Presented at the COMSOL Conference 2008 Hannover

Zinc Corrosion in a Crevice

Comsol Modelling

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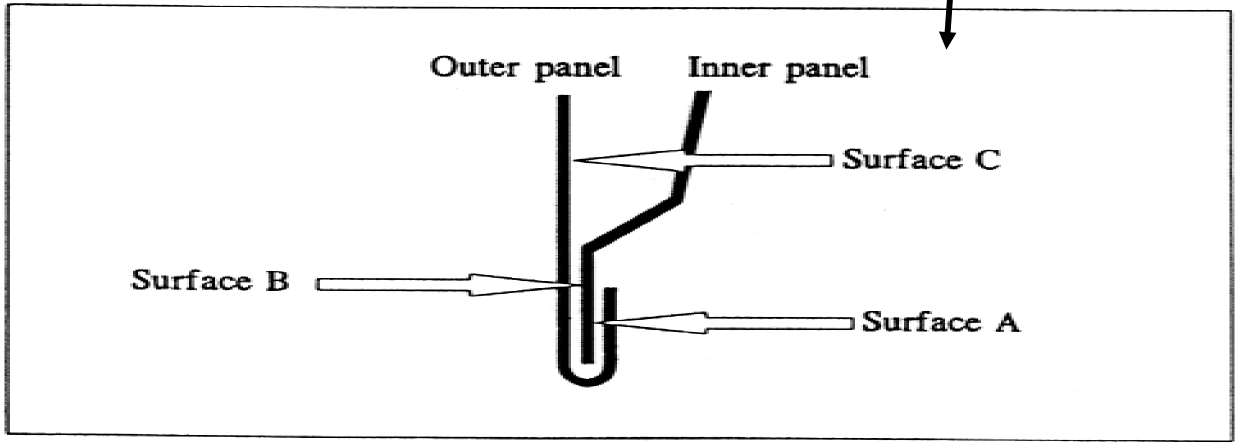
Outline of presentation

- The technical problem
- The corrosion problem and the chemistry
- Formulation of the processes
- Implementation into Comsol
  - Tricks
- Results
- Conclusions

The Technical Problem

- Zinc metal is widely used to protect steel from corrosion
- Galvanized steel is steel covered by a layer of zinc metal
- Zinc is expected to corrode before steel – galvanic protection
- Confined geometries; ’hem flanges’ seem particularly aggressive towards zinc
- Localized corrosion
  - Corrosion depends on local conditions
  - Corrosion changes local conditions

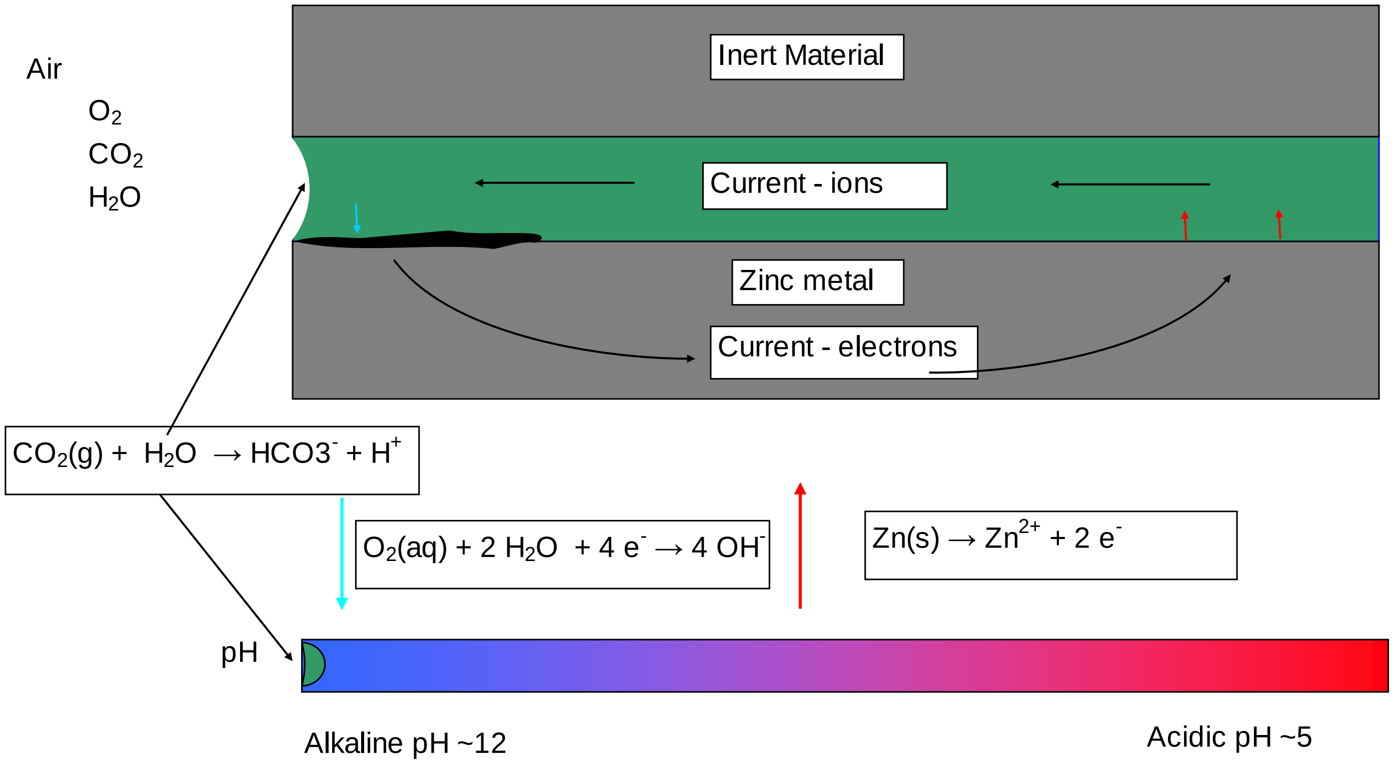
Technical Background-Example



Purpose of the modelling

- Provide a tool for the industry to predict corrosion and evaluate pretreatments
- Alternative/complement to laboratory and field testing
- Automotive industry and building industry
- (Paint industry – Delamination)
- Constant wetness and wet-dry cycles

The corrosion problem and the chemistry



Air

O_2

CO_2

H_2O

Inert Material

Current - ions

Zinc metal

Current - electrons

$CO_2(g) + H_2O \rightarrow HCO3^- + H^+$

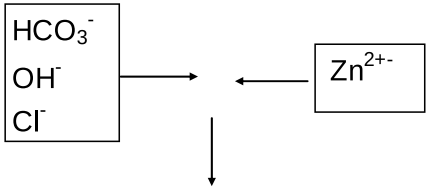
$O_2(aq) + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$

