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

Maalek Mohamed-Saïd and Patrick Namy
SIMTEC- 09 53 51 45 60
patrick.namy@simtecsolution.fr

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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.

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I. Background – Motivations – Objectives

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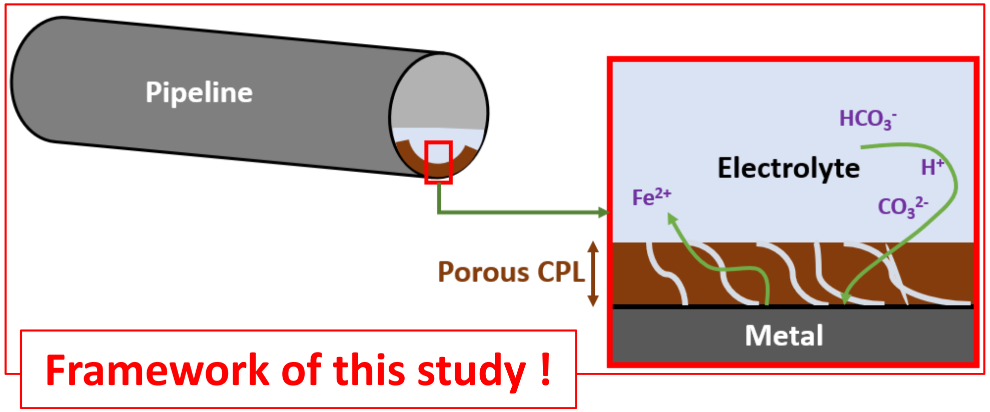
- ***Carbon steel*** is largely used in oil a gas industry
- ***Corrosion*** is the main factor affecting the longevity and reliability of carbon steels tubes and pipelines used for oil & gas production and transportation !
- ***Corrosion*** is the degradation of the metal due to its interaction with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

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:*

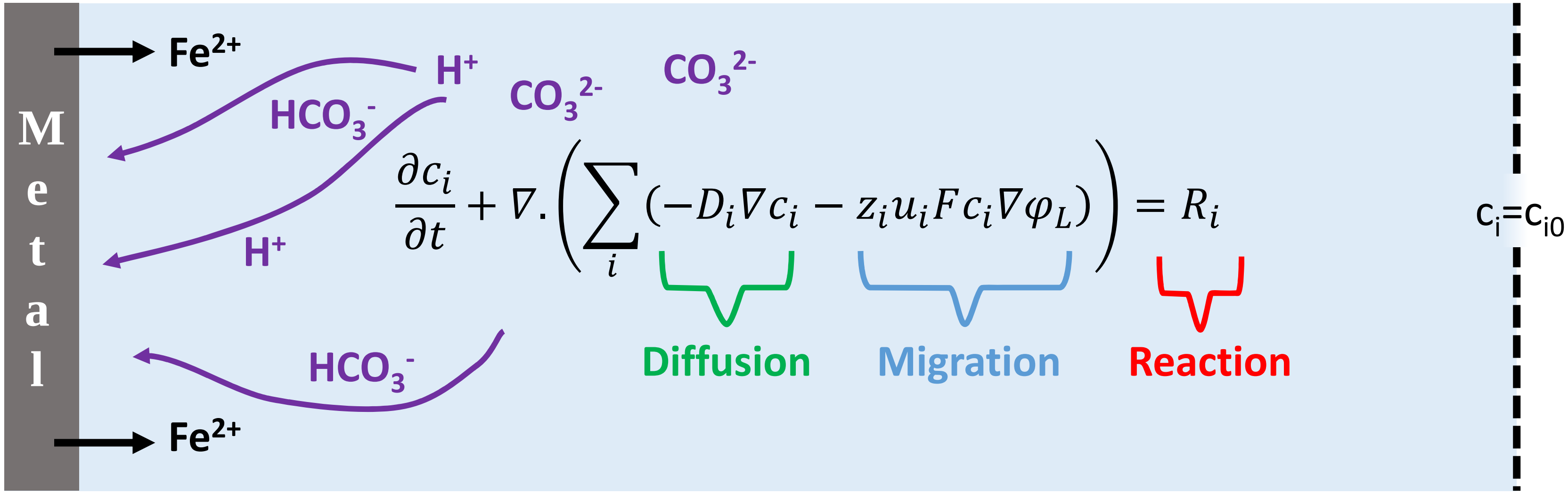
- *the covering effect*
- *the transport limitation of the chemical species through a porous layer ?*

