SIMTEC

Numerical modeling

that predicts, optimizes and innovates

Influence of a Porous Corrosion Product Layer (CPL) on the Corrosion Phenomenon of Carbon Steel Pipelines

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Outline

I. Background – Motivations – Objectives

II. Modelling and Numerical Model : *Corrosion Under Porous CPL*(*)

III. Main Results

IV. Conclusions – Perspectives

Working with SIMTEC

Industry challenges

- R&D sections: experts in their field
  → Expertise in numerical modelling?
- Lack of time
- FE modelling performed by a small group of people

SIMTEC's solutions

- Numerical modelling project
  → SIMTEC's member as your colleague
  → Help improve your modelling knowledge!
  → Cost-effective outsourcing

Our team & Our clients

Numerical modelling / simulation consultants

COMSOL Certified Consultant

6 members all EngD + PhD

- Extensive research background
- Complex problems / various fields of expertise

Successful track record:

- Big compagnies
- Government laboratories

Involved in research consortia

- EU funded projects (REEcover / SHARK)
- PhD projects supervision.

EUROPEAN COMMISSION
SEVENTH FRAMEWORK PROGRAMME
REEcover
SHARK INDUSTRIALISING LASER FUNCTIONAL TEXTURING

Patrick Namy

Vincent Bruyère

Elise Chevallier

Jean-Marc Dedulle

Jean-David Wheeler

Maalek Mohamed-Said

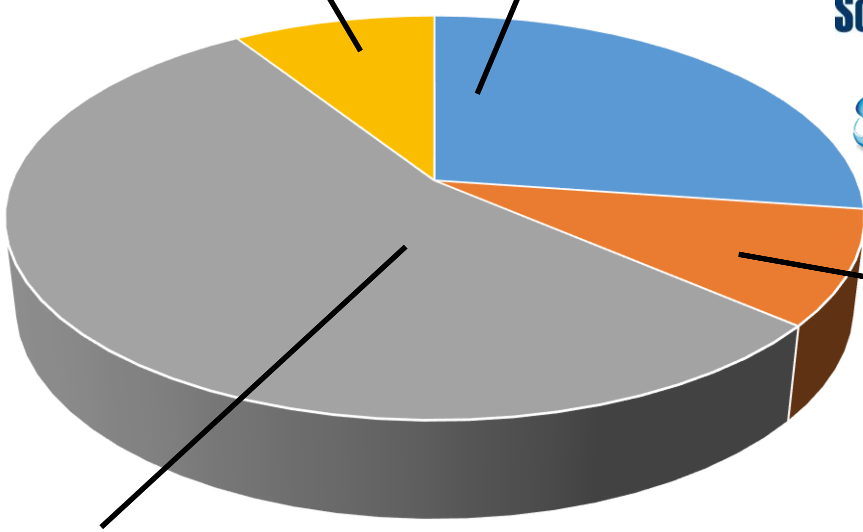
Our team & Our clients

SIMTEC: 15 years of building expertise…

IV. Remote computation

TDA THALES GROUP

I. Numerical Modelling Development



II. Tailored training sessions on numerical modelling

- FEM method training session
- Become an expert with solvers
- Two-phase flow modelling

III. Provide support in numerical modelling

dbv technologies

HORIZON 2020

AIR LIQUIDE, MAN, cea, GROUPE ADP, AIRBUS, ALSTOM, faurecia, Schlumberger, AREVA, TOTAL, Nexans, SOLVAY, novasep, fives, EFD INDUCTION, L'ORÉAL RECHERCHE, KISCO international, SORIN GROUP

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I. Background – Motivations – Objectives

