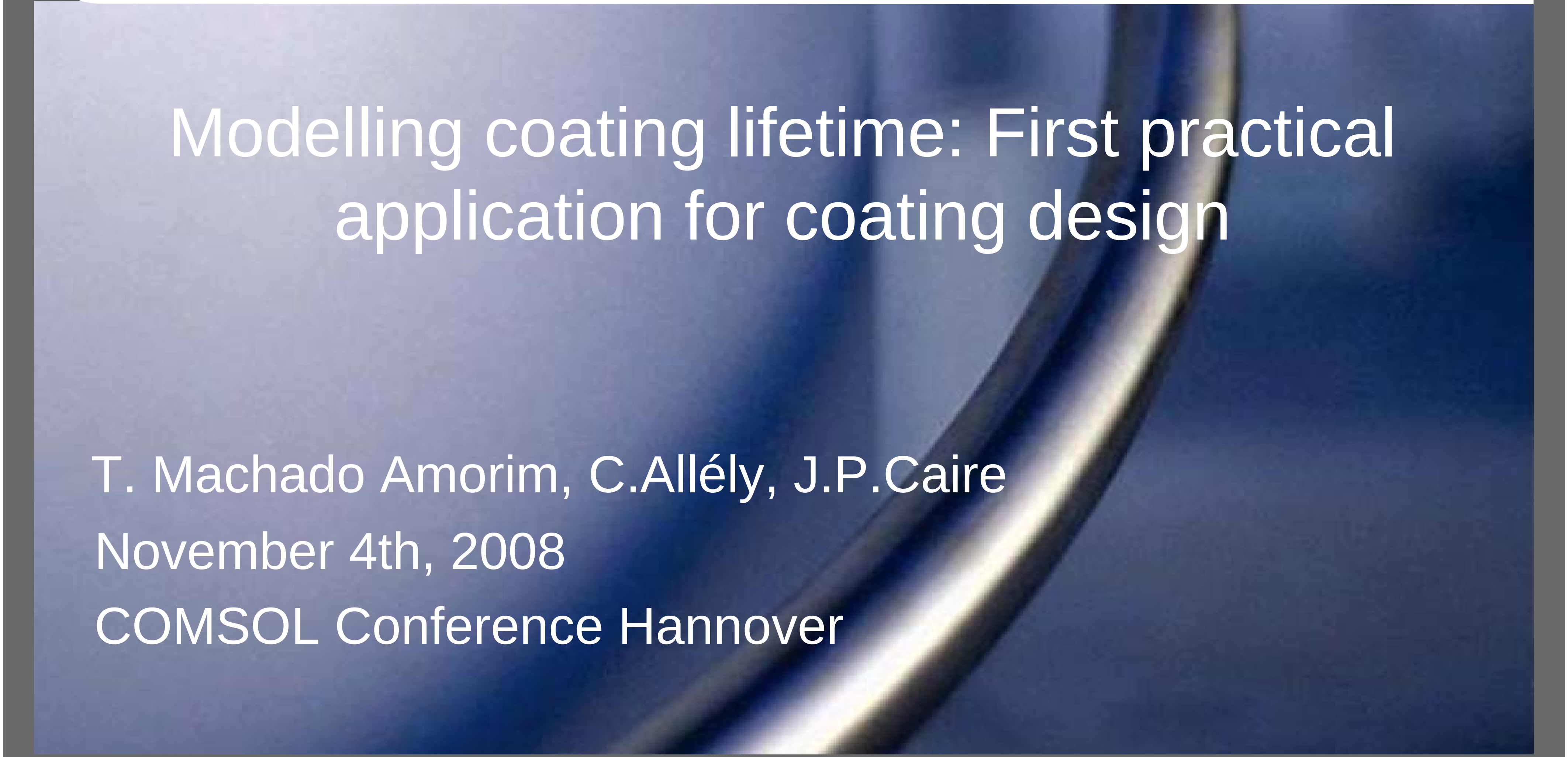
Presented at the COMSOL Conference 2008 Hannover



Modelling coating lifetime: First practical application for coating design

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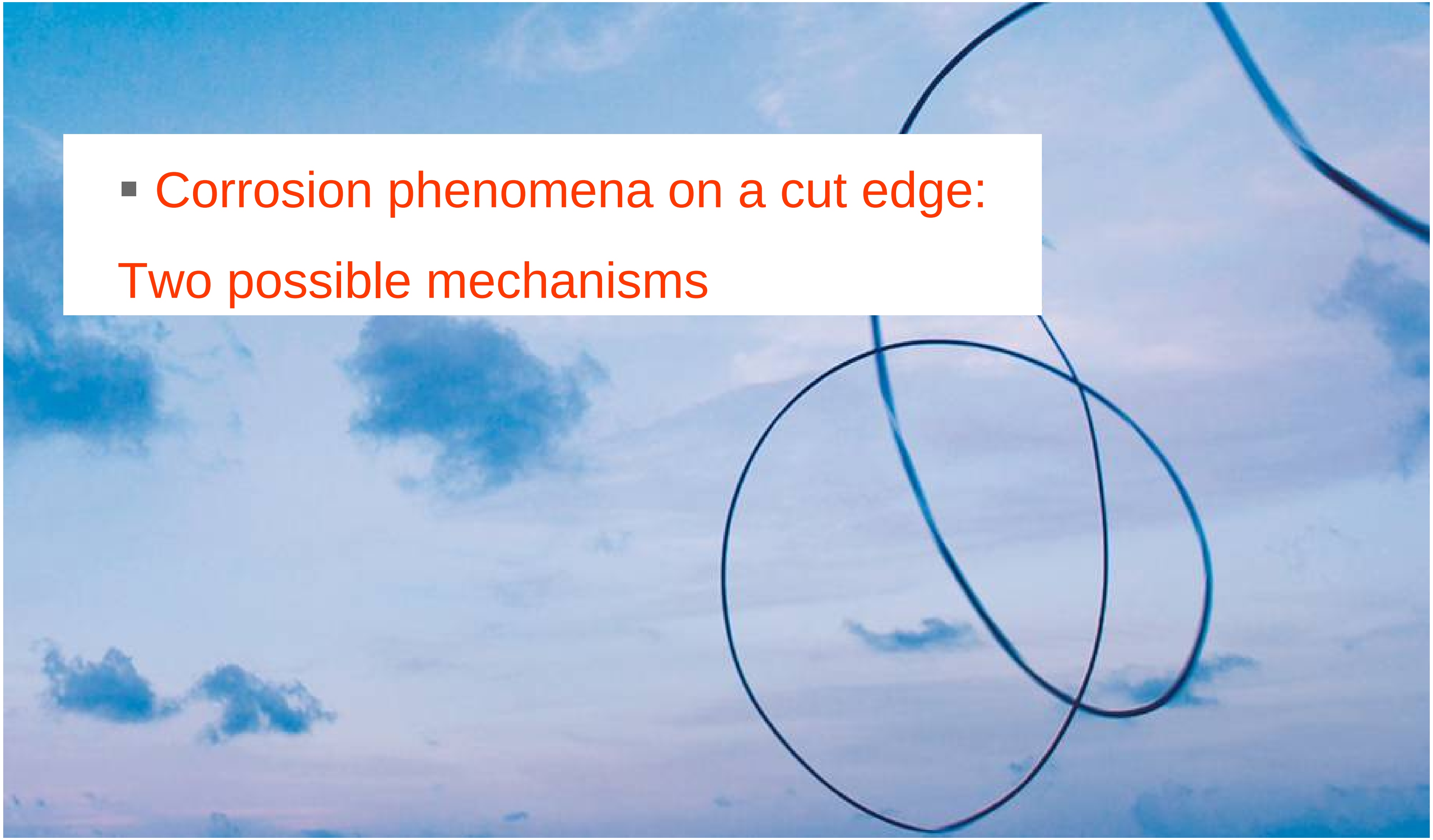
COMSOL Conference Hannover

Summary

- Corrosion phenomena on a cut edge
  - Cathodic or anodic delamination mechanism
- Corroded automotive samples analysis
  - Choice of main underpaint corrosion mechanism
- Cut edge corrosion modelling
  - Modelling corrosion at “initial time”
  - Dynamic corrosion model
- Conclusions

Delamination mechanisms

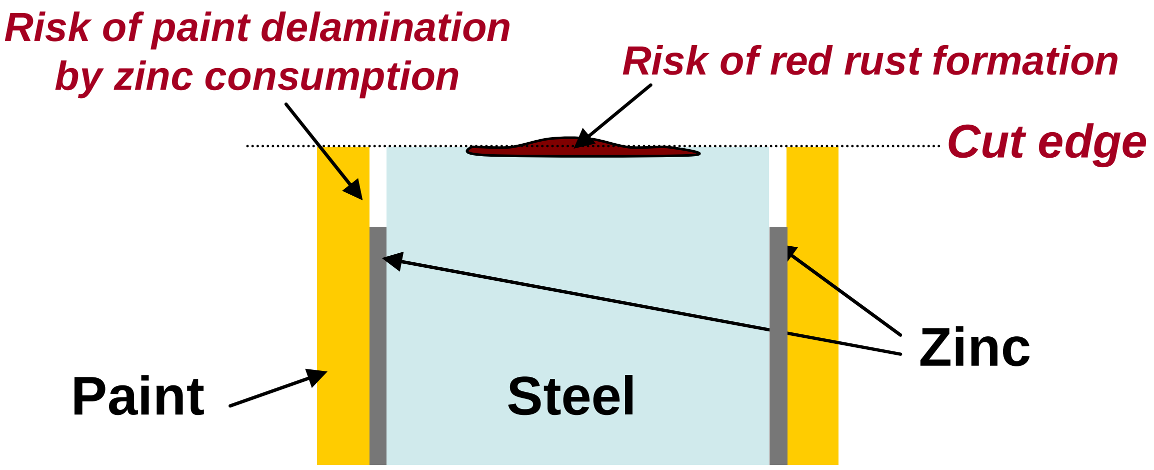


- Corrosion phenomena on a cut edge:

Two possible mechanisms

Corrosion on a cut edge

Red rust formation and paint delamination



Risk of paint delamination by zinc consumption

Risk of red rust formation

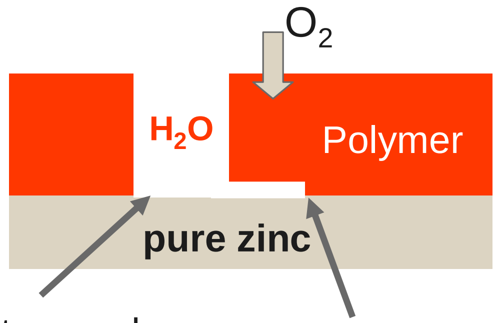
Cut edge

Zinc

Paint

Steel

Cathodic delamination => paint/Zn

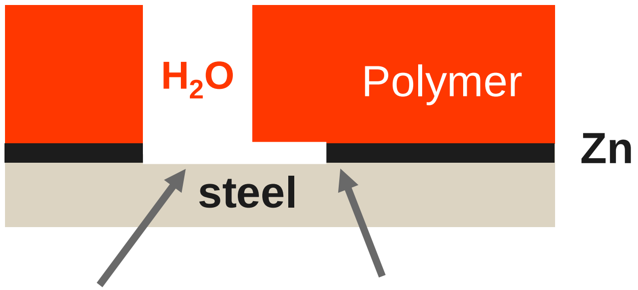


Defect = anode
Zn -> $Zn^{2+} + 2e^-$

Confined zone = cathode
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

➲ **Coupling zinc”defect” / zinc”confined”**

Anodic delamination => paint/EG

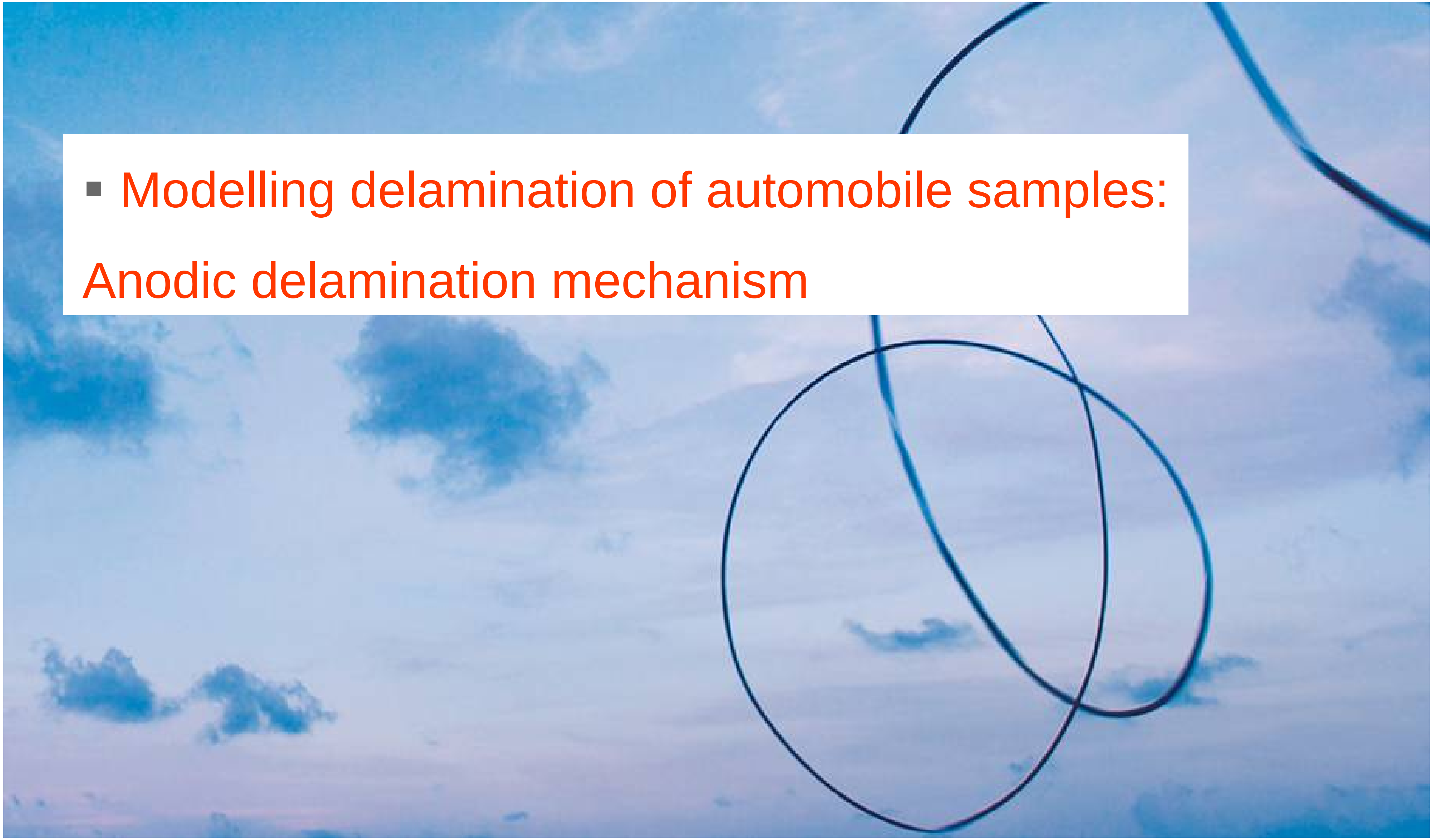


Defect = cathode
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Front of delamination = anode
Zn -> $Zn^{2+} + 2e^-$

➲ **Coupling zinc / steel**

Corrosion modelling

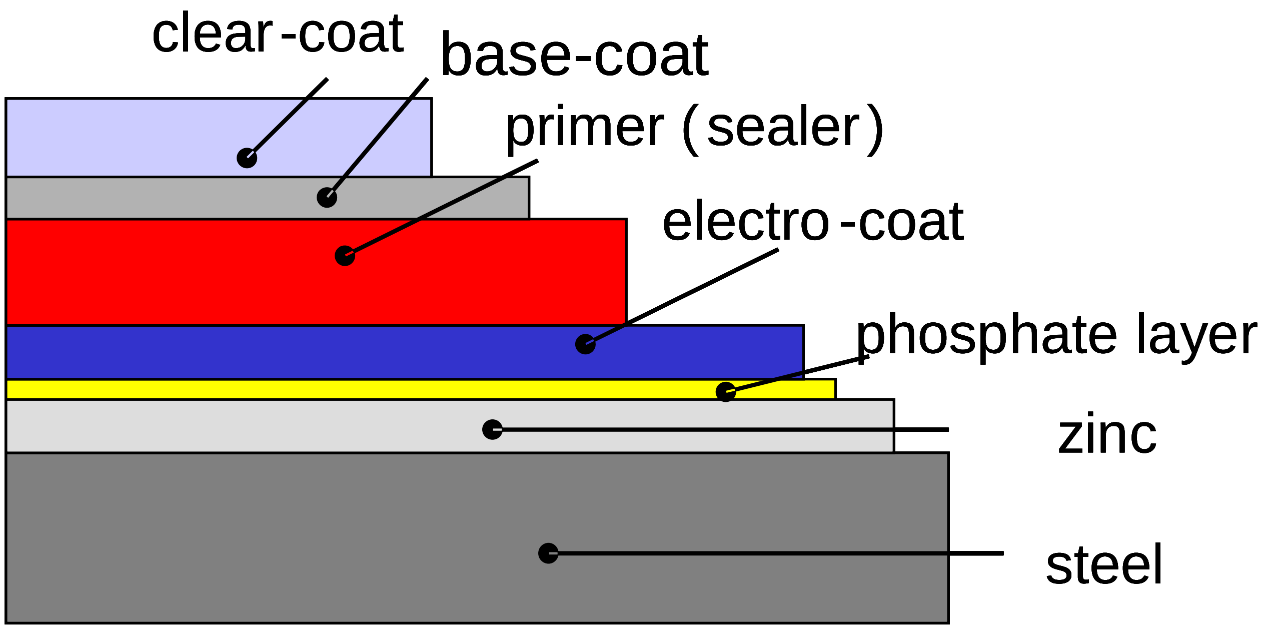


- Modelling delamination of automobile samples:

Anodic delamination mechanism

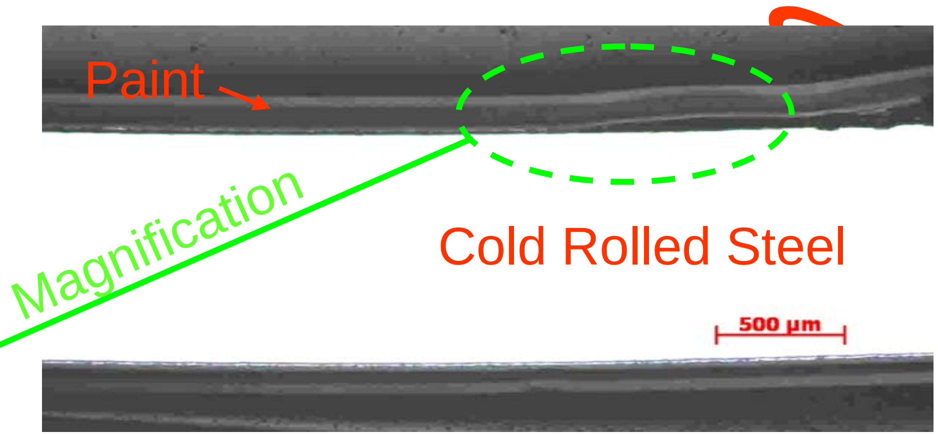
Automotive system configuration

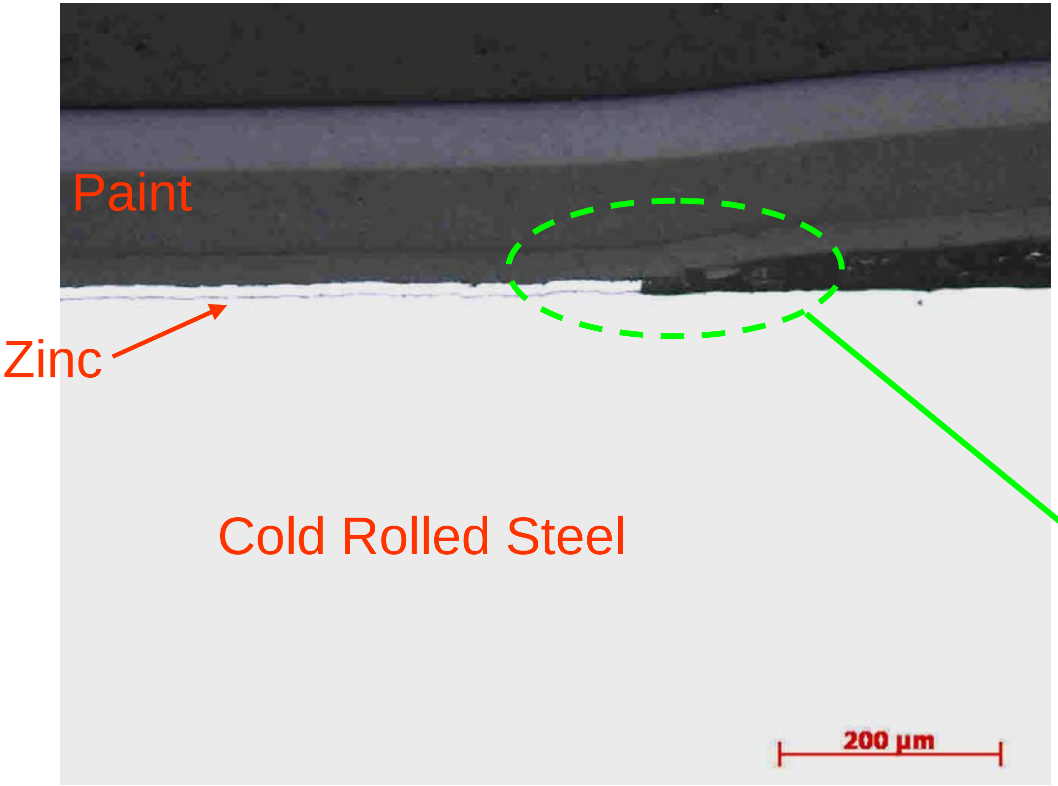
Real auto systems

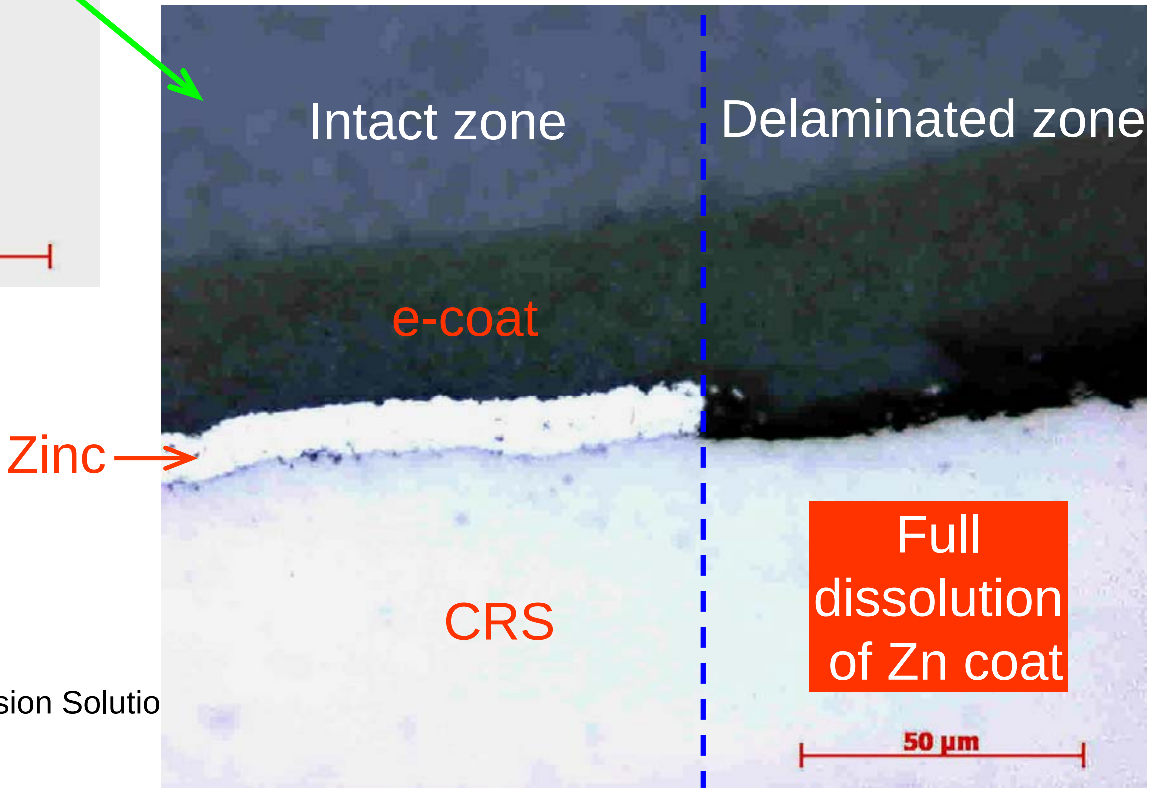


Painted EZ samples

SEM cross section analysis





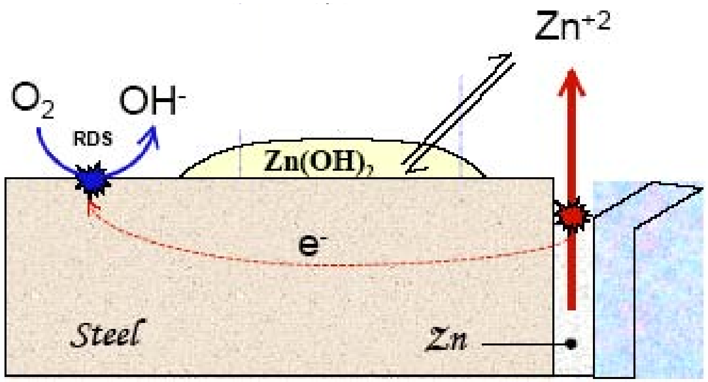


Full dissolution of Zn coat

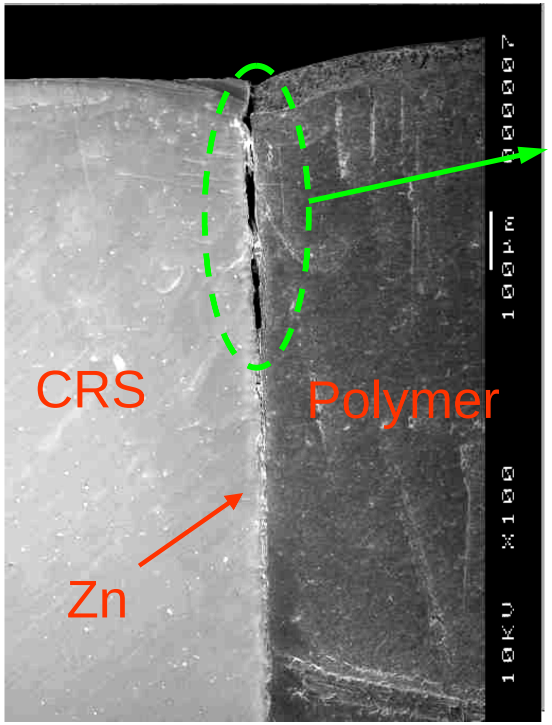
Anodic delamination evolution
=
Complete dissolution of zinc coat

Automotive systems

Same behaviour for cut edge and cosmetic corrosion

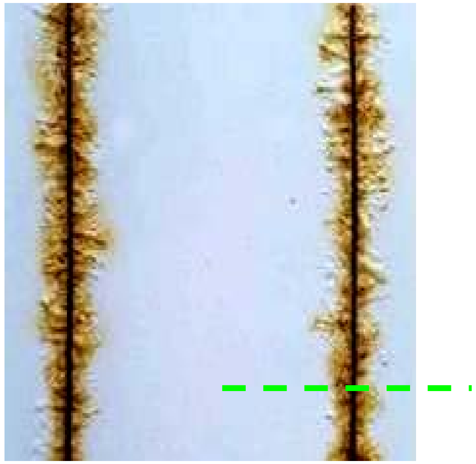


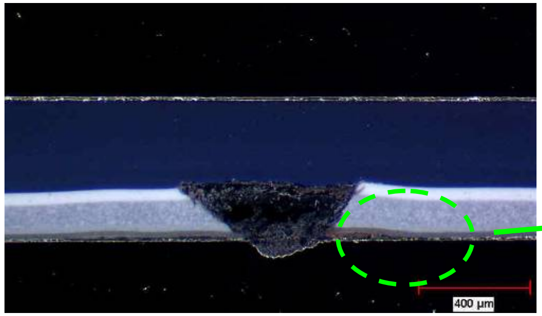
Delamination from a cut edge (EG sample)