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



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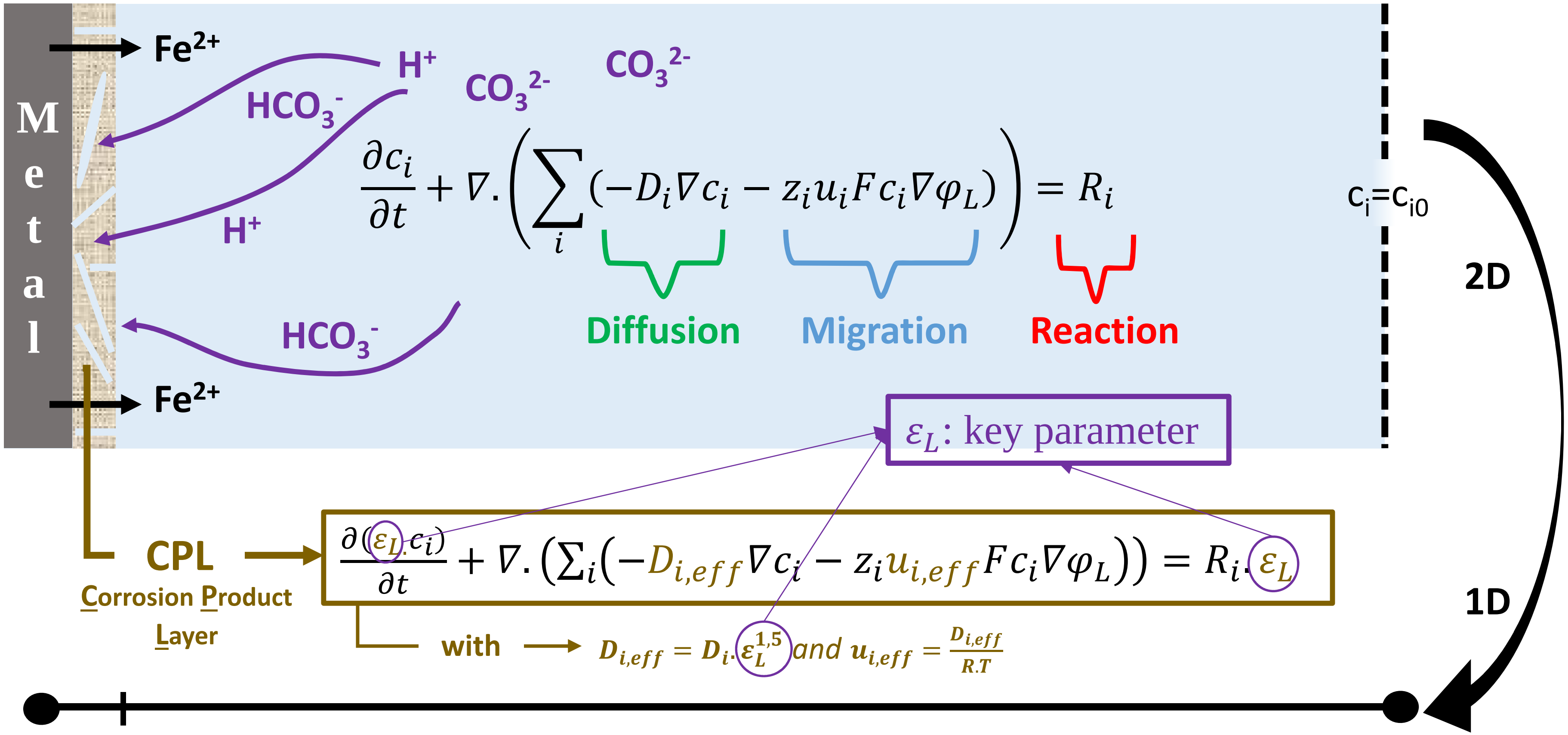

II. Modelling and Numerical Model : Corrosion Under Porous CPL

- 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)
$ia^0_{Fe} = 1.\left(\frac{c_H}{C_{H_{ref1}}}\right)^{a_1}.\left(\frac{c_{CO_2}}{C_{CO_{2ref}}}\right)^{a_2}$ $a_1 = \begin{cases}1, & P_{CO2} < 1\,bar\\ 0, & P_{CO2} \geq 1\,bar\end{cases}$ and $a_2 = \begin{cases}2, & pH \leq 4\\ 1, & pH \in]4;5]\\ 0, & pH > 5\end{cases}$	$C_{H_{ref1}} = 0{,}1$ $C_{CO_{2ref}} = 36{,}6$
$ic^0_{H_2CO_3} = 0{,}06\,.\left(\frac{c_H}{C_{H_{ref2}}}\right)^{-0{,}5}.\left(\frac{c_{H_2CO_3}}{C_{H_2CO_{3ref}}}\right)$	$C_{H_{ref2}} = 0.01$ $C_{H_2CO_{3ref}} = 0{,}1$
$ic^0_{H_2} = 3.10^{-5}.\left(\frac{c_H}{C_{H_{ref3}}}\right)^{0{,}5}$	$C_{H_{ref3}} = 0{,}1$
$ic^0_{H_2O} = 3.10^{-5}$	–