$Zn(s) \rightarrow Zn^{2+} + 2\ e^-$

pH

Alkaline pH ~12

Acidic pH ~5



HCO_3^-

OH^-

Cl^-

Zn^{2+-}

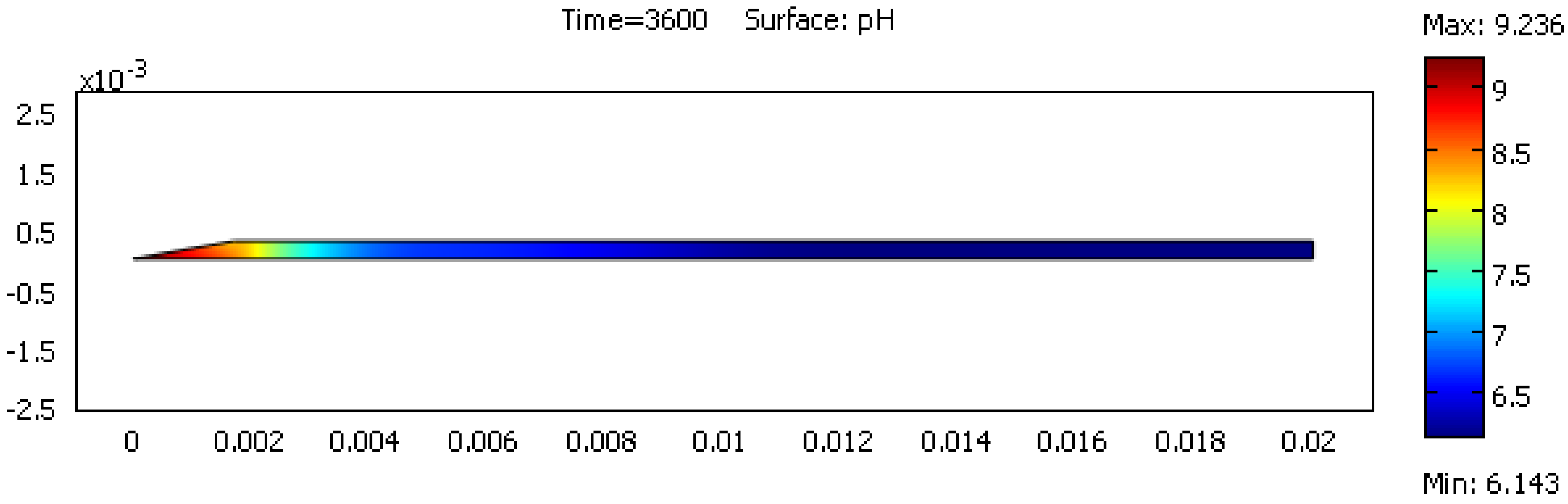
Precipitations at the zinc surface

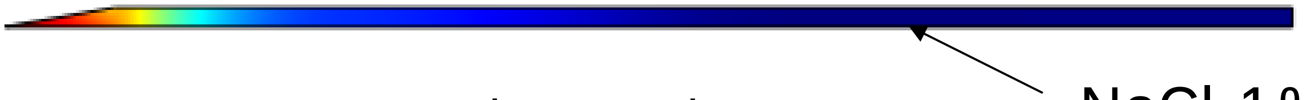
$Zn^{2+} + OH^- \rightarrow 2\ ZnO_2(s)$

$5\ Zn^{2+} + HCO_3^- + 9OH^- \rightarrow Zn_{5C}(CO_3)_2OH_6(s) + H_2O$

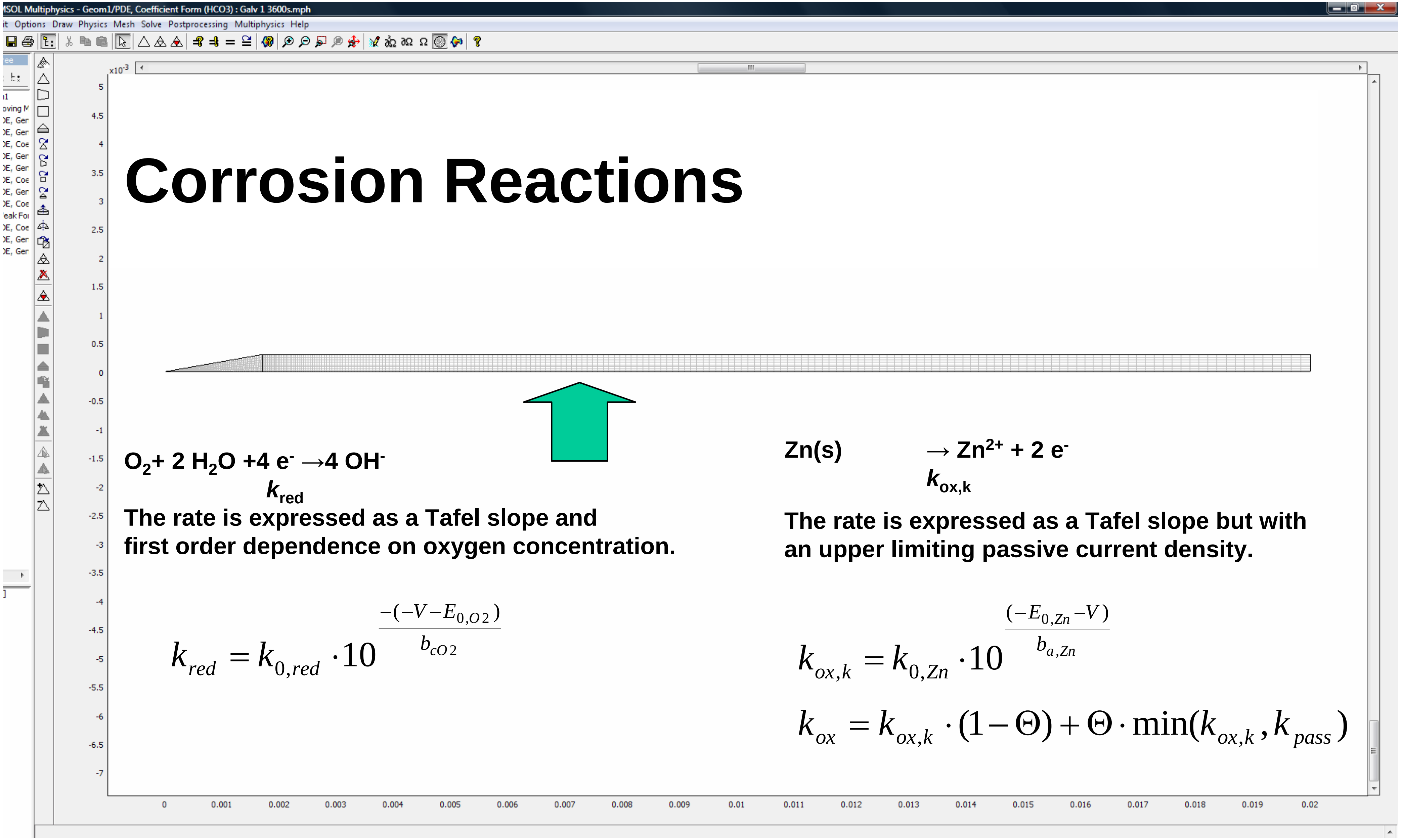
$5\ Zn^{2+} + 2\ Cl^- + 2OH^- \rightarrow Zn_5Cl_2OH_8(s)$

Zinc Corrosion in Confined Zones





- Air
  - O_2
  - CO_2
  - H_2O
- Inert
- Inert
- Zinc Metal
- NaCl 1%



Corrosion Reactions

$O_2 + 2\,H_2O + 4\,e^- \xrightarrow[k_{red}]{} 4\,OH^-$

The rate is expressed as a Tafel slope and first order dependence on oxygen concentration.

$$k_{red} = k_{0,red} \cdot 10^{\frac{-(-V - E_{0,O2})}{b_{cO2}}}$$

$Zn(s) \xrightarrow[k_{ox,k}]{} Zn^{2+} + 2\,e^-$

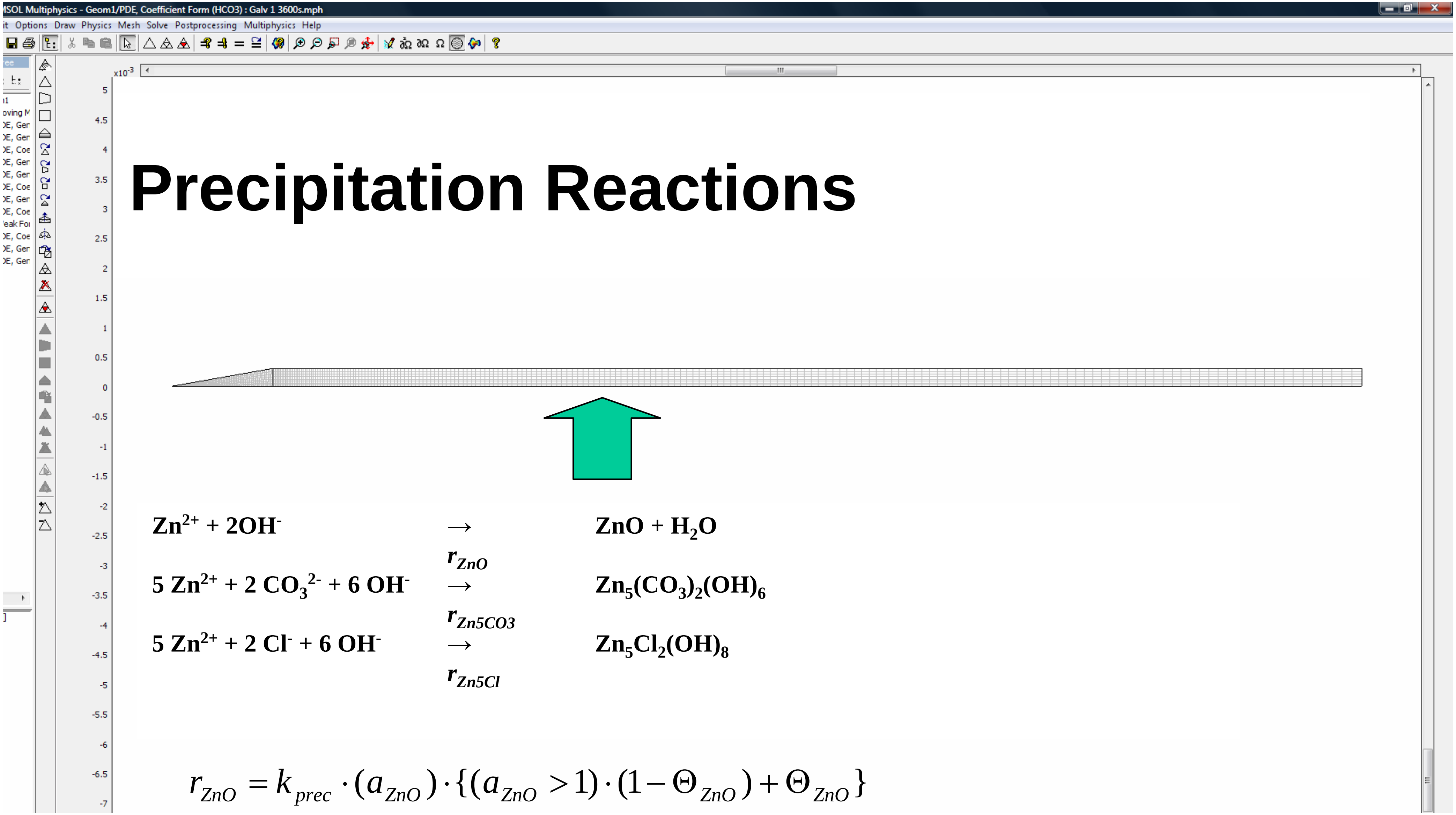
The rate is expressed as a Tafel slope but with an upper limiting passive current density.

