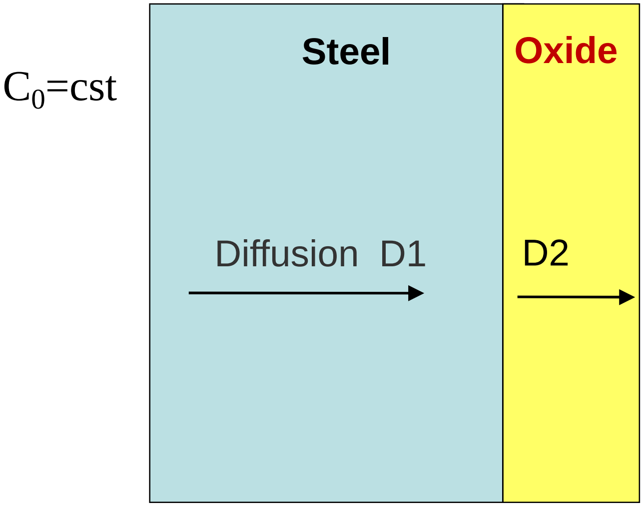
Context

- **Problem:** a passive layer on the exit side can have consequences on the experimental results:
  - Diffusion curves correspond to a multilayered system with two different materials and their own diffusion coefficient *D* (D_1 for the steel and D_2 for the oxide layer).
  - Only an apparent diffusion coefficient D_{app} can be determined experimentally.



- **Our Goal:** Analyze the influence of the oxide layer on the permeability of hydrogen.

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The electrochemical permeation test : Theory