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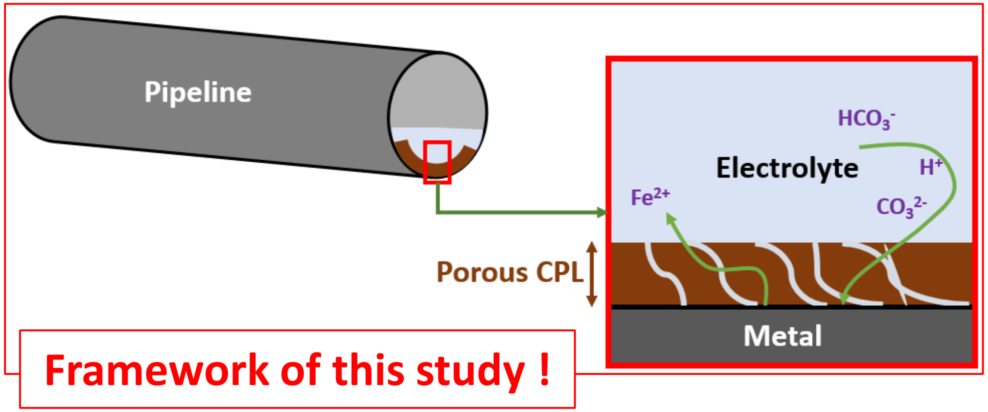
- ***Carbon steel*** is largely used in oil a gas industry
- ***Corrosion*** is the main factor affecting the longevity and reliability of carbon steels tubes and pipelines used for oil & gas production and transportation !
- ***Corrosion*** is the degradation of the metal due to its interaction with an aggressive environment.
- ***Corrosion Product*** is a porous solid that forms by precipitation on the metal surface and **<u>could or not</u>** limit (or even accelerate) the corrosion rate→ ***<u>Objective of this study : how ?</u>***.

I. Background – Motivations – Objectives



The objective is to figure out how a porous corrosion product layer influences the corrosion process: *which of these two processes is predominant on the other:*

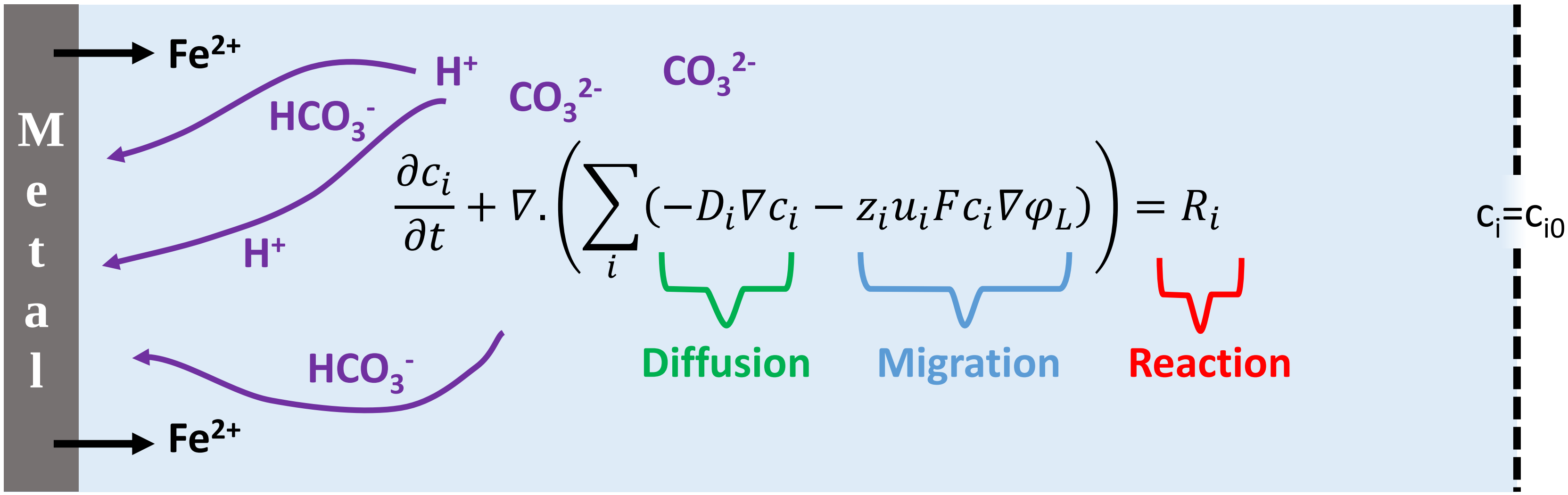
- *the covering effect*
- *the transport limitation of the chemical species through a porous layer ?*

Assumptions:

- an existing electrochemical process for all the kinetics considerations is used. It is specific to the so called "CO_2 corrosion" also called "sweet corrosion" ;
- the CPL does not evolve during the simulation (fixed porosity and thickness): the precipitation phenomenon is not accounted for ;
- a stagnant solution is assumed ;

II. Modelling and Numerical Model : Corrosion Under Porous CPL

- ❑ Model based on the resolution of the Nernst-Planck equation : 1D



$$\frac{\partial c_i}{\partial t} + \nabla . \left(\sum_i (-D_i \nabla c_i - z_i u_i F c_i \nabla \varphi_L) \right) = R_i$$

II. Modelling and Numerical Model : Corrosion Under Porous CPL

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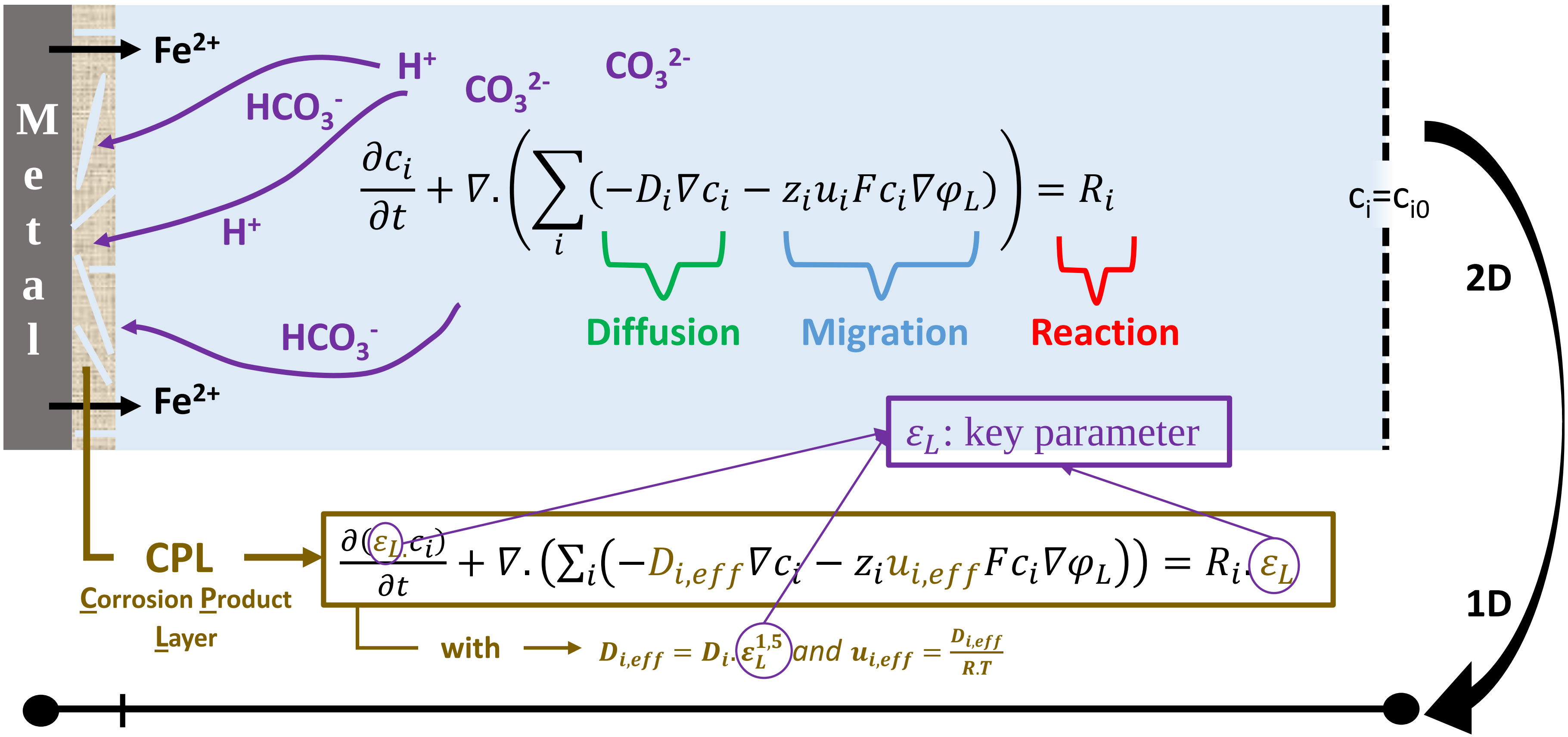