$$k_{ox,k} = k_{0,Zn} \cdot 10^{\frac{(-E_{0,Zn} - V)}{b_{a,Zn}}}$$

$$k_{ox} = k_{ox,k} \cdot (1 - \Theta) + \Theta \cdot \min(k_{ox,k}, k_{pass})$$

Boundary condition for current: flow=$2*k_{ox}-4*k_{red}*cO_2$

Precipitation Reactions



$$Zn^{2+} + 2OH^- \xrightarrow{r_{ZnO}} ZnO + H_2O$$

$$5\ Zn^{2+} + 2\ CO_3^{2-} + 6\ OH^- \xrightarrow{r_{Zn5CO3}} Zn_5(CO_3)_2(OH)_6$$

$$5\ Zn^{2+} + 2\ Cl^- + 6\ OH^- \xrightarrow{r_{Zn5Cl}} Zn_5Cl_2(OH)_8$$

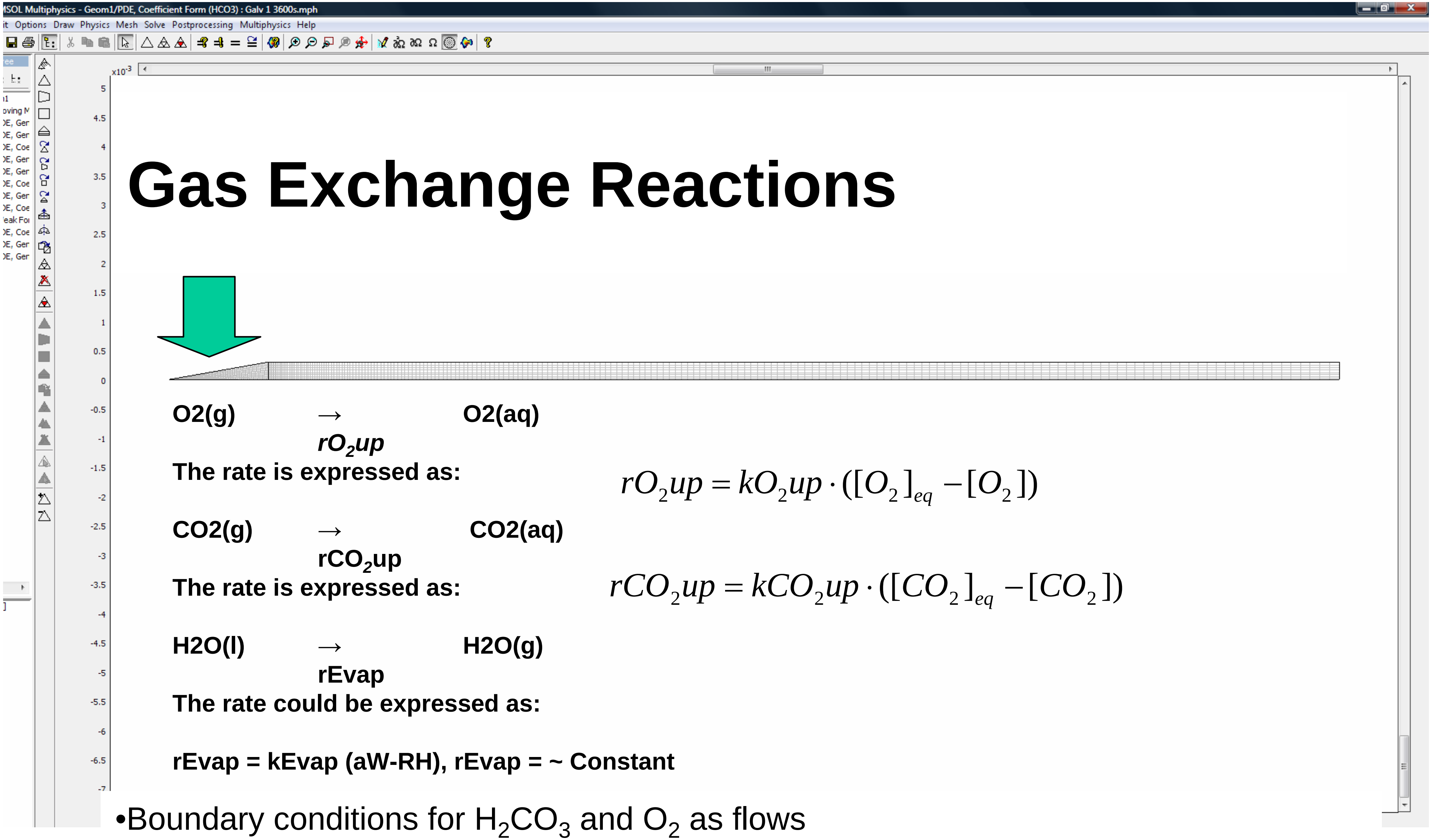
$$r_{ZnO} = k_{prec} \cdot (a_{ZnO}) \cdot \{(a_{ZnO} > 1) \cdot (1 - \Theta_{ZnO}) + \Theta_{ZnO}\}$$

$$r_{Zn5CO3} = k_{prec} \cdot (a_{Zn5CO3}^{1/5} - 1) \cdot \{(a_{Zn5CO3} > 1) \cdot (1 - \Theta_{Zn5CO3}) + \Theta_{Zn5CO3}\}$$

$$r_{Zn5Cl} = k_{prec} \cdot (a_{Zn5Cl}^{1/5} - 1) \cdot \{(a_{Zn5Cl} > 1) \cdot (1 - \Theta_{Zn5Cl}) + \Theta_{Zn5Cl}\}$$

Boundary condition for participating species as flows

Gas Exchange Reactions



O2(g) → O2(aq)

rO_2up

The rate is expressed as:

$$rO_2up = kO_2up \cdot ([O_2]_{eq} - [O_2])$$

CO2(g) → CO2(aq)

rCO_2up

The rate is expressed as:

$$rCO_2up = kCO_2up \cdot ([CO_2]_{eq} - [CO_2])$$

H2O(l) → H2O(g)

rEvap

The rate could be expressed as:

rEvap = kEvap (aW-RH), rEvap = ~ Constant

- Boundary conditions for H_2CO_3 and O_2 as flows
- Water is not included in the model! The geometry decreases and all concentrations increase as water evaporates. Nothing happens; no corrosion, at a dry surface.