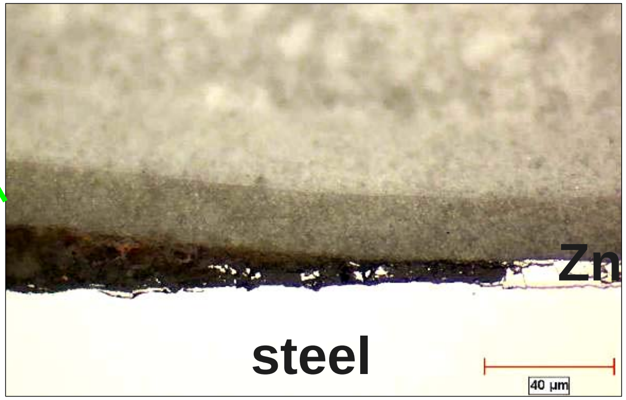


Delamination resulting from Zn film dissolution

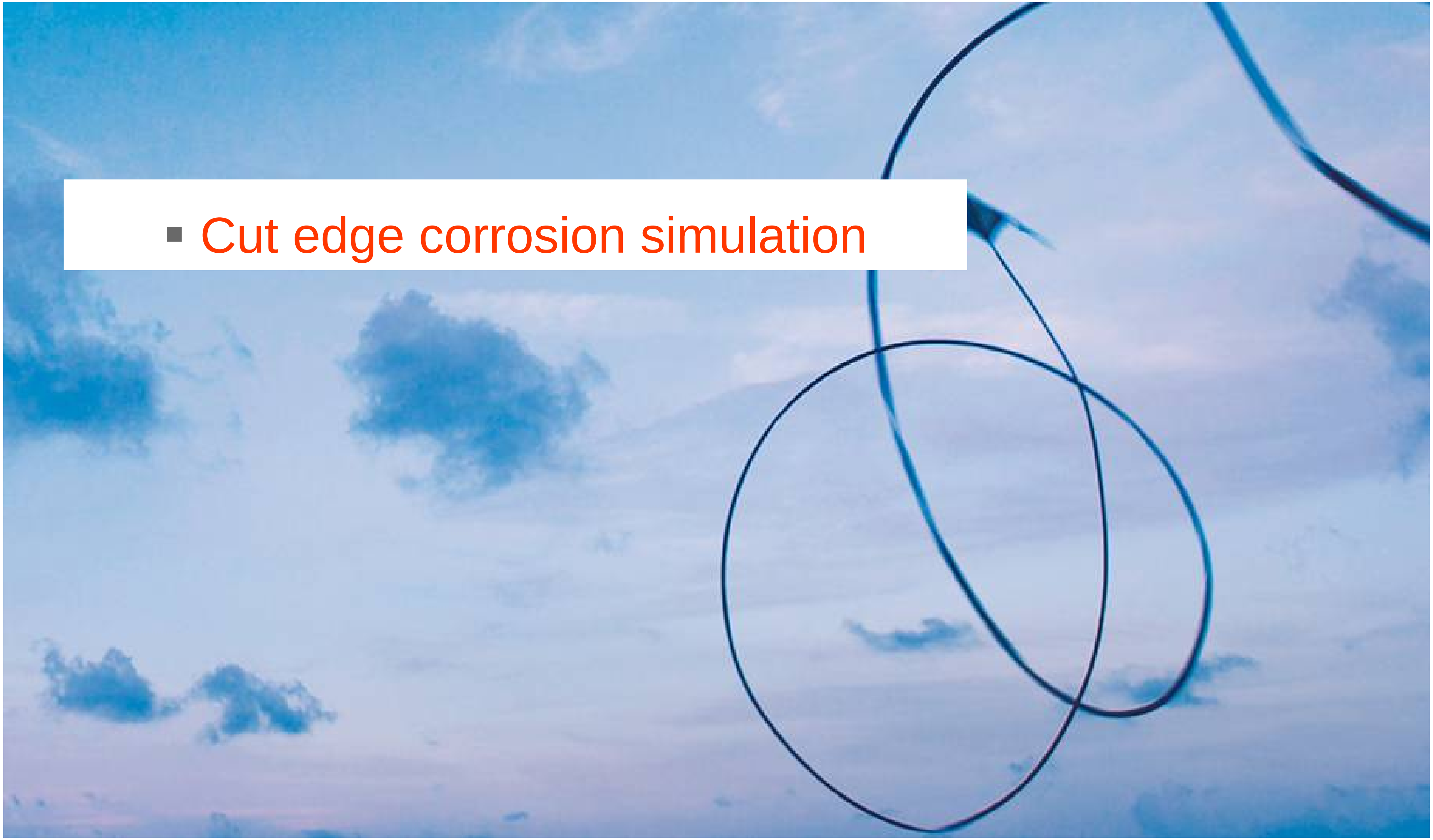
Delamination from a scribe (EG)