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

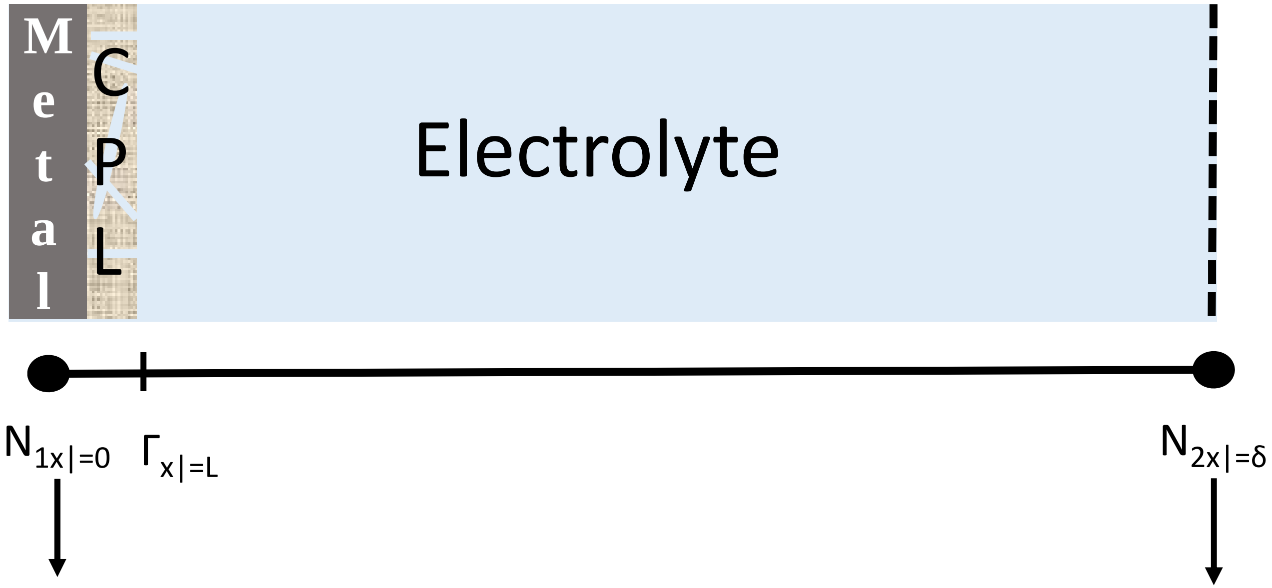
    $$HCO_3^- = CO_3^{2-} + H^+$$

- 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 ($mol.m^{-3}$)	$-\sum z_i.c_i$, $i \neq Na^+$	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.

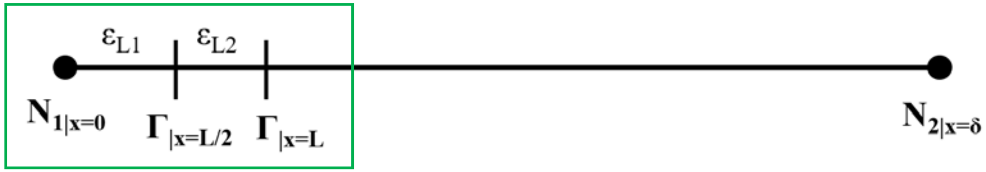
II. Modelling and Numerical Model : Corrosion Under Porous CPL

- 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:**

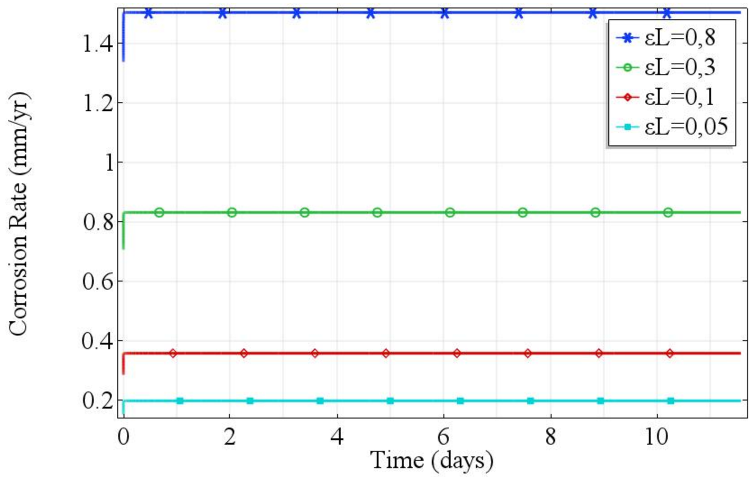


Case A : $\varepsilon_{L1} > \varepsilon_{L2}$: ε_{L1}=0,8 and ε_{L2}=0,05 : internal part **<u>less dense</u>** than the external part