Local Equilibrium-During mass tranport

- Reactions between dissolved species fast!
- Laws of conservation applied to groups of species e.g. Total carbonate,$cCO2T = [CO_3^{2-}]+[HCO_3^{-}]+[H_2CO_3]$

$$\frac{\partial cCO2T}{\partial t} + \nabla (j_{CO2T,x}, j_{CO2T,y}) = 0$$

$$\frac{\partial cCO2T}{\partial t} + \nabla (cCO2Tdx - \frac{F}{R \cdot T} cCO2Tmig \cdot Vx + u \cdot cCO2T,\ cCO2Tdy - \frac{F}{R \cdot T} cCO2Tmig \cdot Vy + v \cdot cCO2T) = 0$$

$$cCO2Tmig = -cHCO3 \cdot DHCO3 - 2 \cdot cCO3_x \cdot DCO3$$

$$cCO2Tdx = cHCO3_x \cdot DHCO3 + cH2CO3_x \cdot DH2CO3 + cCO3_x \cdot DCO3$$

- *cH=cHT+cOH+cZnOH+2*cZn(OH)2+3*Zn(OH)3+4*cZn(OH)4-cH2CO3+cCO3*
- *cHCO3=cCO2T-cH2CO3-cCO3*
- *cZn=cZnT-cZnOH-cZnOH2-cZnOH3-cZnOH4-cZnCl*
- *cCl=cClT-cZnCl*
- **These algebraic expressions are solved together with all transport equations!**

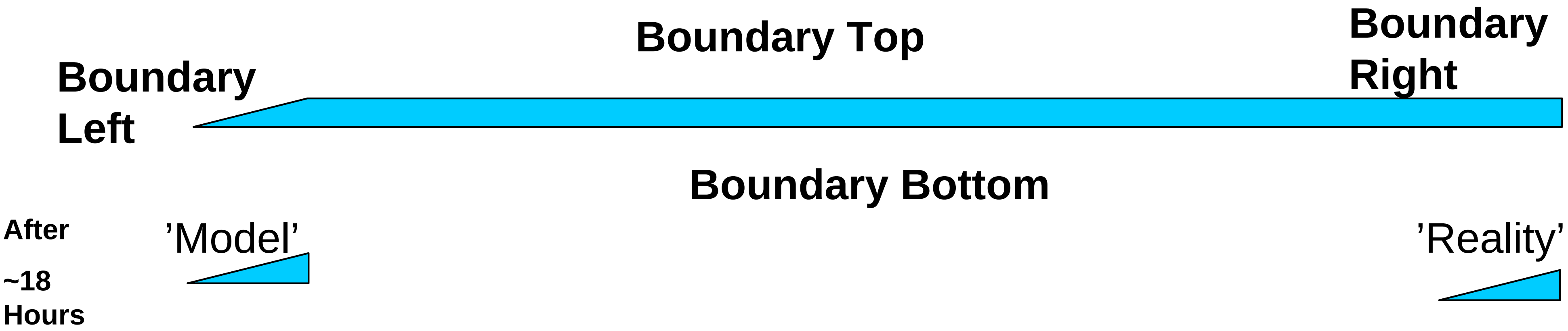
Summary of Equations as PDE:s

• **Moving Mesh(ALE)**	**-Ruling application**
• Nernst-Planck expression	-all charged species incl. Na^+
• Transport expression Total Zn^{2+}	-Zn^{2+}, $ZnOH^+$, $ZnOH_2$ $ZnOH_3^-$, $ZnOH_4^{2-}$, $ZnCl^+$
• Transport expression Total CO_3^{2-}	-H_2CO_3, HCO_3^-, CO_3^{2-}
• Transport expression Total Cl^-	-Cl^-, $ZnCl^+$
• Transport expression Total H^+	-H^+,OH^-,H_2CO_3,CO_3^{2-},$ZnOH^+$,$ZnOH_{2,}$$ZnOH_3^-$$ZnOH_4^{2-}$
• Algebraic expression Free Zn^{2+}	
• Algebraic expression Free CO_3^{2-}	
• Algebraic expression Free Cl^-	
• Algebraic expression Free H^+	
• Weak form, boundary	-Zn, ZnO, $Zn_5(CO_3)_2(OH)_6$, $Zn_5Cl_2OH_8$

Tricks

In reality: Boundary Left Moves to the RIGHT with evaporation

In the Model: Boundary Left is stationary, All other boundaries and the solution volume moves to the LEFT with evaporation



Boundary Top

Boundary Left

Boundary Right

Boundary Bottom

After

~18 Hours

’Model’

’Reality’

Purpose: Avoid ’Inverted Mesh’ ERROR

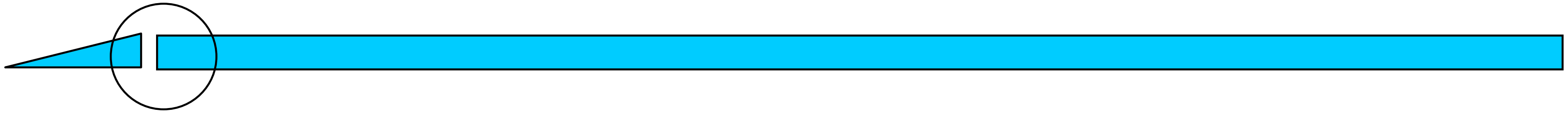
Fast processes at Boundary Left require fine mesh

’Inverted Mesh’ ERROR difficult to avoid at fine mesh

Coarse mesh at Boundary Right – No ’Inverted Mesh’ ERROR

Tricks

Two Domains – Only one deformed by Moving Mesh



No
Deformation

Deformed from the right

Number of Mesh elements reduced at intervals

-similar resolution at both domains within the circle

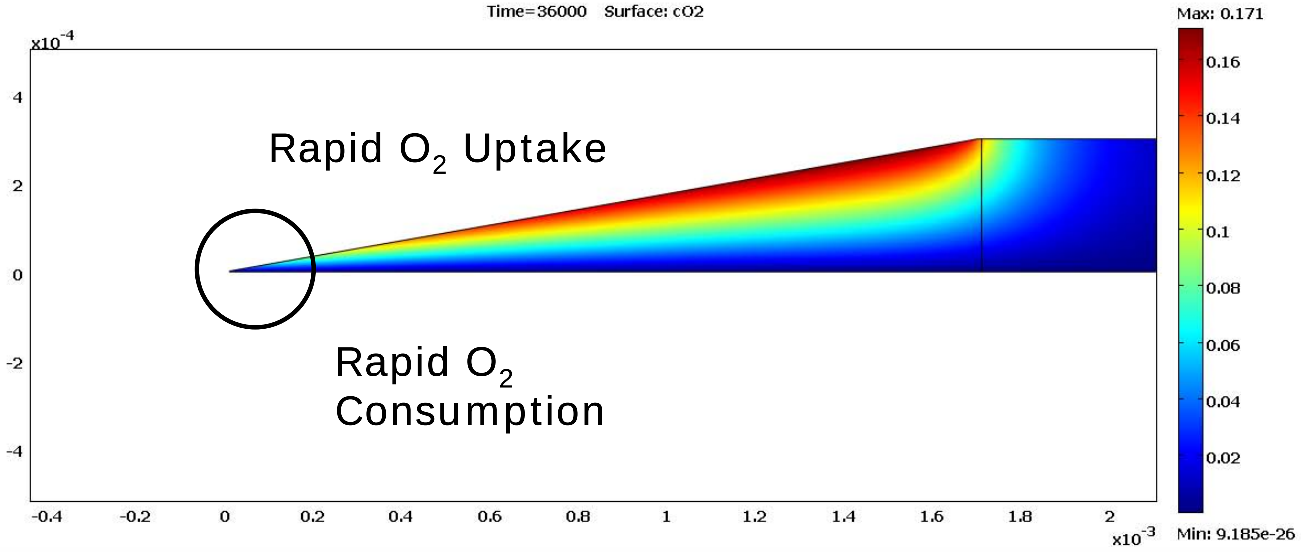
Several intervals of remeshing at increasing frequency before the right domain becomes insignificant in relation to the left domain.

Tricks

Problem:(?)

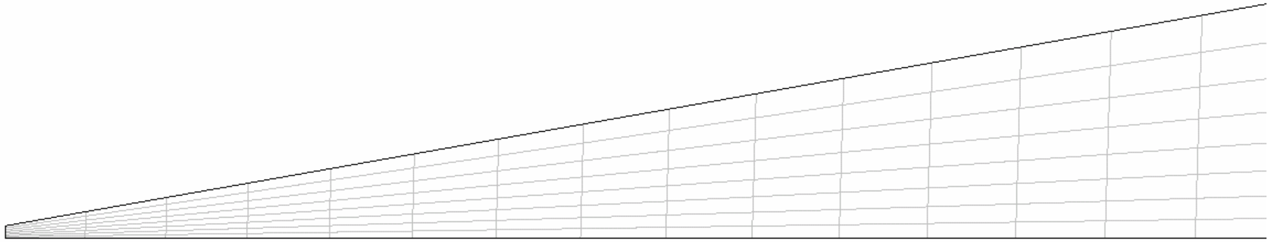
What happens at the point of the ’arrow’?

Resolution: Chop it off!