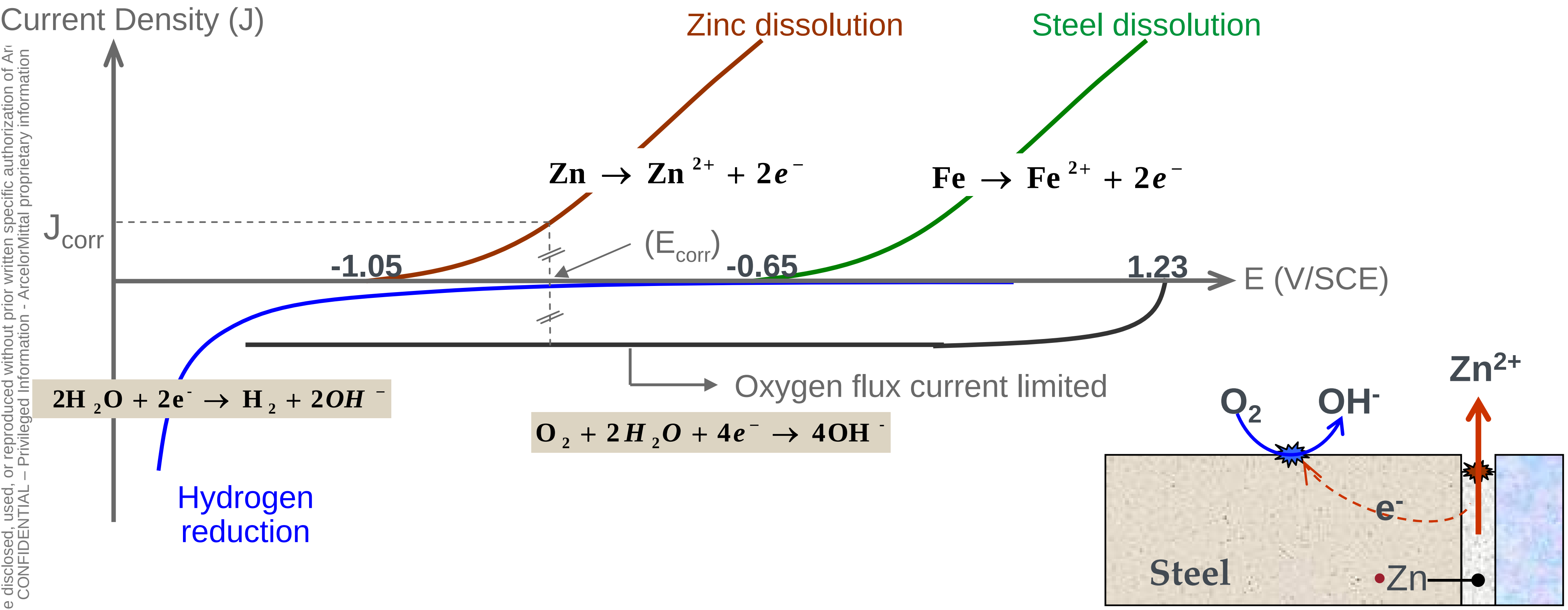
Corrosion modelling



- Cut edge corrosion simulation

Cut edge protection mechanisms

- Galvanic coupling between Steel and Zinc

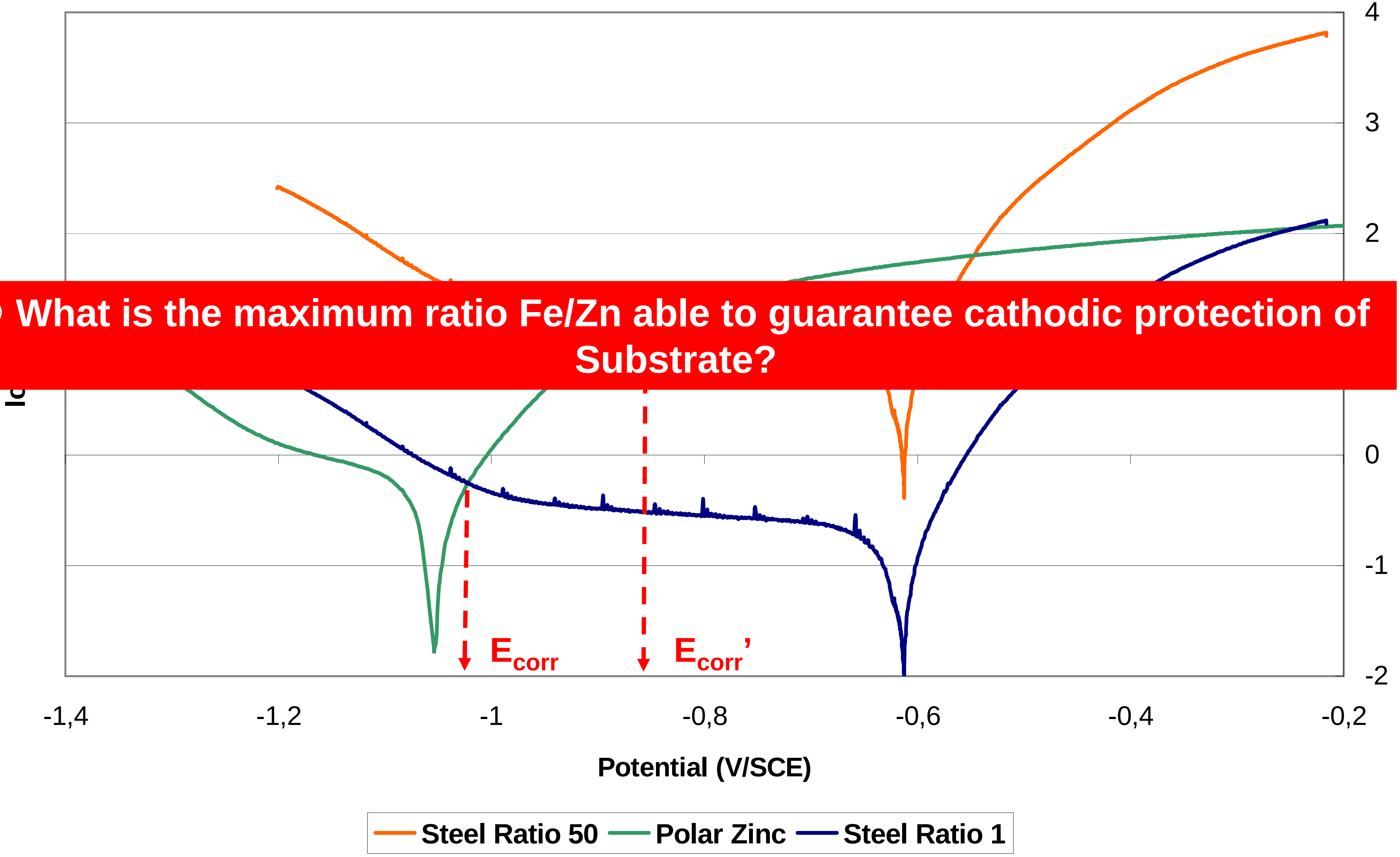


- Analyze made using thermodynamics considerations

$$E_{eq_i} = E_{0_i} + \frac{RT}{zF} \log\left(n_i^{z+}\right)$$

$Zn \leftrightarrow Zn^{2+} + 2e^-$	$E^0 = -0.76$ (V/SHE)
$Fe \leftrightarrow Fe^{2+} + 2e^-$	$E^0 = -0.44$ (V/SHE)
$O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^-$	$E^0 = 1.23$ (V/SHE)
$2H_2O + 2e^- \leftrightarrow H_{2(g)} + 2OH^-$	$E^0 = 0$ (V/SHE)

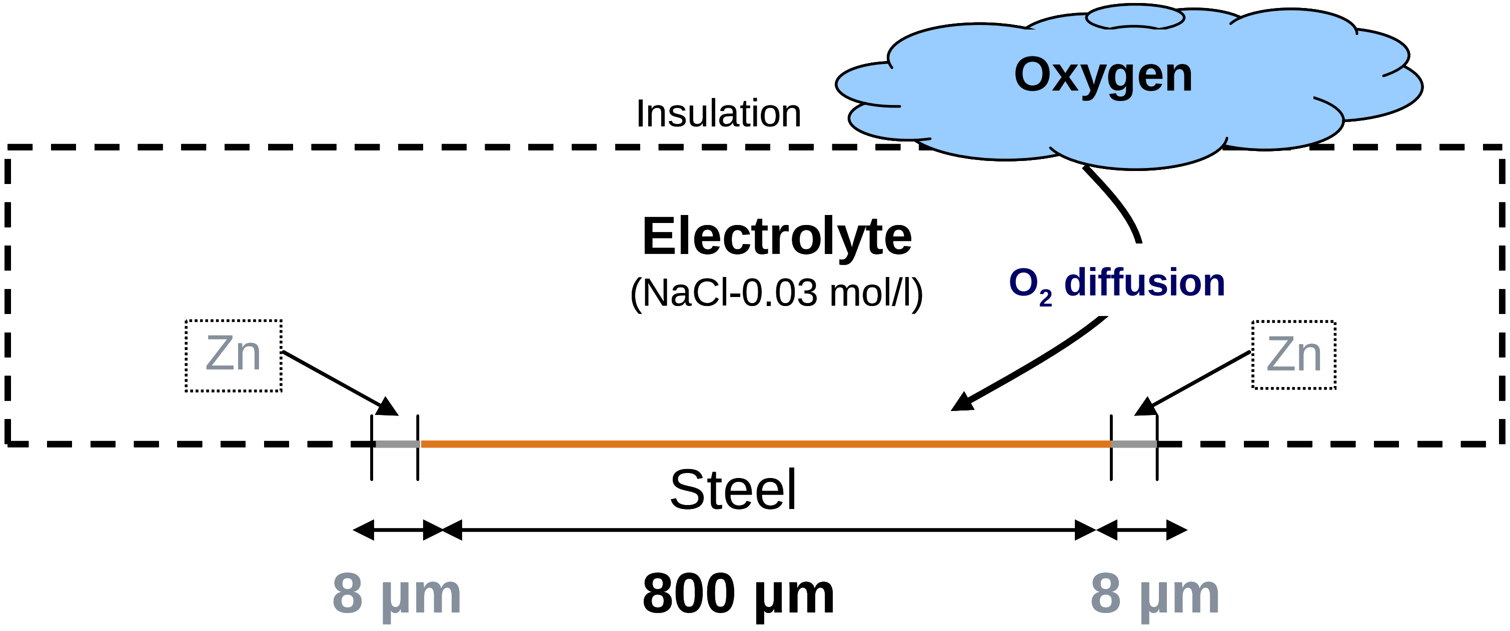
Ratio Fe/Zn influence on Galvanic coupling



➲ What is the maximum ratio Fe/Zn able to guarantee cathodic protection of Substrate?

« Time Zero » Cut edge modeling

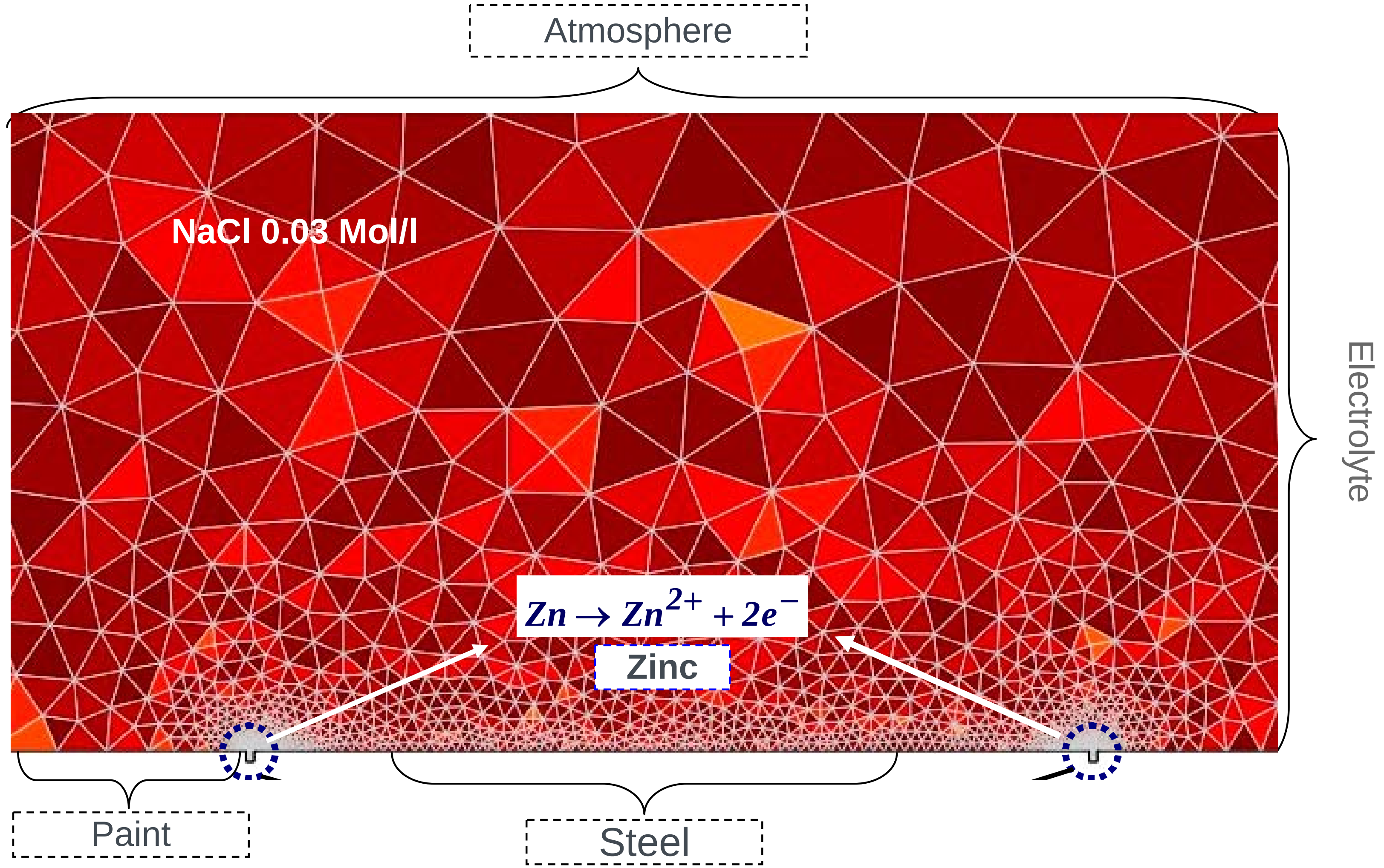
- Model configuration sketch



Steel thickness (µm)	Zinc thickness (per face) (µm)	Ratio Fe/Zn
800	8	50
800	2	200
800	0.5	800