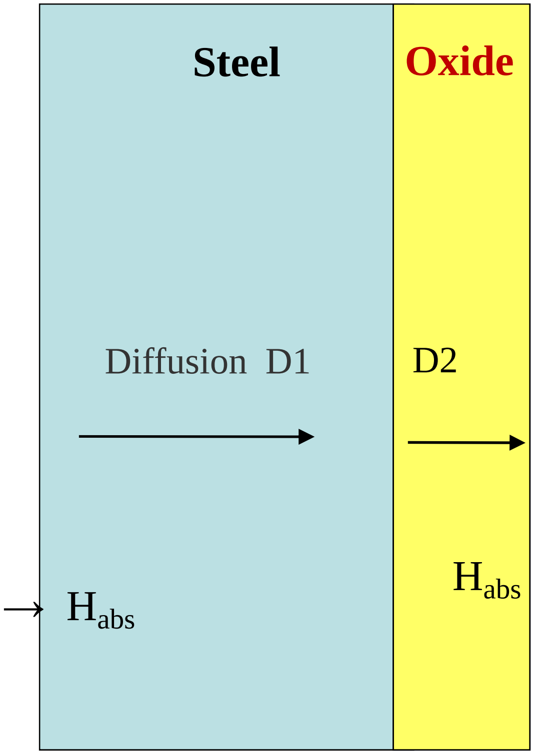
Charging Cell

H_2SO_4

Cathodic Polarisation

$2H^+ + 2e^- \rightarrow H_2$

$H_{ads} \rightarrow H_{abs}$



Steel

Oxide

Diffusion D1 →

D2 →

$H_{abs} \rightarrow H_{ads}$

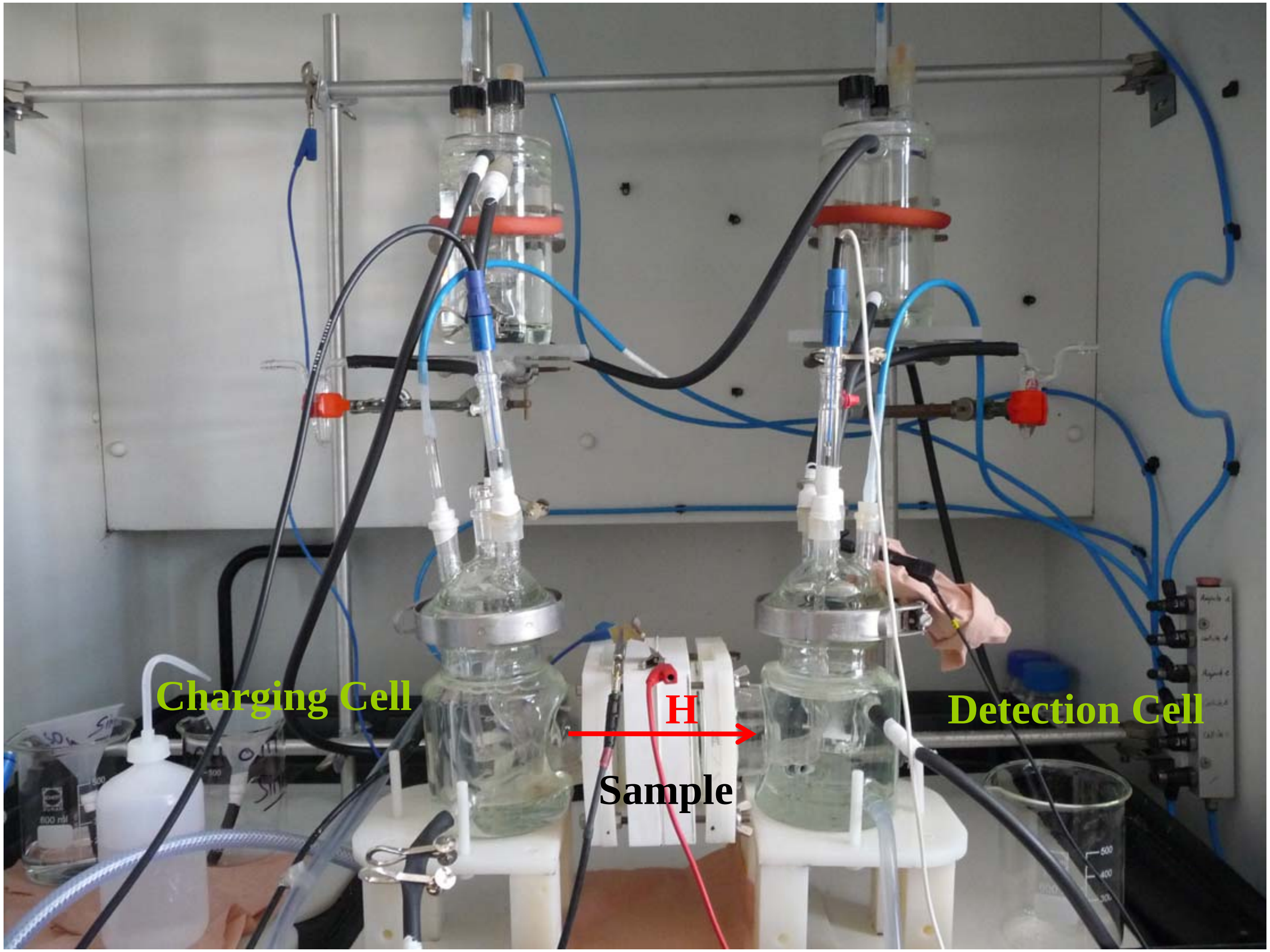
Detection Cell

NaOH

Anodic Polarisation

$H_{ads} \rightarrow H^+ + e^-$

The electrochemical permeation test : Experimental set up



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Diffusion : Fick’s Laws

Fick's laws describe diffusion into the multilayered system assuming that there is no hydrogen trapping and the diffusion is unidirectional:

$$J(x,t) = -D_{app} \frac{\partial C(x,t)}{\partial x} \qquad \frac{\partial C}{\partial t} = D_{app} \frac{\partial^2 C}{\partial x^2}$$

Two analytical solutions of Fick’s laws are employed to fit the diffusion phenomenon when the hydrogen concentration is supposed to be constant beneath the entry side $C=C_0$ and equals to zero on the exit side $C=0$:

$$J_t = J_\infty \frac{2}{\sqrt{\pi\tau}} \exp\left[\frac{-1}{4\tau}\right] \quad \text{for} \quad \tau = \frac{D_{app} t}{e^2} \leq 0.3$$

$$J_t = J_\infty (1 - \exp(-\pi^2 \tau)) \quad \text{for} \quad \tau = \frac{D_{app} t}{e^2} \geq 0.2$$