Rapid O_2 Uptake

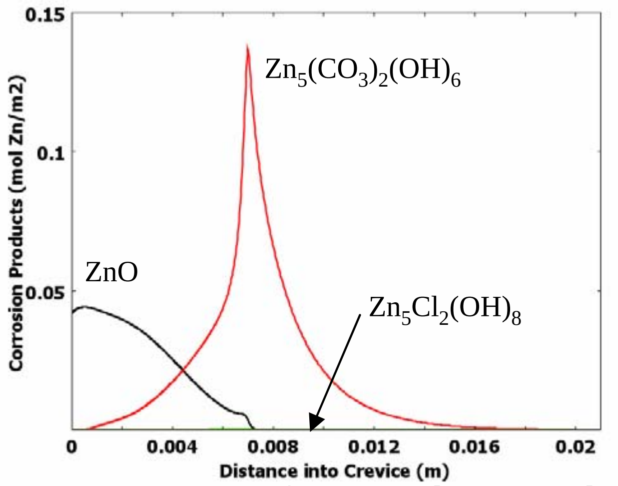
Rapid O_2 Consumption



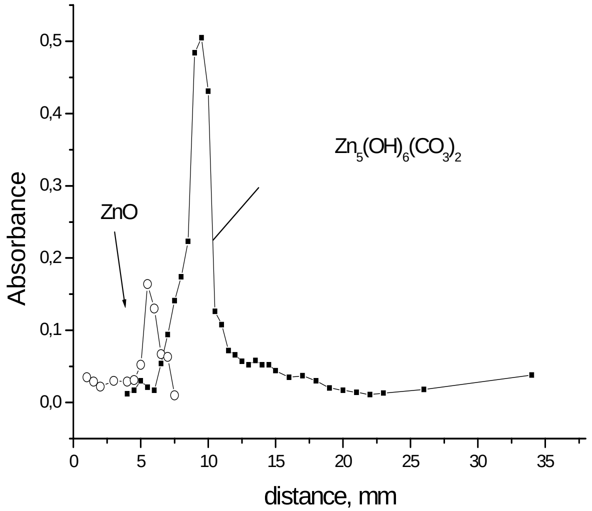
Rectangular mesh

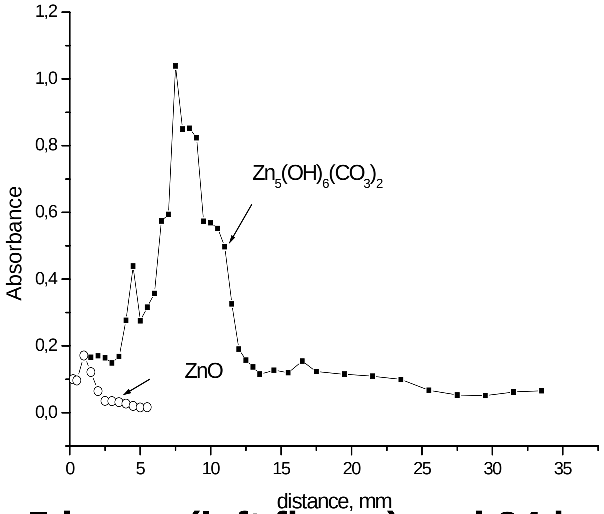
Results - Solid Corrosion Products – No Drying

Model results compared to experimental observations



Amounts of corrosion products after 20 hours exposure without drying.

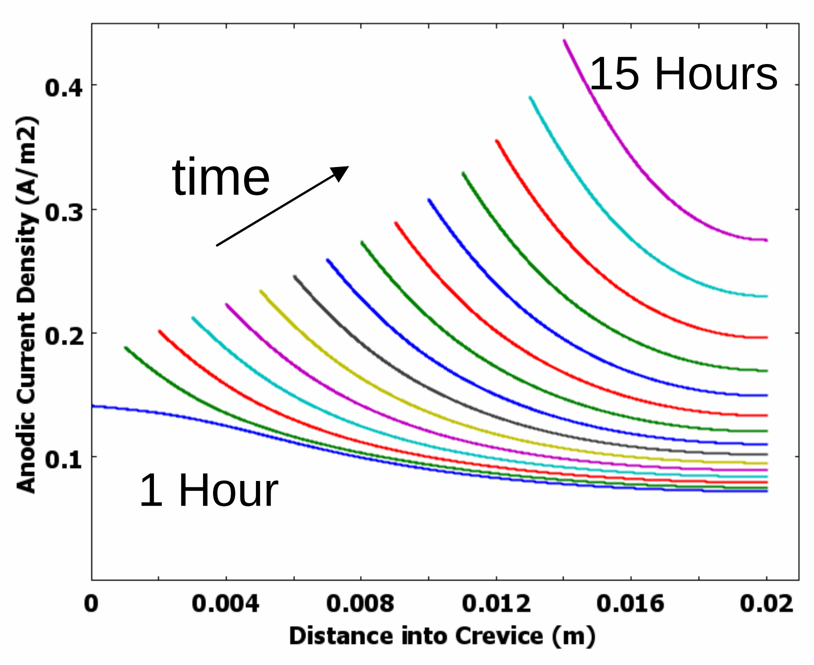




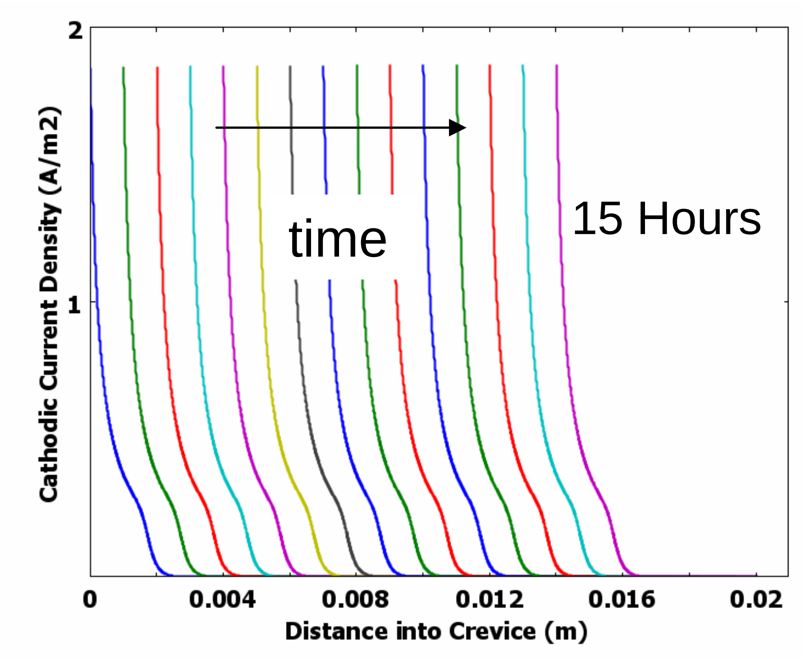
Distribution of corrosion products in crevice after 5 hours (left figure) and 24 hours (right figure) of exposure. 350 ppm CO2, 100 % RH (no drying). Gap height = 0.3 mm

Results – Current densities – Drying at 1mm/hour

Zinc oxidation



Oxygen reduction



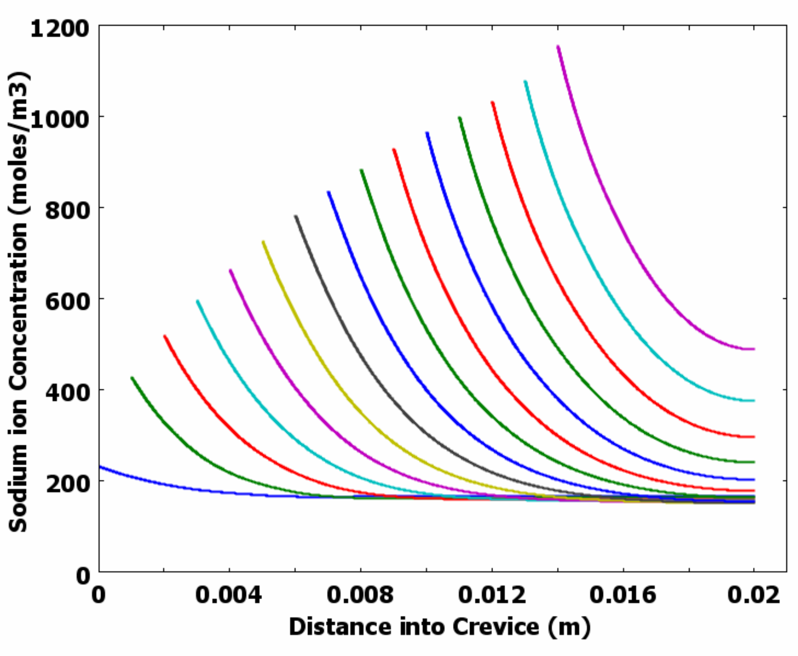
Zinc oxidation over the whole wet surface- highest at the left boundary