Model Configuration

COMSOL environment



Atmosphere

NaCl 0.03 Mol/l

Electrolyte

$Zn \rightarrow Zn^{2+} + 2e^{-}$

Zinc

Paint

Steel

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$$

$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$$

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$

Governing equations in the electrolyte

→2 Modules from COMSOL MULTIPHYSICS

- Diffusion
- Nernst Planck with electroneutrality

- Nernst-Planck (species flux)

$$N_i = \underbrace{-z_i F \frac{D_i}{RT} c_i \nabla \Phi}_{\text{Migration}} \underbrace{- D_i \nabla c_i}_{\text{Diffusion}} \underbrace{+ c_i v}_{\text{Convection}}$$

- Mass balance

$$\frac{\partial c_i}{\partial t} + \nabla N_i = R_i \xrightarrow{\text{In steady-state}} -\nabla N_i + R_i = 0$$

- Inside electrolyte neutrality

$$\sum z_i c_i = 0$$

Boundary settings

❑Zinc oxidation : Butler-Volmer equation

$$j_{Zn} = j_{0Zn}\left(e^{\left(\frac{\alpha zF}{RT}(V - E_{0Zn})\right)} - e^{\left(\frac{-\beta zF}{RT}(V - E_{0Zn})\right)}\right)$$

❑Oxygen and water reduction

- **Water reduction**

  (Butler-Volmer equation)

$$j_{H_2} = j_{0H_2}\left(-e^{\left(\frac{-\beta zF}{RT}(V - E_{0H_2})\right)}\right)$$

- **Oxygen reduction**
  - Mass transfer limitation (Fick's law)

$$j_{\lim_{O_2}} = \frac{zFDC_{O_2}}{\delta}$$

❑Steel oxidation: Butler-Volmer equation

Physical & kinetic data (literature)

Physics data

	Zn^{2+}	OH^-	Na^+	Cl^-	O_2
Diffusion coefficient $D*10^9$ (m²/s)	0.712	5.24	1.33	2.03	1.90
Ionic Mobility u_m*10^{13} (s*mol/K)	2.86	21.04	5.31	7.84	

Kinetics Data

Butler Volmer	Zn oxidation	H_2O reduction
J° (A/m²)	0.71	10^{-4}
β (V/decade)	0.0256	0.0513
E_{eq} (V/SHE)	-0.765	-0.42

Species Flux: Faraday's law

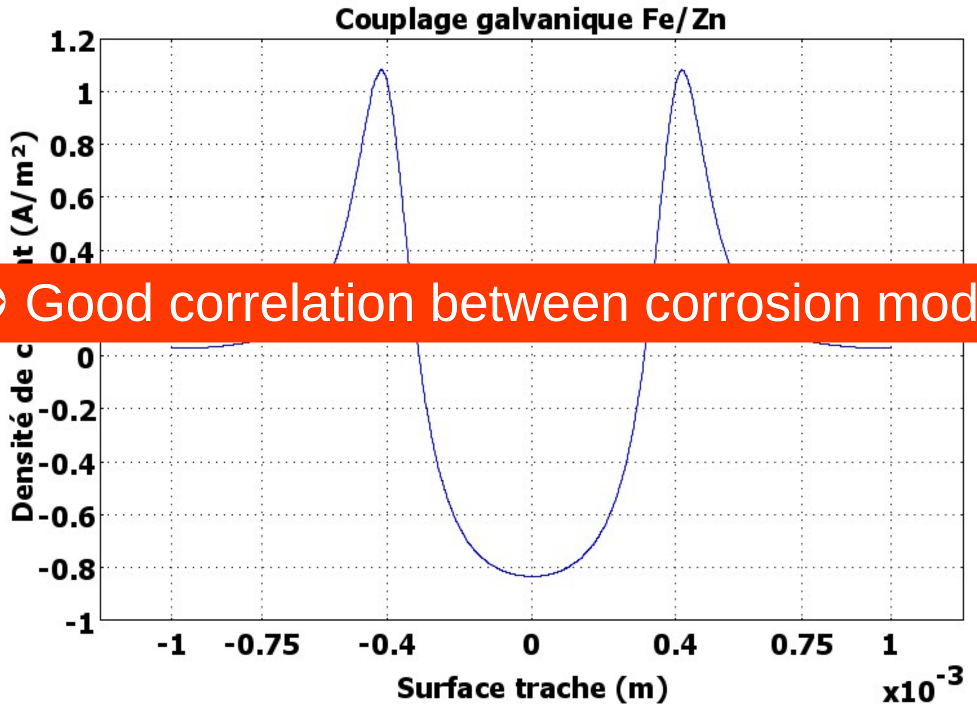
$$(Zn^{2+}) = \frac{J_{Zn}}{2*F} \qquad (OH^-) = \frac{-J_{O_2}}{F}$$