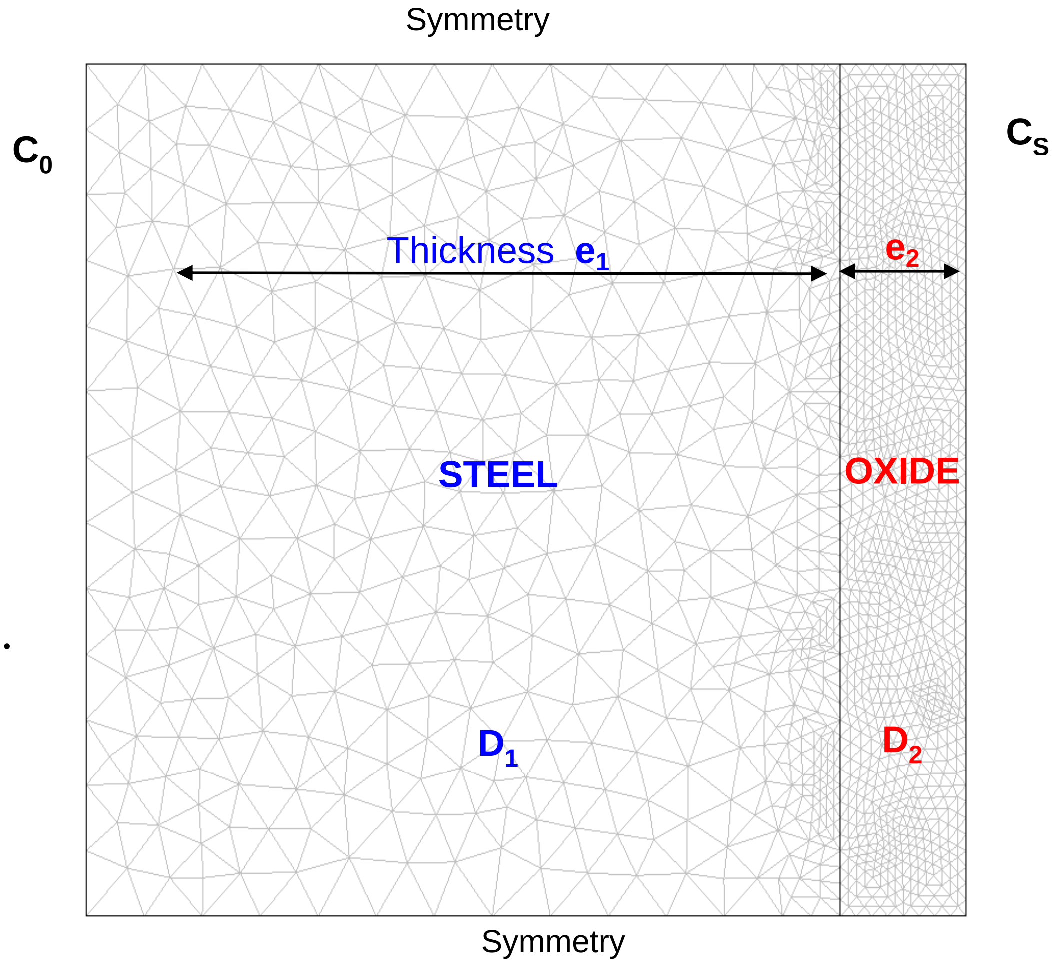
The electrochemical permeation test : Simulation

<u>Boundary conditions</u>

C_0=5 mol/m^3,
C_S=0 mol/m^3.
e_1=1mm

Two types of steels:
- Ferritics D_1=1.10^{-8} m^2/s
- Martensitic D_1=7.10^{-10} m^2/s.

Two thicknesses
- e_2 = 100nm,
- e_2 = 500 nm.



$$R = \frac{D_{oxide}}{D_{steel}} = \frac{D_2}{D_1} \quad \text{With } R \in \left[10^{-4};1\right] \text{ and } D_{oxide} \le D_{steel}$$

COMSOL Conference, October 14th-16th 2009, Milan, Italy.