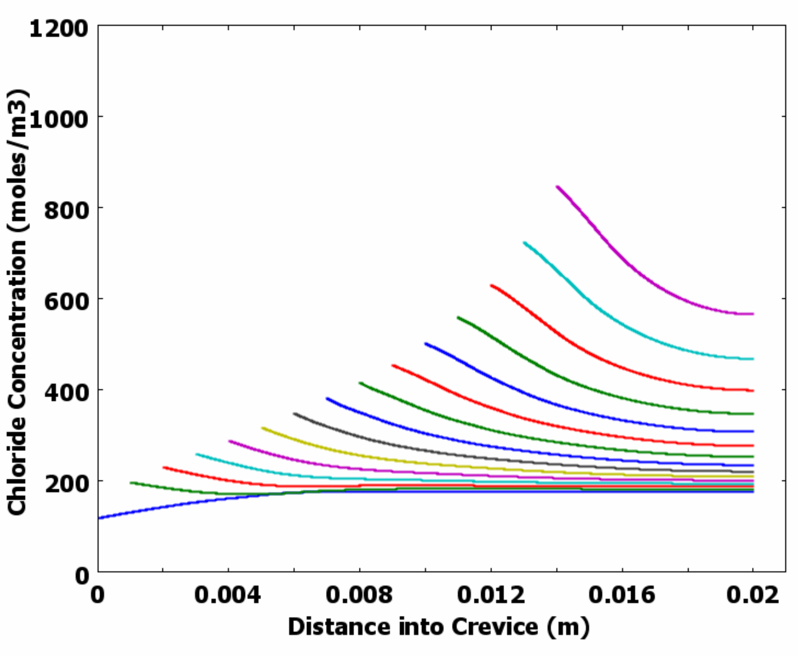
Oxygen reduction only close to the left boundary

Results – NaCl Concentrations – Drying at 1mm/hour

Sodium Concentration

Chloride Concentration

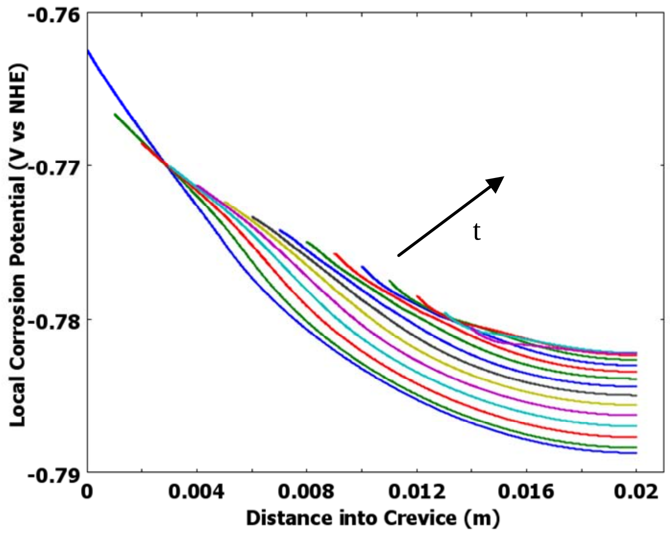




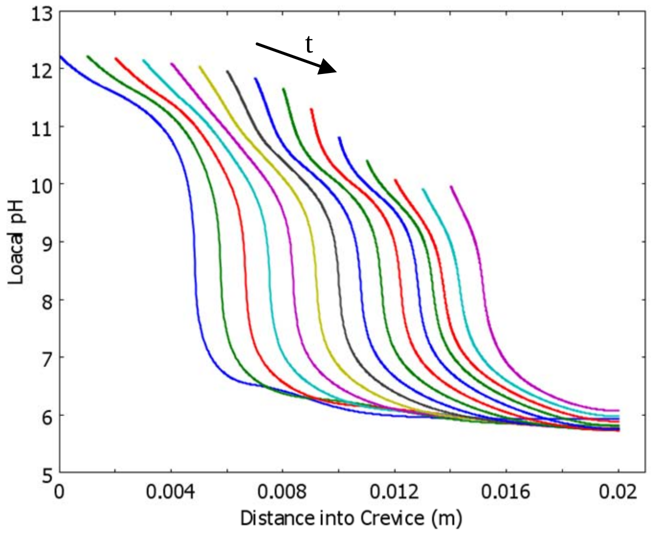
Cl^- initially depleted from the water/air interface, Na^+ enriched

Drying counters tendency to depletion, enhances enrichment

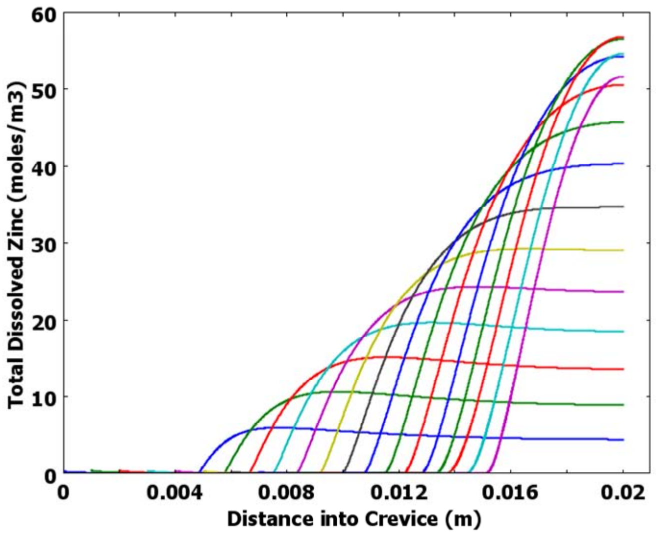
Results-Details



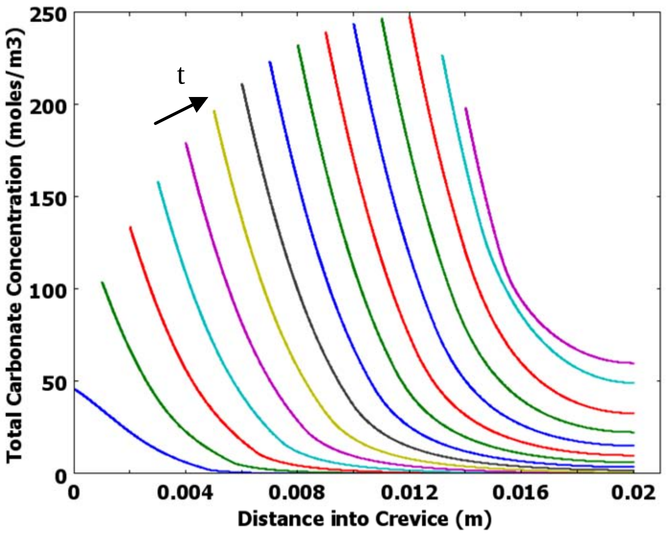
c. Local corrosion potential.



d. Local pH at the zinz surface.



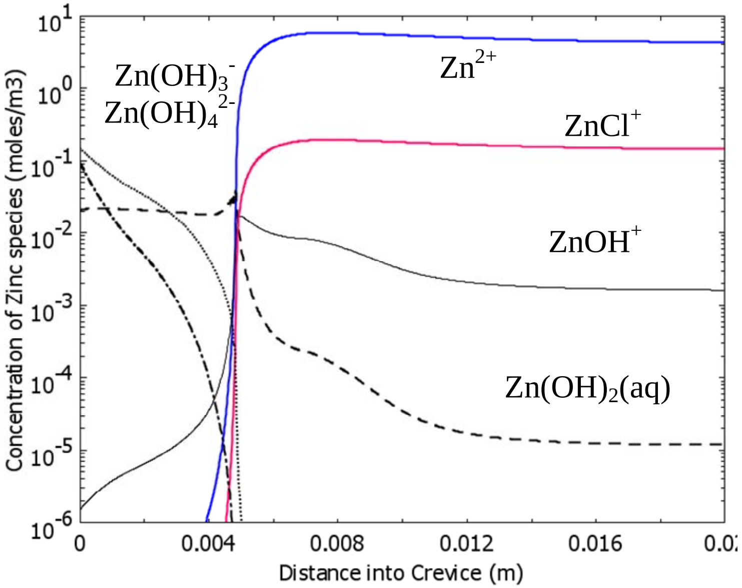
e. Total concentration of dissolved zinc at the surface.