$$\frac{\partial c_i}{\partial t} + \nabla.\left(\sum_i \left(-D_i \nabla c_i - z_i u_i F c_i \nabla \varphi_L\right)\right) = R_i$$

$$\frac{\partial(\varepsilon_L.c_i)}{\partial t} + \nabla.\left(\sum_i \left(-D_{i,eff} \nabla c_i - z_i u_{i,eff} F c_i \nabla \varphi_L\right)\right) = R_i.\varepsilon_L$$

with $D_{i,eff} = D_i.\varepsilon_L^{1,5}$ and $u_{i,eff} = \frac{D_{i,eff}}{R.T}$

II. Modelling and Numerical Model : Corrosion Under Porous CPL

- Electrochemical process (CO_2 corrosion) : from the petroleum literature [**1-9**]

Electrochemical reaction	Current density	Tafel slope (mV)	Reference mV/ENH
$Fe_{(s)} \rightarrow Fe^{2+} + 2e^-$	$ia_{Fe} = (\varepsilon_L).ia^0_{Fe}.10^{\frac{\eta}{\beta_a}}$	$\beta_a = 40$	$E_{refFe} = 447$
$2H_2CO_3 + 2e^- \rightarrow H_2 + 2HCO_3^-$	$ic_{H_2CO_3} = -(\varepsilon_L).ic^0_{H_2CO_3}.10^{-\frac{\eta}{\beta_{cH_2CO_3}}}$	$\beta_{cH_2CO_3} = 120$	$E_{refH_2CO_3} = 381$
$2H^+ + 2e^- \rightarrow H_2$	$ic_{H_2} = -(\varepsilon_L).ic^0_{H_2}.10^{-\frac{\eta}{\beta_{cH_2}}}$	$\beta_{cH_2} = 118$	$E_{refH_2} = 0$
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$ic_{H_2O} = -(\varepsilon_L).ic^0_{H_2O}.10^{-\frac{\eta}{\beta_{cH_2O}}}$	$\beta_{cH_2O} = 118$	$E_{refH_2O} = 827$

$\eta = \varphi_m - \varphi_L - E_{iref}$ with φ_m: potential of the metal

ε_L : porosity of the CPL at the metal surface (x=0)

Apparent current density

Expression of the apparent current density (A.m^{-2})	Concentration (mol.m^{-3})
$ia^0_{Fe} = 1.\left(\frac{c_H}{C_{Href1}}\right)^{a_1}.\left(\frac{c_{CO_2}}{C_{CO_2ref}}\right)^{a_2}$ $a_1 = \begin{cases}1, & P_{CO2} < 1\ bar\\ 0, & P_{CO2} \geq 1\ bar\end{cases}$ and $a_2 = \begin{cases}2, & pH \leq 4\\ 1, & pH \in]4;5]\\ 0, & pH > 5\end{cases}$	$C_{Href1} = 0{,}1$ $C_{CO_2ref} = 36{,}6$
$ic^0_{H_2CO_3} = 0{,}06.\left(\frac{c_H}{C_{Href2}}\right)^{-0{,}5}.\left(\frac{c_{H_2CO_3}}{C_{H_2CO_3ref}}\right)$	$C_{Href2} = 0.01$ $C_{H_2CO_3ref} = 0{,}1$
$ic^0_{H_2} = 3.10^{-5}.\left(\frac{c_H}{C_{Href3}}\right)^{0{,}5}$	$C_{Href3} = 0{,}1$
$ic^0_{H_2O} = 3.10^{-5}$	–

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II. Modelling and Numerical Model : Corrosion Under Porous CPL