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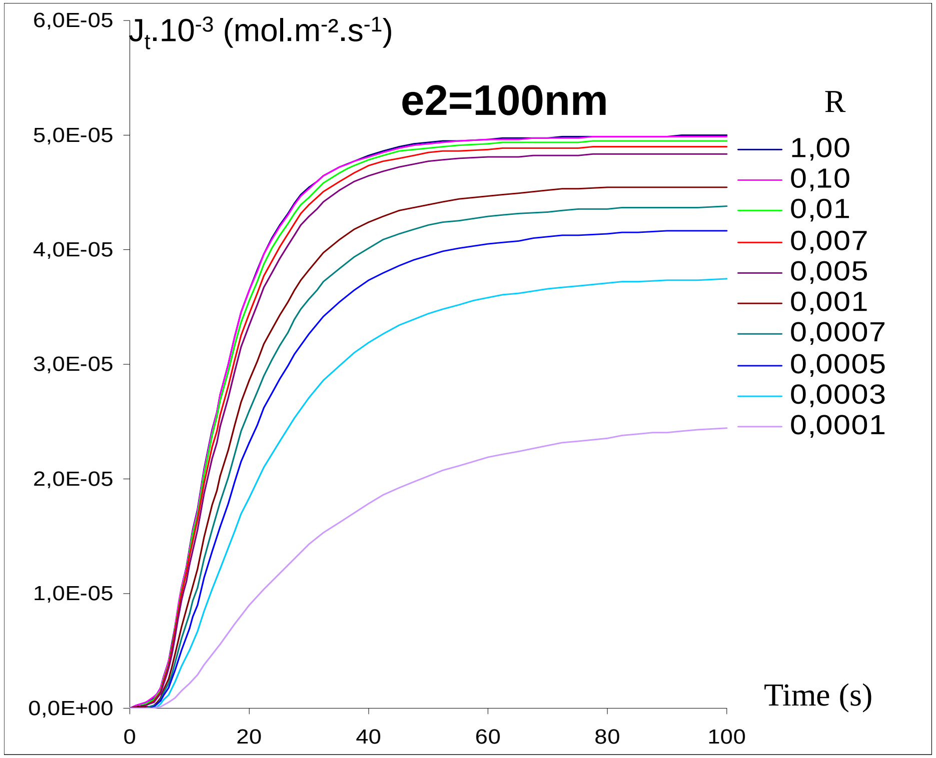
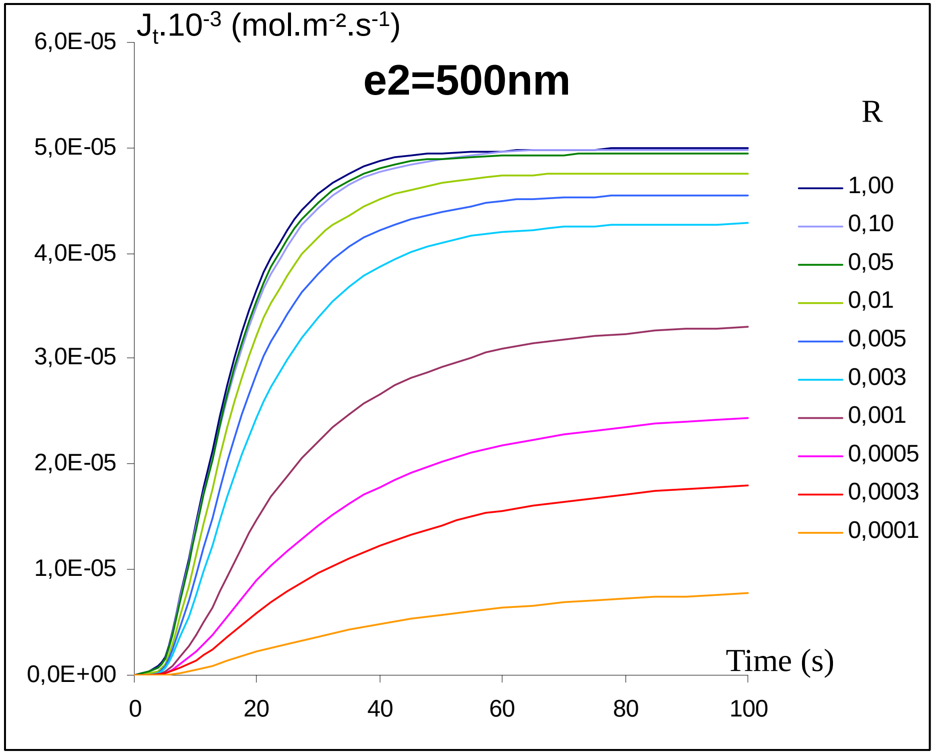
Results: Evolution of the permeation curves