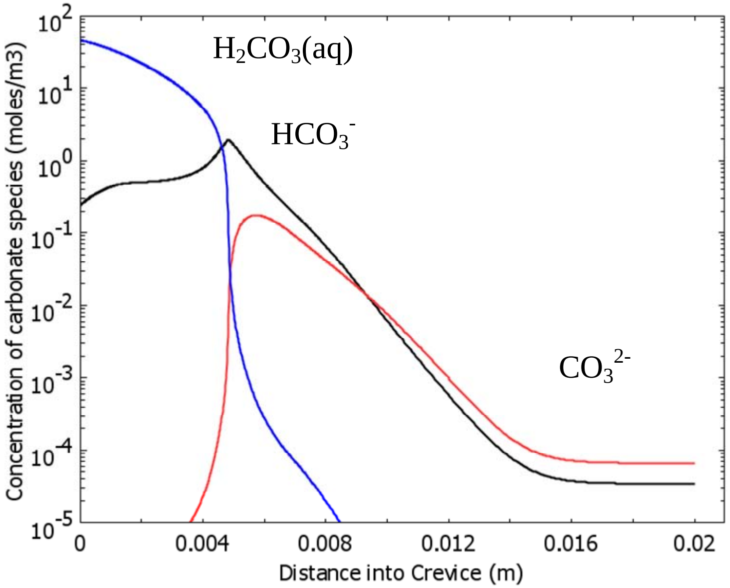
f. Total concentration of carbonate in the solution at the zinc surface.

Results - Dissolved Species

Concentrations of zinc and carbonate species after 1 hour exposure without evaporation. Data for the first cycle.



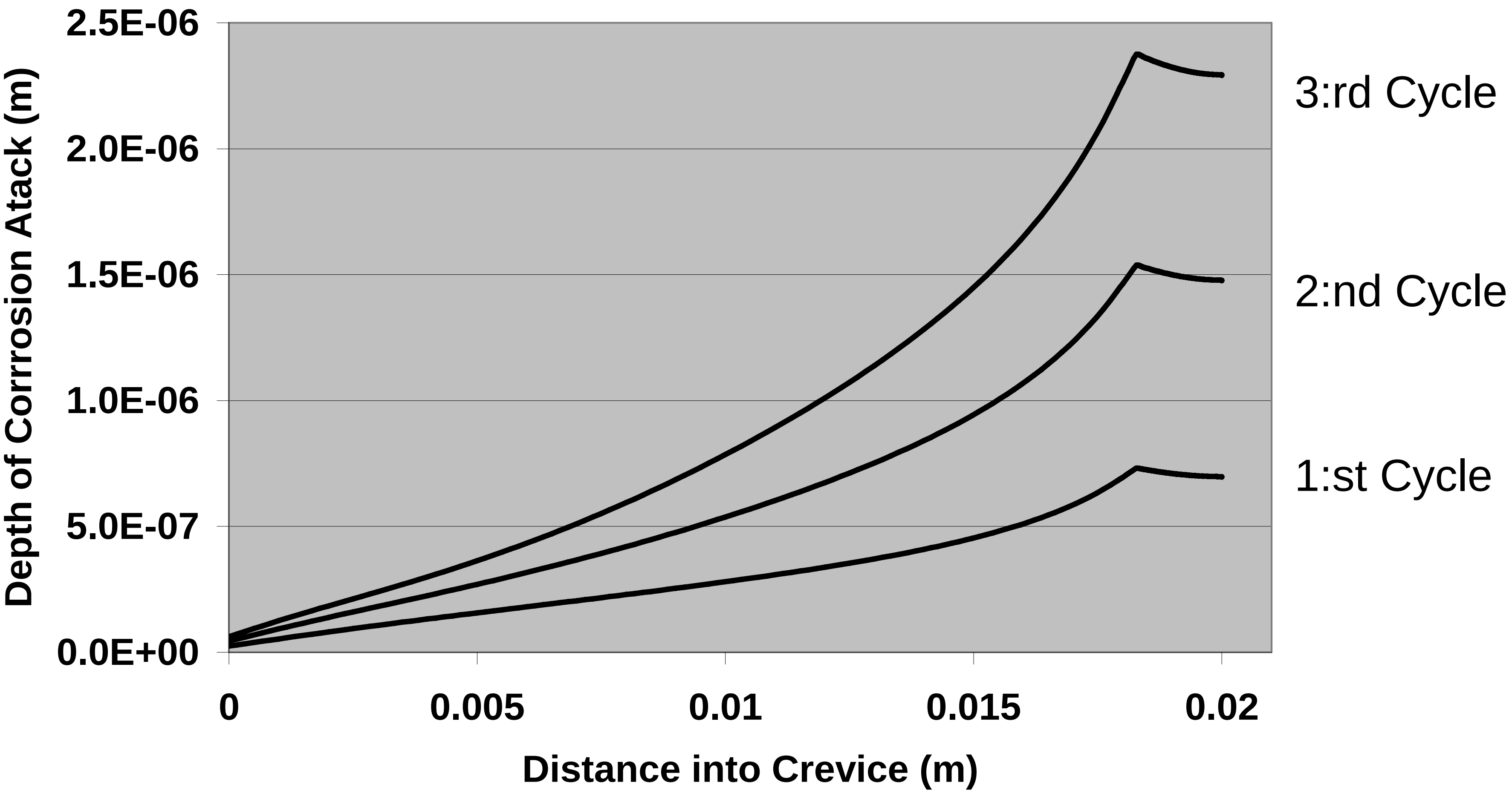
a. Concentration of zinc species



b. Concentration of carbonate species.

All aqueous species included are important for the aqueous chemistry! ($ZnOH^+$)

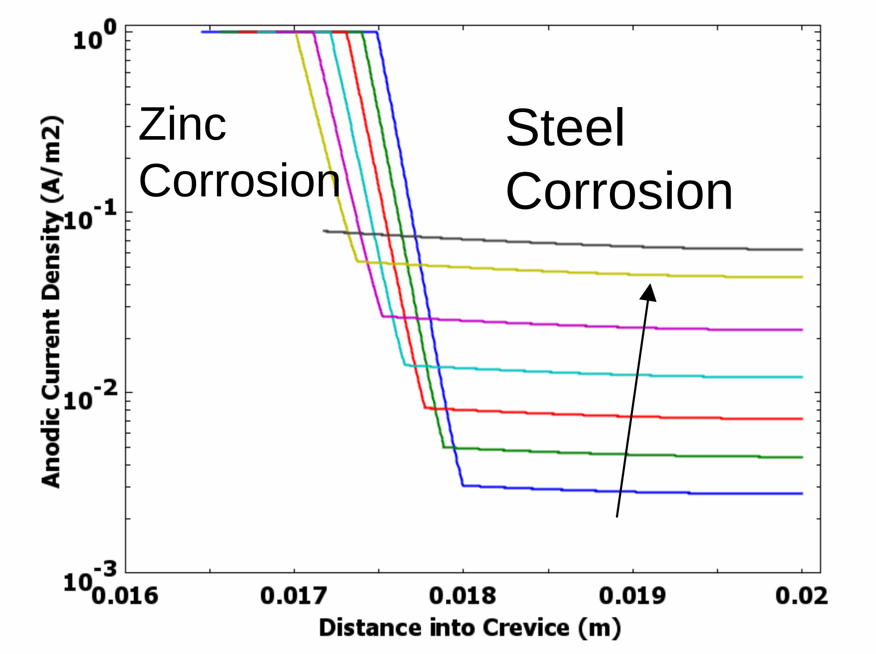
Results-Depth of the corrosion attack



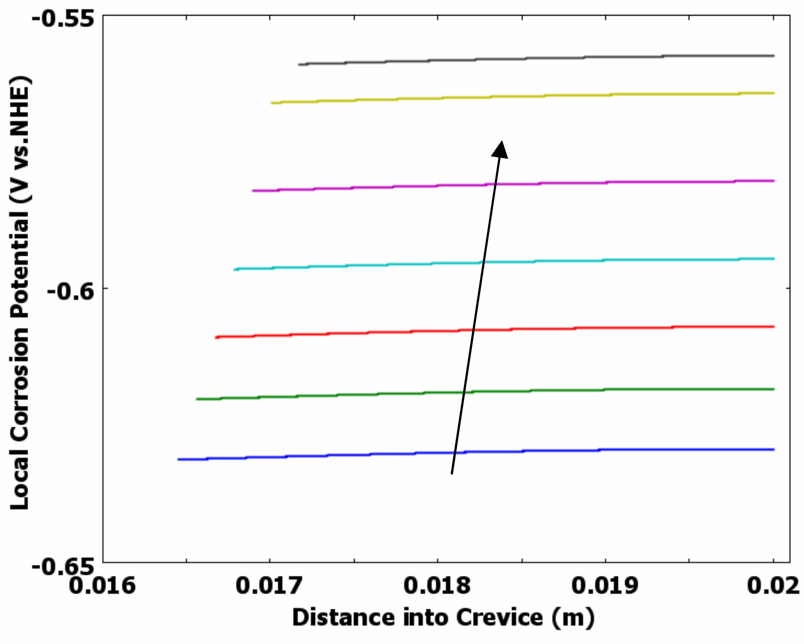
Results

Galvanic Protection of Exposed Steel: 2 μm Zinc layer, Penetration during the 3:wet-dry cycle

Corrosion currents



Corrosion potential



Galvanic protection of steel while electrolytic contact with Zinc!