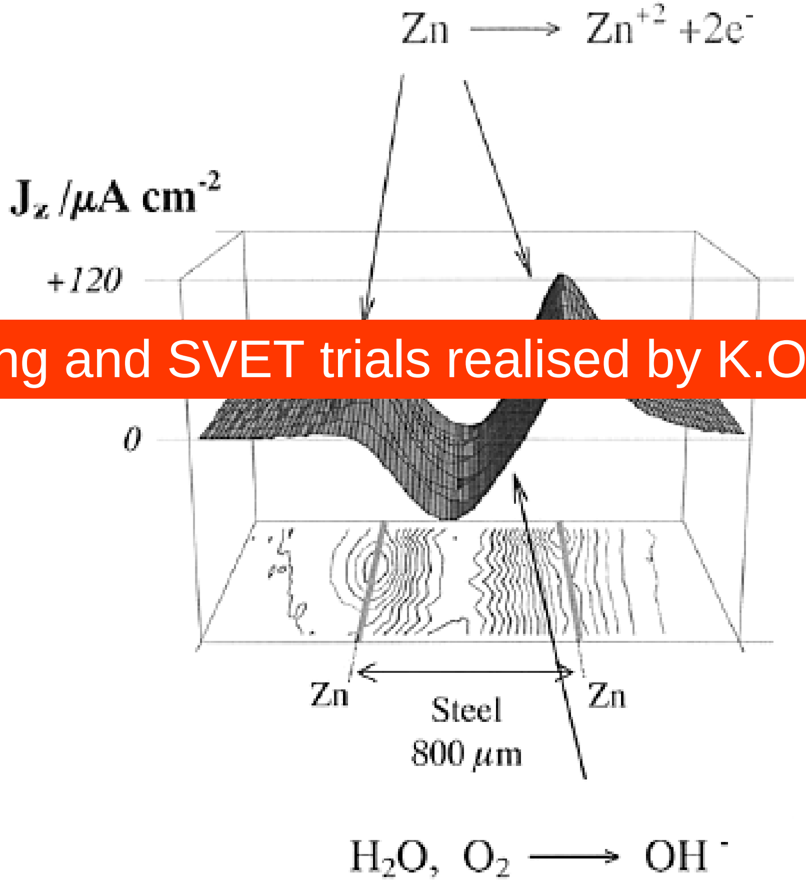
Results

Total current density on the Cut edge

➔ Simulation validation with SVET results

Distance from cut edge surface 150 µm



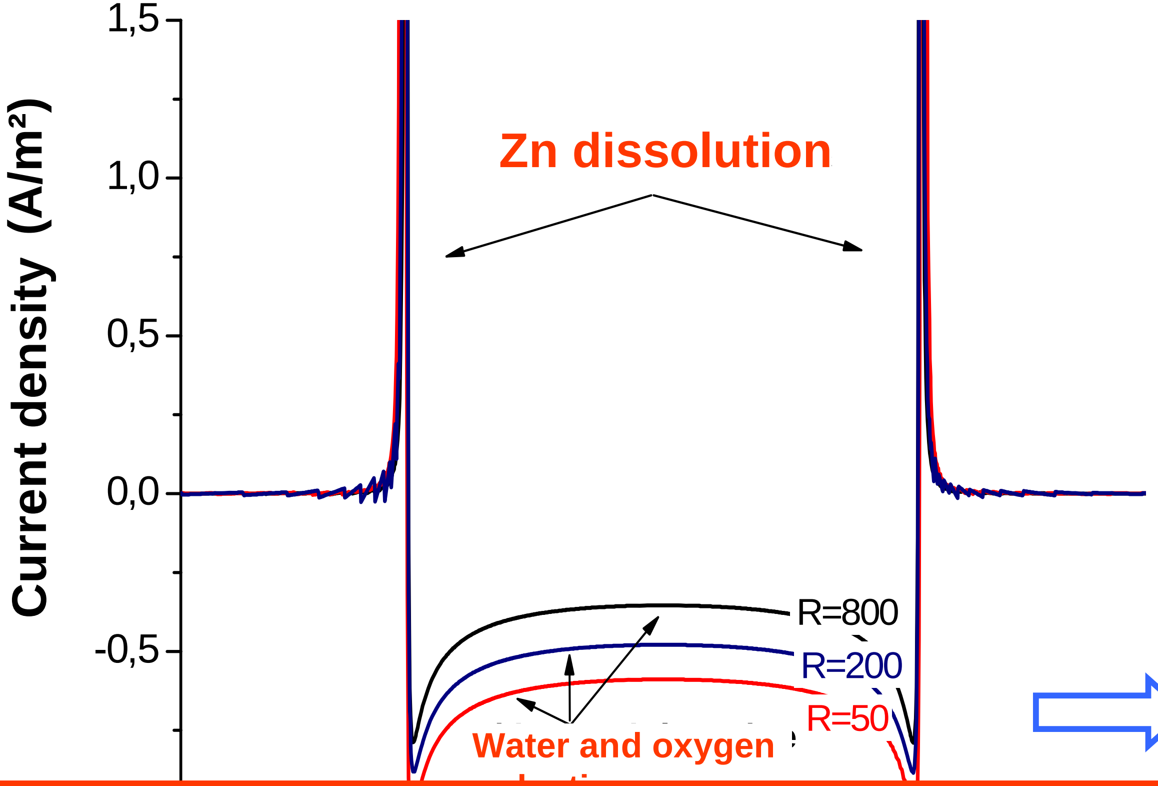


➲ Good correlation between corrosion modeling and SVET trials realised by K.Ogle

- **ARSA model**
- **K. Ogle**

Results

Total current density on the Cut edge



•Steel under protection by galvanic coupling in time Zero for all ratio Fe/Zn

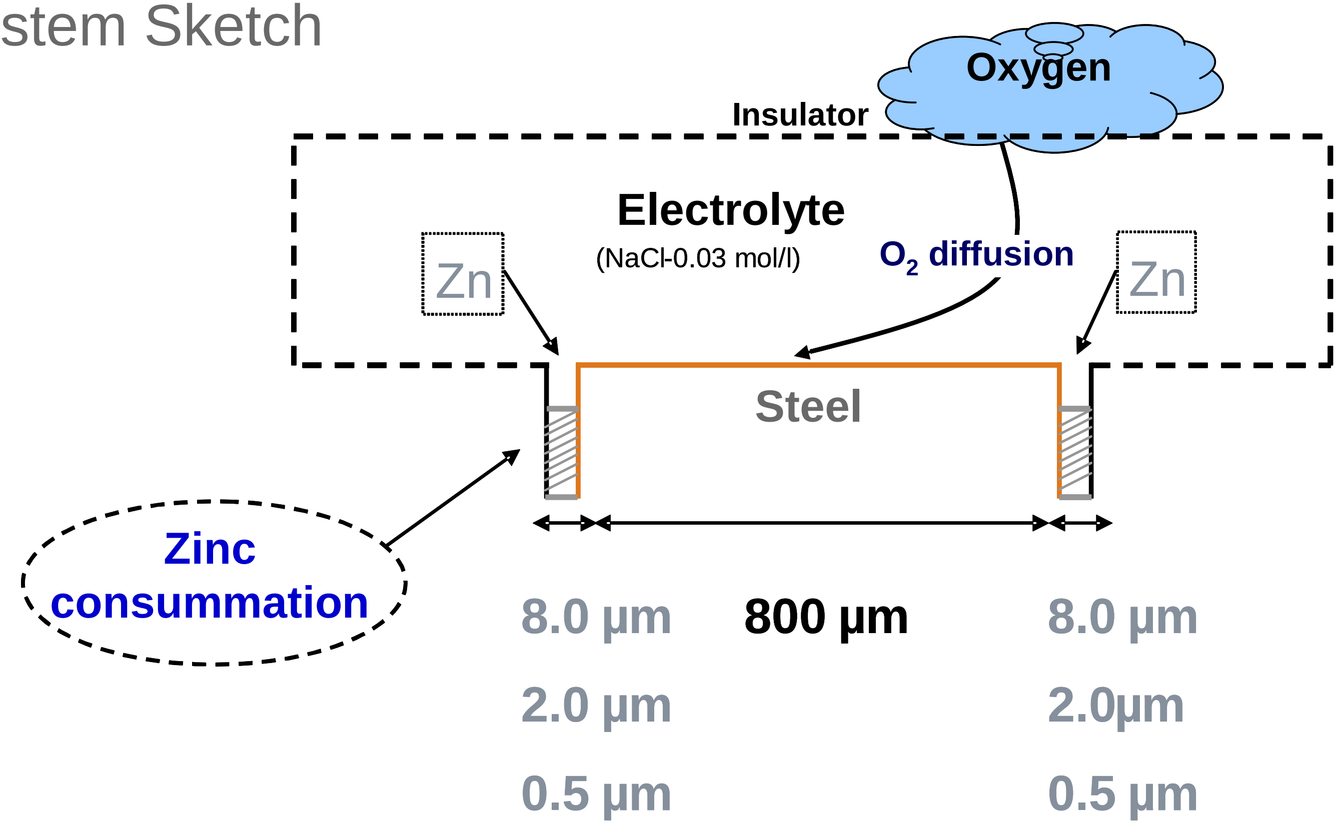
➲ Weak steel corrosion values = cathode protection excepted for ratio 800

➲ J_{Fe} of model R=800 is 100x more important then that from R=50

	Ratio Fe/Zn=50	Ratio Fe/Zn=200	Ratio Fe/Zn=800	Pure Steel
Steel corrosion kinetics (jFe(A/m²))	0,0006	0,0018	0,062	0,40
Current value relative to pure steel	0,15%	0,45%	15,5%	100%

Dynamic cut edge modelling
Zn consummation in a coupling situation

System Sketch

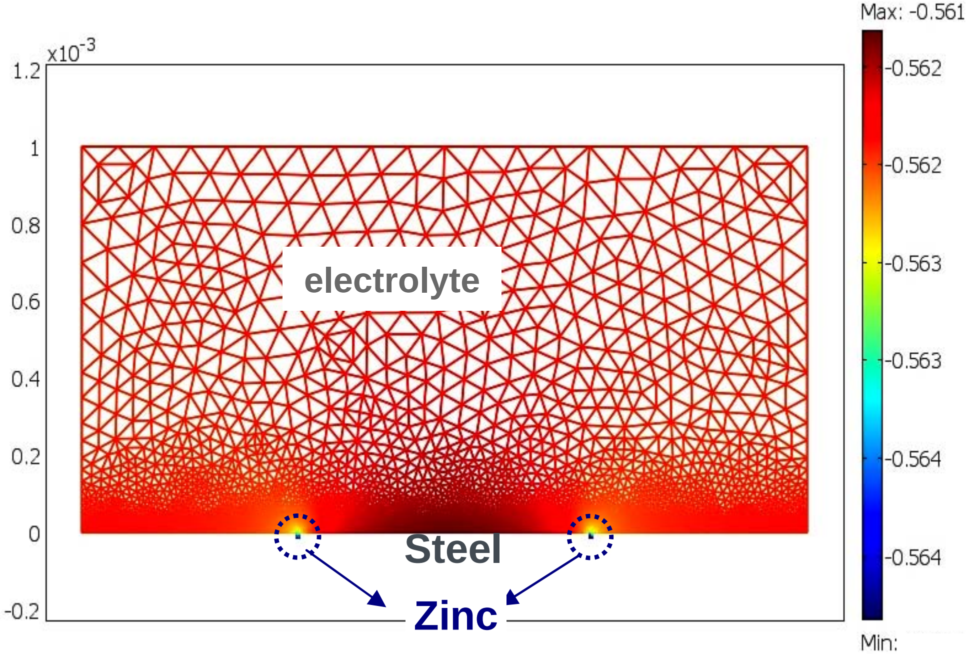


Simulation tools

- Mesh mobile (COMSOL MULTIPHYSICS)
- Faraday’s law (Zn consummation)