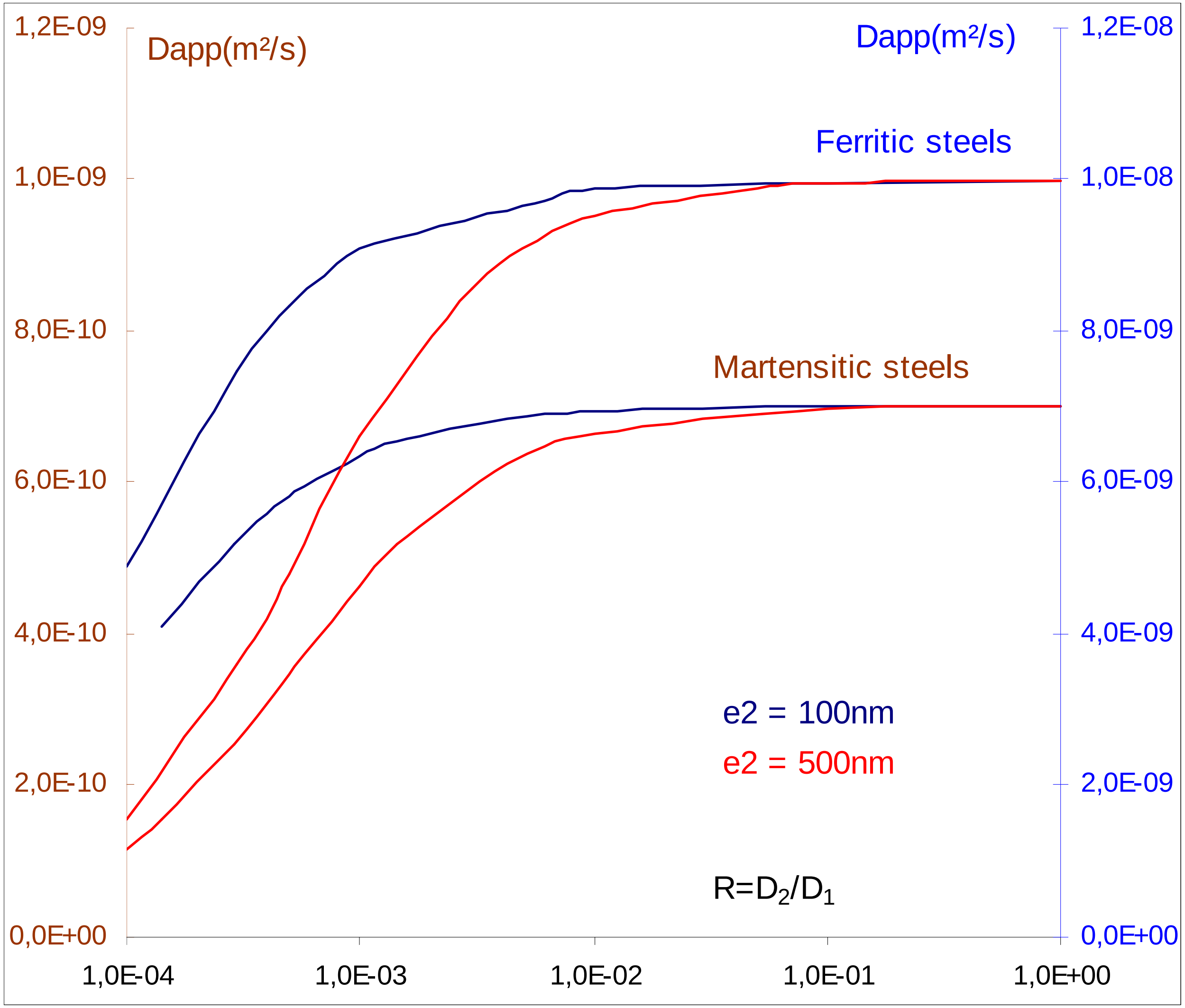
- The decrease of the flux as R diminishes, and it is much more visible for the thicker layer.