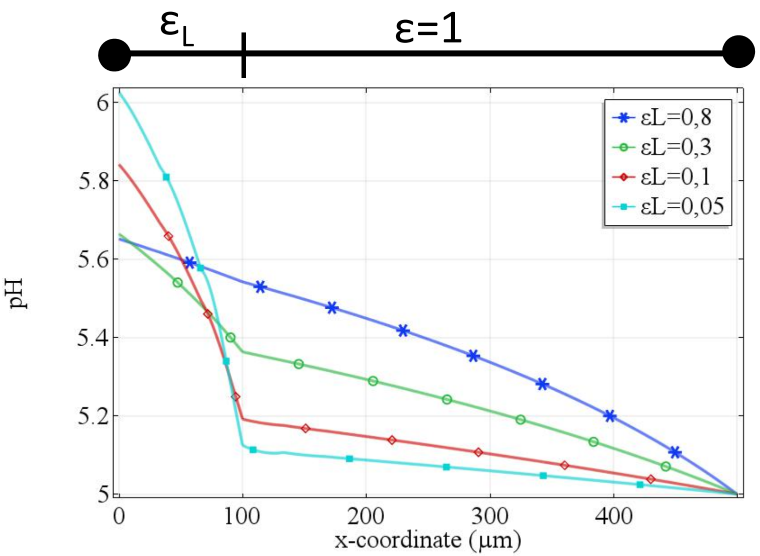
Case B : $\varepsilon_{L1} < \varepsilon_{L2}$: ε_{L1}=0,05 and ε_{L2}=0,8 : internal part **<u>denser</u>** than the external part

III. Main Results

1. Influence of the CPL porosity



Evolution of the corrosion rate

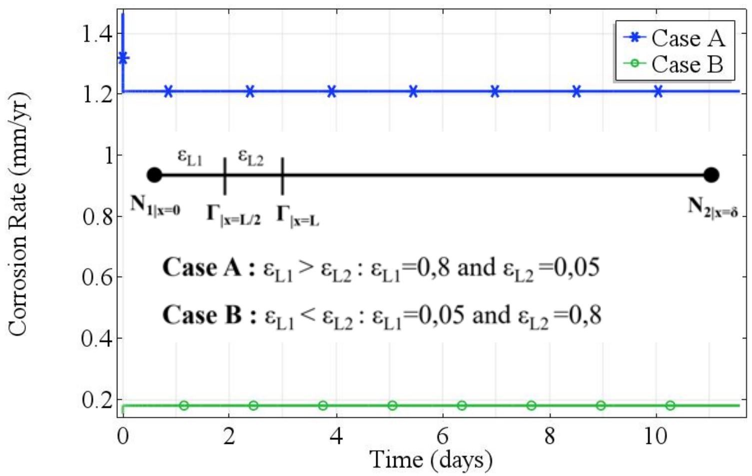


Distribution of the pH

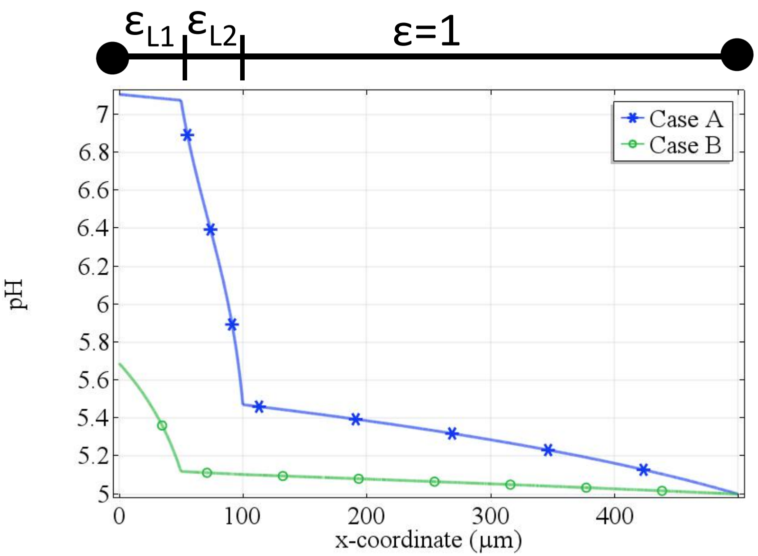
- Evolution of the corrosion rate shows that ***a dense layer involves high surface coverage and thus a low corrosion rate***.
- ***A denser layer limits the transport*** within the CPL and thus the pH increases significantly. In fact, pH increase's is due to the limitation of the bicarbonate diffusion 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.

Questions pouvant être posées :

→ pourquoi la circulation n'est pas prise en compte ? Hypothèse forte ?

→ pourquoi avoir choisi L = 100 µm ? et δ = 500 µm ?

→ comment prévoyez-vous l'évolution en cas de prise en compte de la précipitation des produits de corrosion ?