- Evolution of species within the electrolyte (**at equilibrium at T=25°C**) :
  - *Autoprotolysis of Water :* $\mathbf{K_w = 10^{-14}}$

    $$H_2O = H^+ + OH^-$$

  - *Hydration of CO_2 :* $\mathbf{K_{CO_2} = 2{,}580.10^{-3}}$

    $$CO_2 + H_2O = H_2CO_3$$

  - *First dissociation of H_2CO_3 :* $\mathbf{K_{H_2CO_3} = 1{,}251.10^{-4}}$

    $$H_2CO_3 = HCO_3^- + H^+$$

  - *Second dissociation of H_2CO_3 :* $\mathbf{K_{HCO_3} = 1{,}382.10^{-10}}$

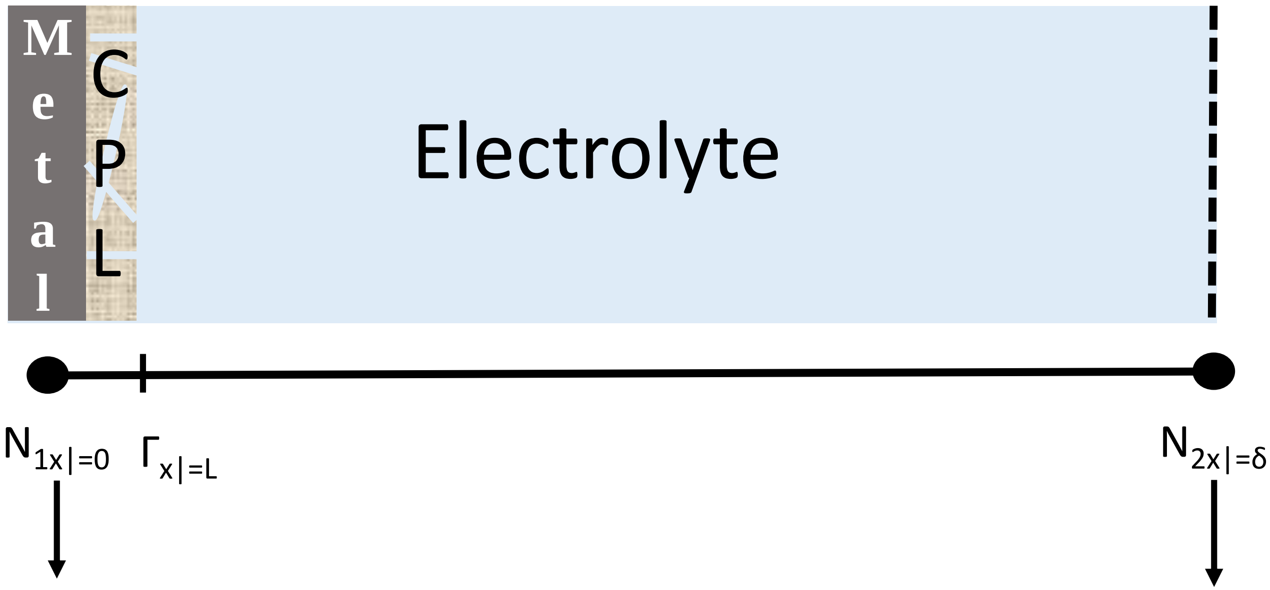
    $$HCO_3^- = CO_3^{2-} + H^+$$

- Initial condition and composition of the medium (**satisfying the equilibrium**) :
  - Thickness of the CPL: **L=100 µm**
  -

Species	Na^+	Cl^-	Fe^{2+}	OH^-	H^+	CO_2	H_2CO_3	HCO_3^-	CO_3^{2-}
Concentration ($mol.m^{-3}$)	$-\sum z_i.c_i$, i ≠ Na^+	10	$1{,}79.10^{-2}$	9.10^{-7}	10^{-2}	33,3	$8{,}6.10^{-2}$	2,34	$3{,}17.10^{-5}$

II. Modelling and Numerical Model : Corrosion Under Porous CPL

- Boundary conditions



Neumann condition (fluxes) :

- $N_i=f(i_a, i_c)$ for the electroactive species ;
- $N_i=0$ for all non-electroactive species.

Dirichlet condition (concentration) :

- diffusion boundary layer: $\mathbf{c_i=c_{i0}}$;
- δ= 500 µm.