$$R = \frac{D_{oxide}}{D_{steel}} = \frac{D_2}{D_1}$$

Results: Evolution of D_{app}



$$R = \frac{D_{oxide}}{D_{steel}} = \frac{D_2}{D_1}$$

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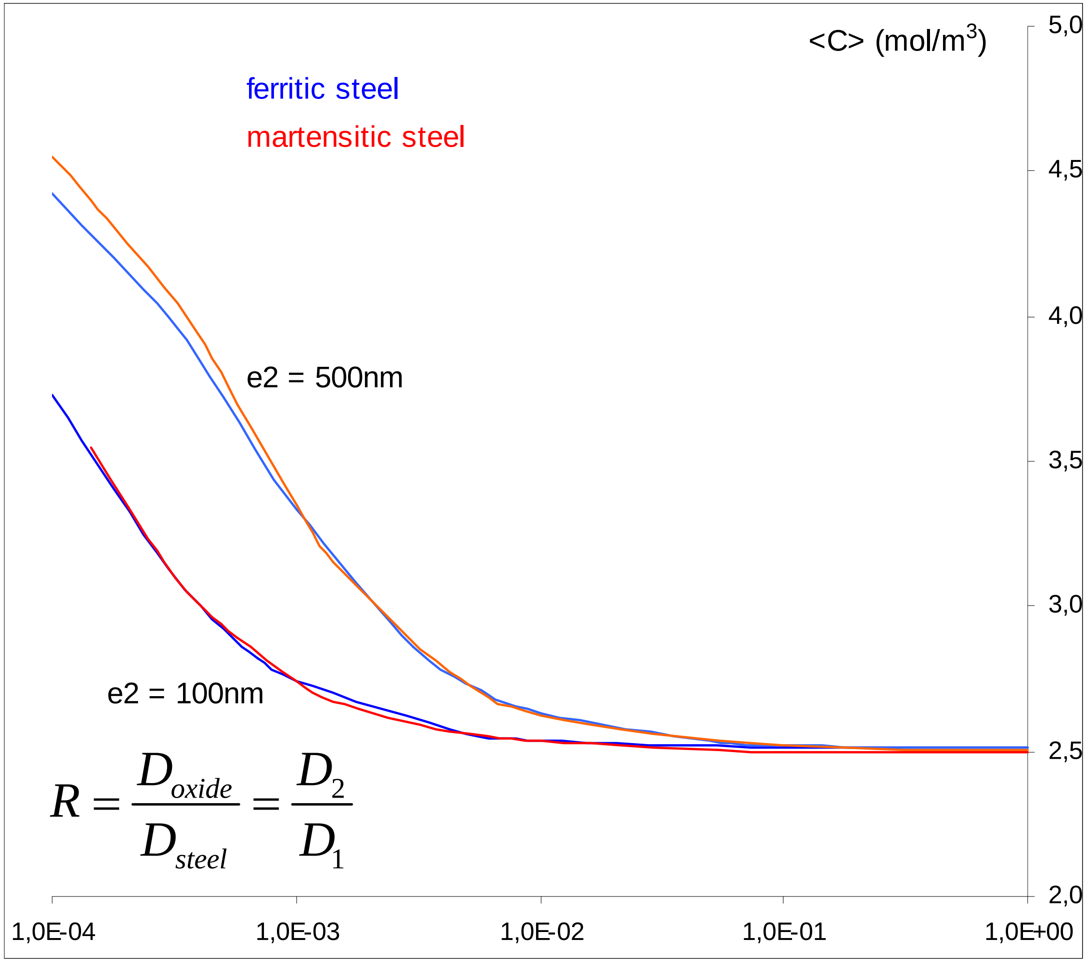
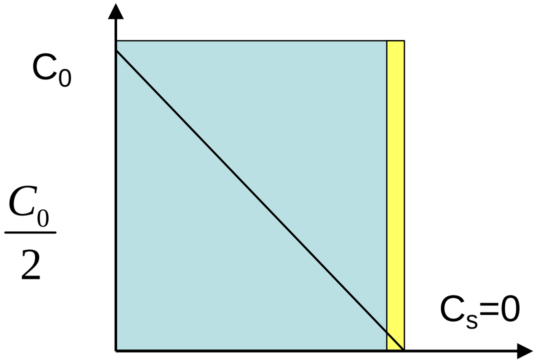
Results: Evolution of <C>