$$V_{cons\,Zn} = J \cdot \frac{Mol}{\rho \cdot z \cdot F}$$

Modelling cut edge corrosion
11 days salt spray test simulation

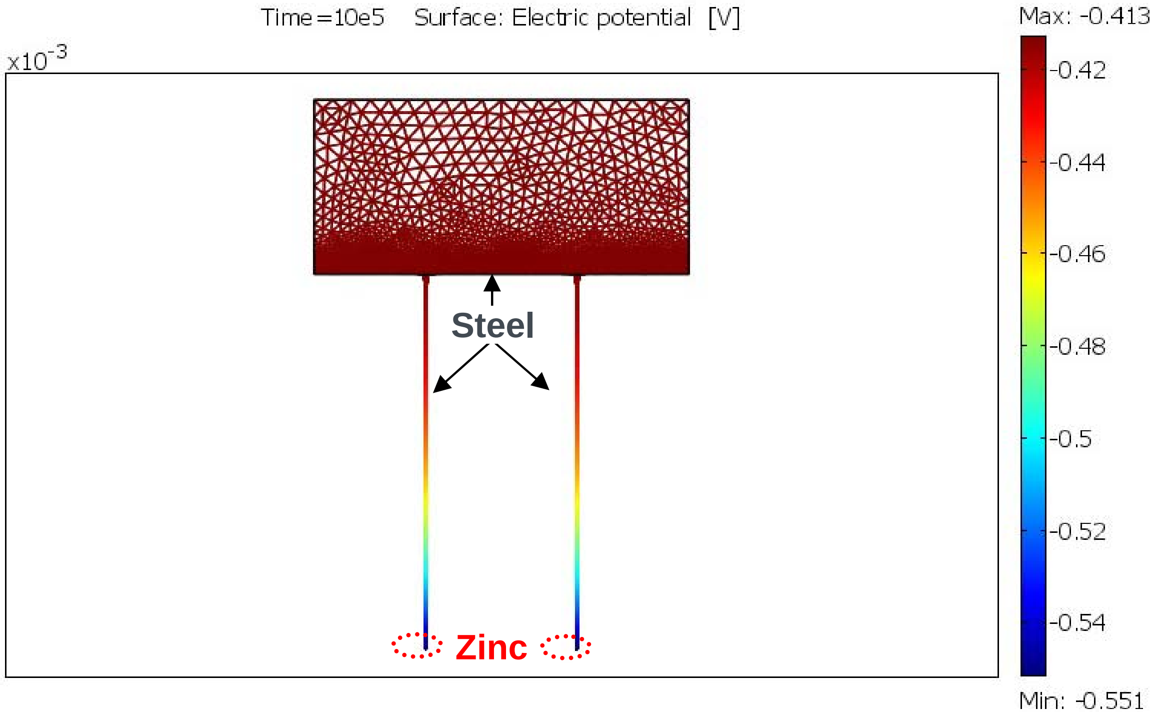


Data:
Corrosion potential t=0

Simulation

Cut edge after 11 days salt spray test

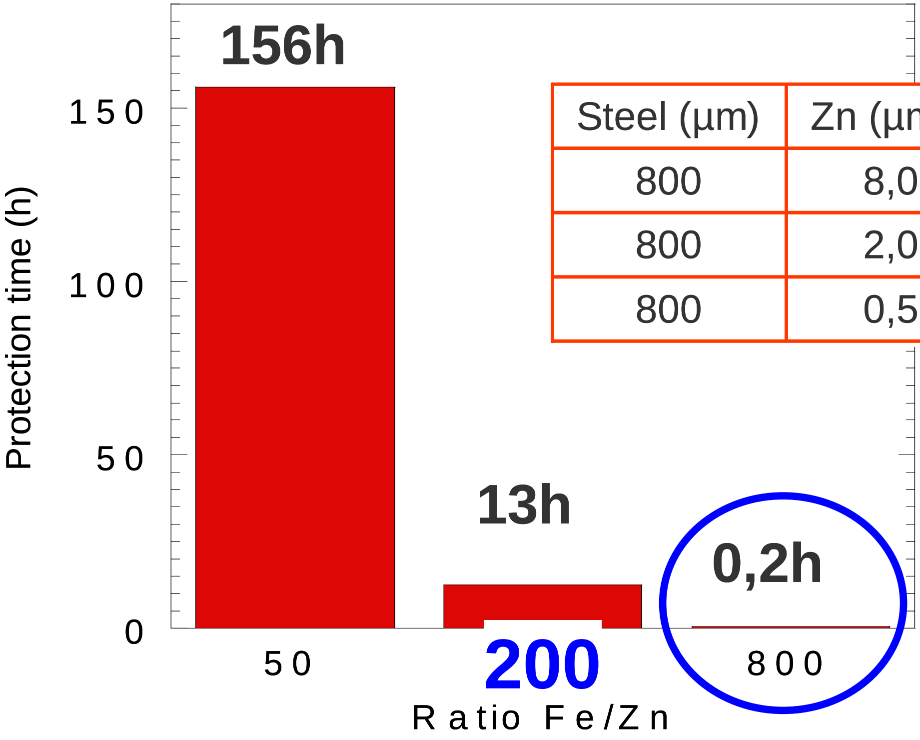
- Corrosion potential
- Zn consumption



Cut edge corrosion modelling
Main results

- Reduction of Zn thickness without loosing cathodic protection properties

Cathodic protection duration



Steel (µm)	Zn (µm)	Fe/Zn
800	8,0	50
800	2,0	200
800	0,5	800

Not enough corrosion protection

Effect of Fe/Zn ratio

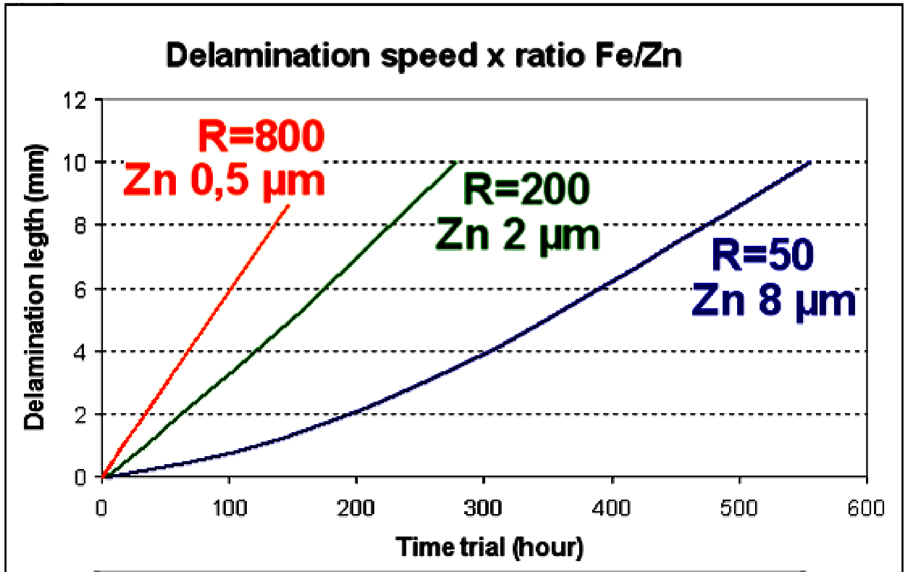
- Max Fe/Zn ratio for steel cathodic protection < 800

Modeling cut edge corrosion

Influence of Fe/Zn thickness ratio on delamination rate

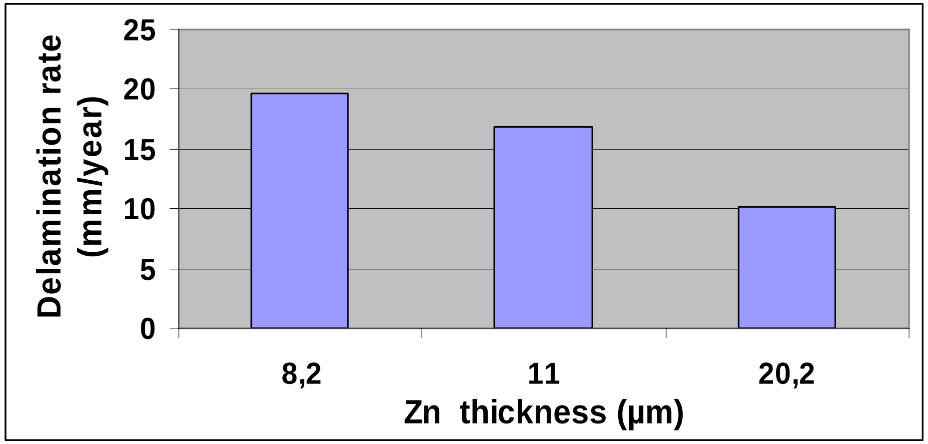
→ For a given steel thickness, the delamination rate increases with the decrease of coating thickness

Anodic delamination modelling

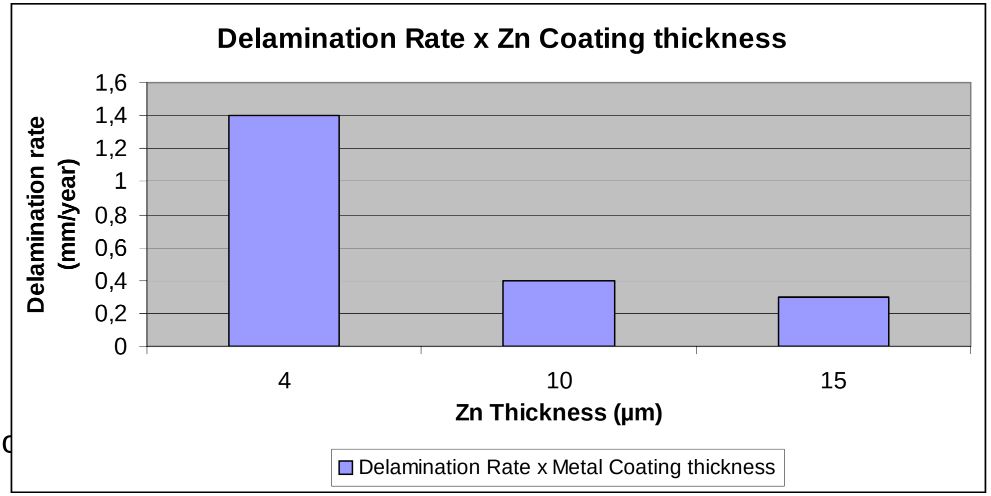


Fe/Zn ratio	Delamination rate (mm/day)
50	0,34
200	0,72
800	1,49

Accelerated corrosion tests results



On-vehicle results



Conclusions

- The 2D cut edge delamination model simulates a steady state corrosion situation

  - ✓ It simulates corrosion on cut edges by using Nenrst-Planck Module + Mobile Mesh in COMSOL MULTI PHYSICS
  - ✓ It Calculates cathodic protection evolution with Zn dissolution for different ratio Fe/Zn
  - ✓ Its tendencies are in good agreement with literature data and results obtained from accelerated corrosion tests
  - ✓ It shows that anodic delamination is the main underpaint corrosion mechanism for automotive samples configuration

- Ongoing development: undermining corrosion simulation in cyclic corrosion configuration