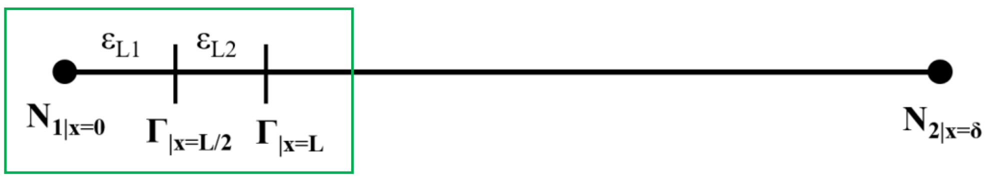
II. Modelling and Numerical Model : Corrosion Under Porous CPL

- Targeted studies : two numerical experiments

1. **Influence of the CPL porosity :**

   ε_L = 0,8 ; 0,3 ; 0,1 and 0,05

2. **Influence of a bilayer structure of the CPL:**

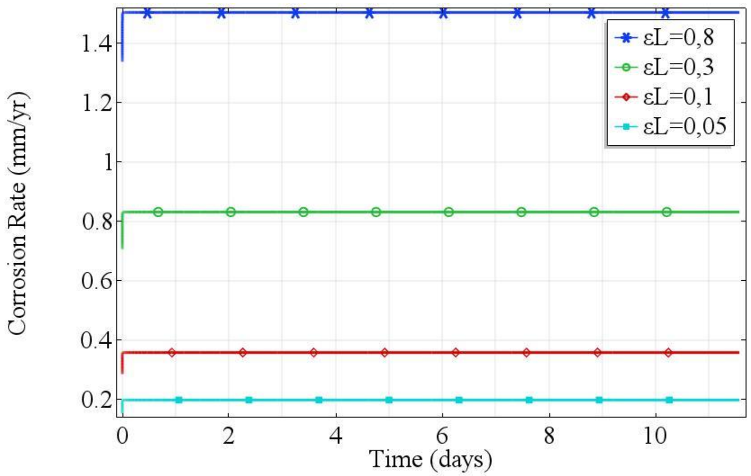


Case A : $\varepsilon_{L1} > \varepsilon_{L2}$: ε_{L1}=0,8 and ε_{L2}=0,05 : internal part **<u>less dense</u>** than the external part

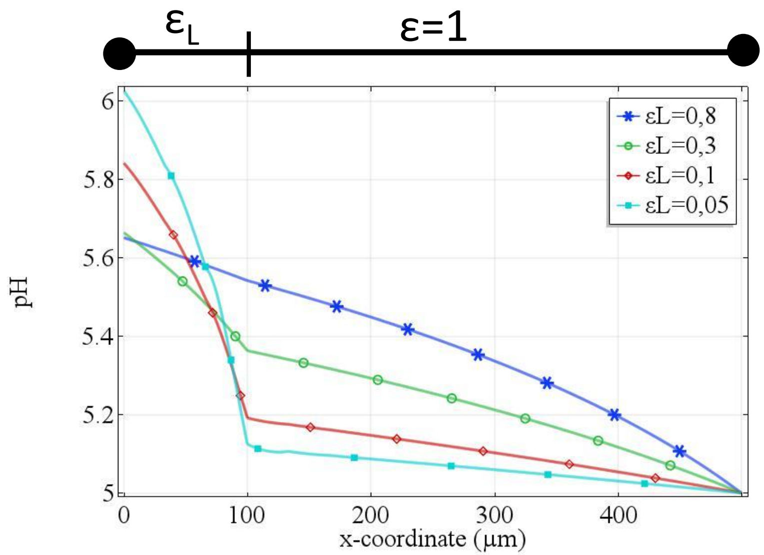
Case B : $\varepsilon_{L1} < \varepsilon_{L2}$: ε_{L1}=0,05 and ε_{L2}=0,8 : internal part **<u>denser</u>** than the external part