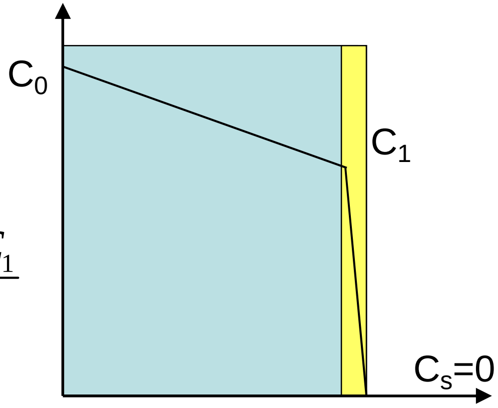
<C>, the average concentration, depends only on R and the thickness of the oxide layer. Up to R=0.01, the variation of D_{app} is insignificant and would correspond to the “real” diffusion coefficient of the substrate (D_1).



$$R = \frac{D_{oxide}}{D_{steel}} = \frac{D_2}{D_1}$$



$$< C > = \frac{C_0}{2}$$



$$< C > = \frac{C_0 + C_1}{2}$$

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Results: Extrapolation

The oxide layer could be as thin as 2.8nm.

By fitting the obtained curves (<C> *vs* R and D_{app} *vs* R), we were able to acquire their expression:

$$D = D_{app}\left[1-\exp\left[-\left(\frac{R}{B}\right)^{n}\right]\right]^{-1}$$

where $B = B_0 e + B_1$ and n a constant

$$<C>=\frac{C_0}{2}\left[1+\exp\left[-\left(\frac{R}{B}\right)^{n}\right]\right]$$