III. Main Results

1. Influence of the CPL porosity



Evolution of the corrosion rate

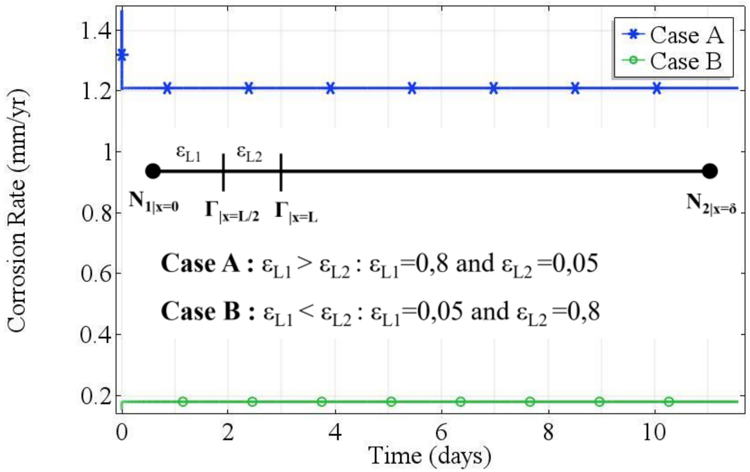


Distribution of the pH

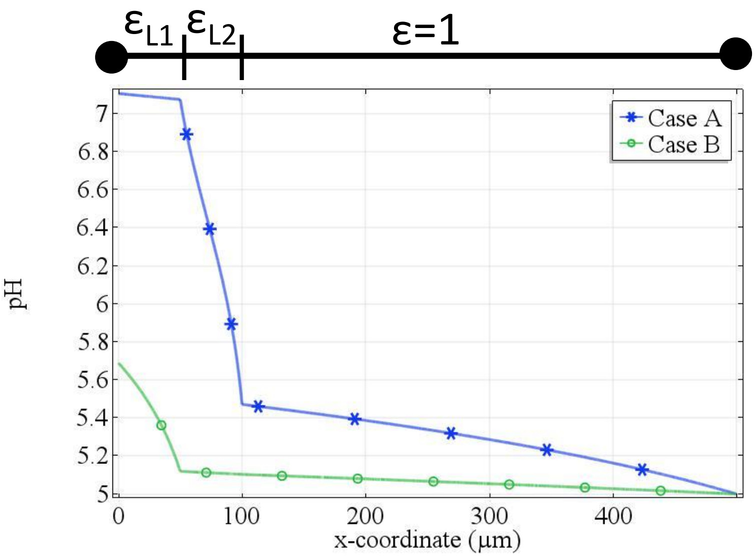
- Evolution of the corrosion rate shows that ***a dense layer involves high surface coverage and thus a low corrosion rate***.
- ***A denser layer limits the transport*** within the CPL and thus the pH increases significantly. In fact, pH increase's is due to the limitation of the bicarbonate diffusion through the CPL.
- The denser the CPL :
  - ✓ *The more the reduction of the corrosion rate it is;*
  - ✓ *The more the reaching of favorable condition to the precipitation of corrosion product it is*.

III. Main Results

2. Influence of a bilayer structure of the CPL



Evolution of the corrosion rate



Distribution of the pH

- Even if in the **Case A** the corrosion rate decreases from 1,5 mm/yr to 1,2 mm/yr, ***the corrosion rate is mainly controlled by the internal porosity of the CPL.***
- ***The transport phenomenon has a marginal effect on the corrosion rate*** with respect to the effect of the metal covering as clearly highlighted in the second case (**Case B**).
- However, this marginal effect is no longer true concerning the chemical evolution of the medium. ***In the case B, the pH*** (=7) ***and the saturation level (>>1) increase significantly*** indicating more favorable conditions for the corrosion products to precipitate.

IV. Conclusions – Perspectives

- Study of the corrosion of carbon steel pipelines using COMSOL Multiphysics® 1D numerical model.
- The influence of a fixed CPL is figured out by studying :
  - a "homogeneously" porous CPL ;
  - a "heterogeneously" porous CPL : bilayer structure.
- Two results are highlighted :
  - the corrosion rate depends largely on the porosity of the internal part of the CPL that covers the metal surface ;
  - an external dense layer affects mainly the chemical composition and thus the corrosion process by limiting the transport at the external part.
- Further developments will consist in taking into account the precipitation of the corrosion products that could influence, in large extend, the corrosion process.