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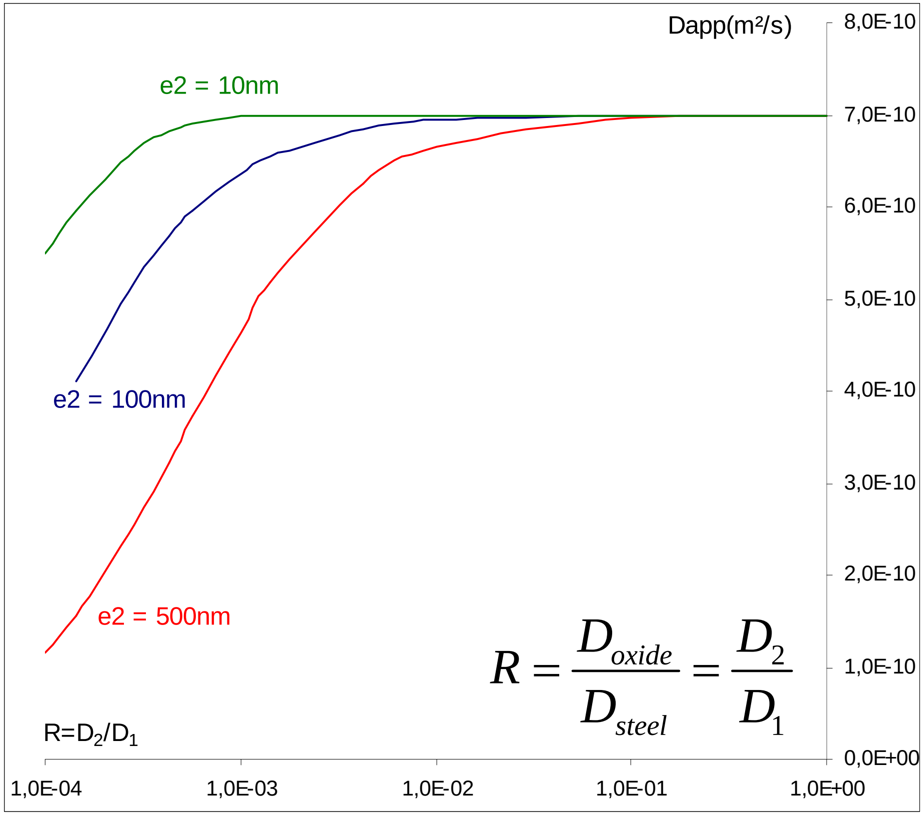
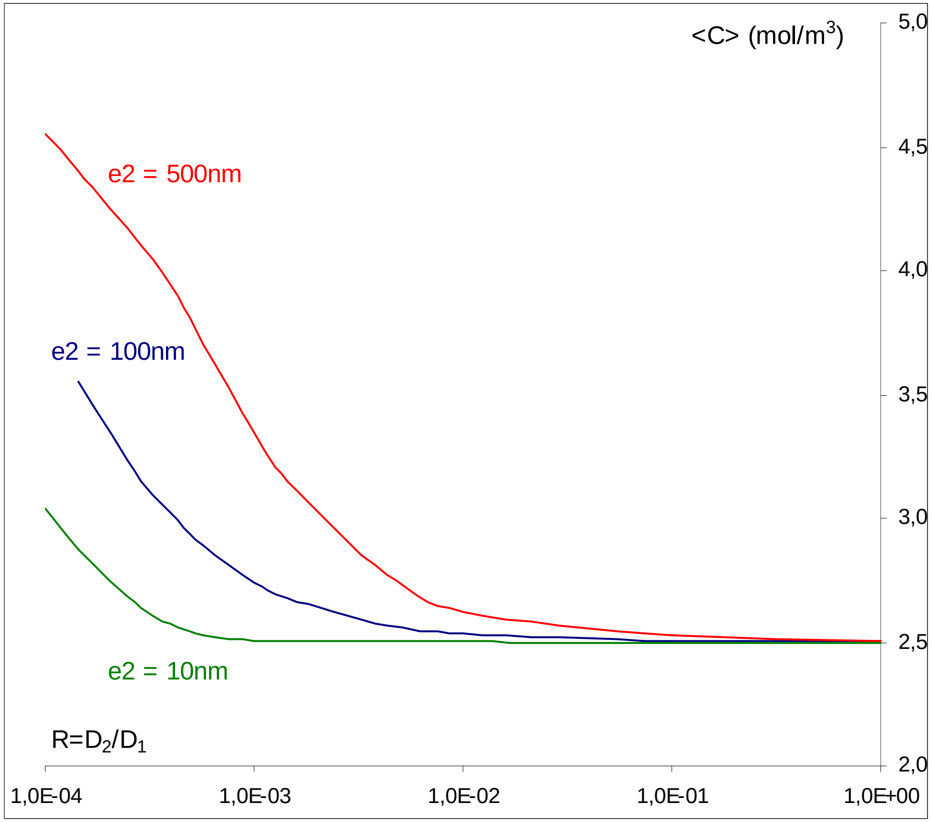
Results: fitted curves

Evolution of the fitted curves of Dapp and <C> in function of R
for a martensitic steel for e2=10nm



$$R = \frac{D_{oxide}}{D_{steel}} = \frac{D_2}{D_1}$$



The smaller the oxide layer the bigger the difference between D_1 (substrate) and D_2 (oxide) can be without altering neither D_{app} nor <C>.

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Conclusions

- Exhibit the relationship between the oxide layer characteristics and the apparent hydrogen diffusion.

- D_{app} and <C> rely on both the thickness and the diffusion coefficient of the oxide layer.

- The thinner is the layer, the smaller is the error committed on the diffusion coefficient of the substrate.

- FEM calculations using Comsol Multiphysics offer the opportunity to correct experimental data and the evolution of true diffusion coefficient.

- Perspectives: Studying the effects of trapping of hydrogen

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Thank you for your attention