Conclusions

- **Main conclusions**
- The corrosion of zinc and galvanized steel under the conditions studied is almost completely under cathodic control. **The supply of oxygen determines the corrosion rate.**
- The availability of **carbon dioxide** from the atmosphere has a big influence on the distribution of the **corrosion products** formed and on the local pH at the water/air interface. However, this seems to have a **small if any influence on the total corrosion rate**.
- With a certain geometry of the confined zone, similar to the geometry studied here, the **deepest corrosion attack is to be found deep into the crevice** when wet-dry cycles are applied. However, at constant wetness, the deepest corrosion attack is to be found at the mouth of the crevice.
- A certain zinc layer will last longer if the anodic dissolution is localised to a region close to the water/air interface when wet-dry cycles are applied. Thus **a low conductivity solution is more beneficial than a high conductivity solution for wet-dry cycles.**

Conclusions

- **Main conclusions(2)**
- During constant wetness, a certain zinc layer will last longer if the anodic dissolution is distributed over the whole metal surface in the crevice. Thus, a high conductivity solution is more beneficial than a low conductivity solution for constant wetness.
- Fe(III) formed when the zinc layer on galvanized steel is penetrated by corrosion does not seem to have any detrimental effects. In the solid forms, e.g. FeOOH(s) is likely to be too inert to behave as an oxidant for zinc. The solubility of Fe(III) is very low in the solutions formed in the confined zone so the concentration of dissolved Fe(III) will be too low to be of any significance compared with the direct effects of oxygen. Thus there are no thermodynamic grounds for a corrosive effect of so called Fe(II)/Fe(III) cycles under the conditions studied.
- The **results of the numerical model are in good agreement with the experimental results** concerning the general corrosion behaviour and the composition and distribution of corrosion products as well as the localization of the corrosion attack.

Conclusions

- **Other significant findings**
- Drying by evaporation causes loss of water from one side of the water volume. The salts, of course, remain in the solution. Thus, there is a **local concentrating effect at the sites of evaporation.** Evaporation builds up a concentration gradient that is only partly countered by diffusion. At the rates of evaporation studied here, diffusion rates can keep up with the concentrating effect of the evaporation but **significant gradients in NaCl**, which is the main salt in the solution, **arise**.
- As a consequence of the concentration gradient, **a diffusion potential arises**. Sodium and chloride ions have a tendency to diffusion at different rates so a diffusion potential arises so that the local solution maintains electro-neutrality.
- The magnitude of the diffusion potential displays a maximum at a drying stage approximately half way. Initially the concentration gradient is negligible and at the later stages of drying the solution is rather concentrated everywhere and only low diffusion potentials arise.
- The polarity of this diffusion potential is such that sites further into the crevice are becoming more anodic and more prone to anodic dissolution. The magnitude of the diffusion potential may be similar or higher than the iR-drop that results from the corrosion current.

Conclusions

- **Other significant findings(2)**
- The uptake of carbon dioxide from the atmosphere seems to proceed with a limited rate. The rate limitation could by kinetic or it could be mass transport limited, by gas phase diffusion. Experiments show pH values higher than pH 10 at the mouth of the crevice. Equilibrium with CO_2(g) from the air would establish a much lower pH.
- Model studies with facile kinetics of CO_2 uptake reveals $Zn_5(CO_3)_2(OH)6$ as the main solid corrosion product. Na_2CO_3 is not formed and neither is $Zn_5Cl_2(OH)_8$ although both may be found experimentally.
- Only at low rates of CO_2 uptake does the pH at the mouth of the crevice exceed pH 10. Paradoxically, a low rate of CO_2 uptake is a prerequisite for the formation of Na_2CO_3. If the pH is too low, almost all carbonate in the solution is present as HCO3- and eventually ends up in $Zn_5(CO_3)_2(OH)_6$. Only at the lower rates of uptake is the pH so high that a significant fraction of the aqueous carbonate is present as CO_3^{2-} and Na_2CO_3 can form

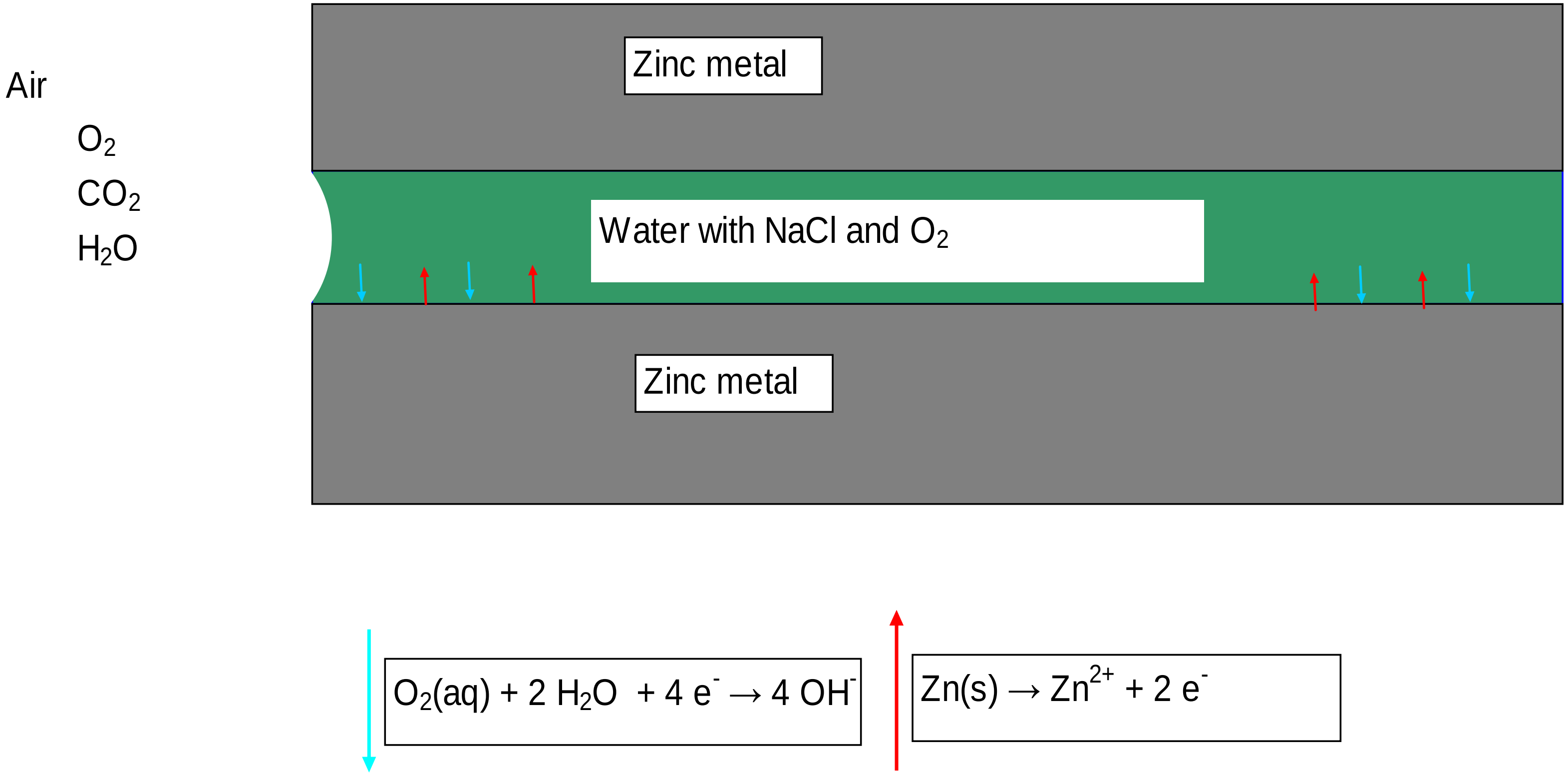
Extras

Modelling Zinc Corrosion in Confined Zones

Contents

- Confined zone
- Qualitative description
- Zinc - Zn^{2+}, equilibrium properties
  - Diagram aq/s
  - Distribution diagram- Baes Mesmer
- Zinc corrosion, Kinetic parameters
  - Zinc dissolution
  - Oxygen reduction
  - Precipitation kinetics
- Preliminary results
- Calibration/Verification

Confined zone (1)



Air

O_2

CO_2

H_2O

Zinc metal

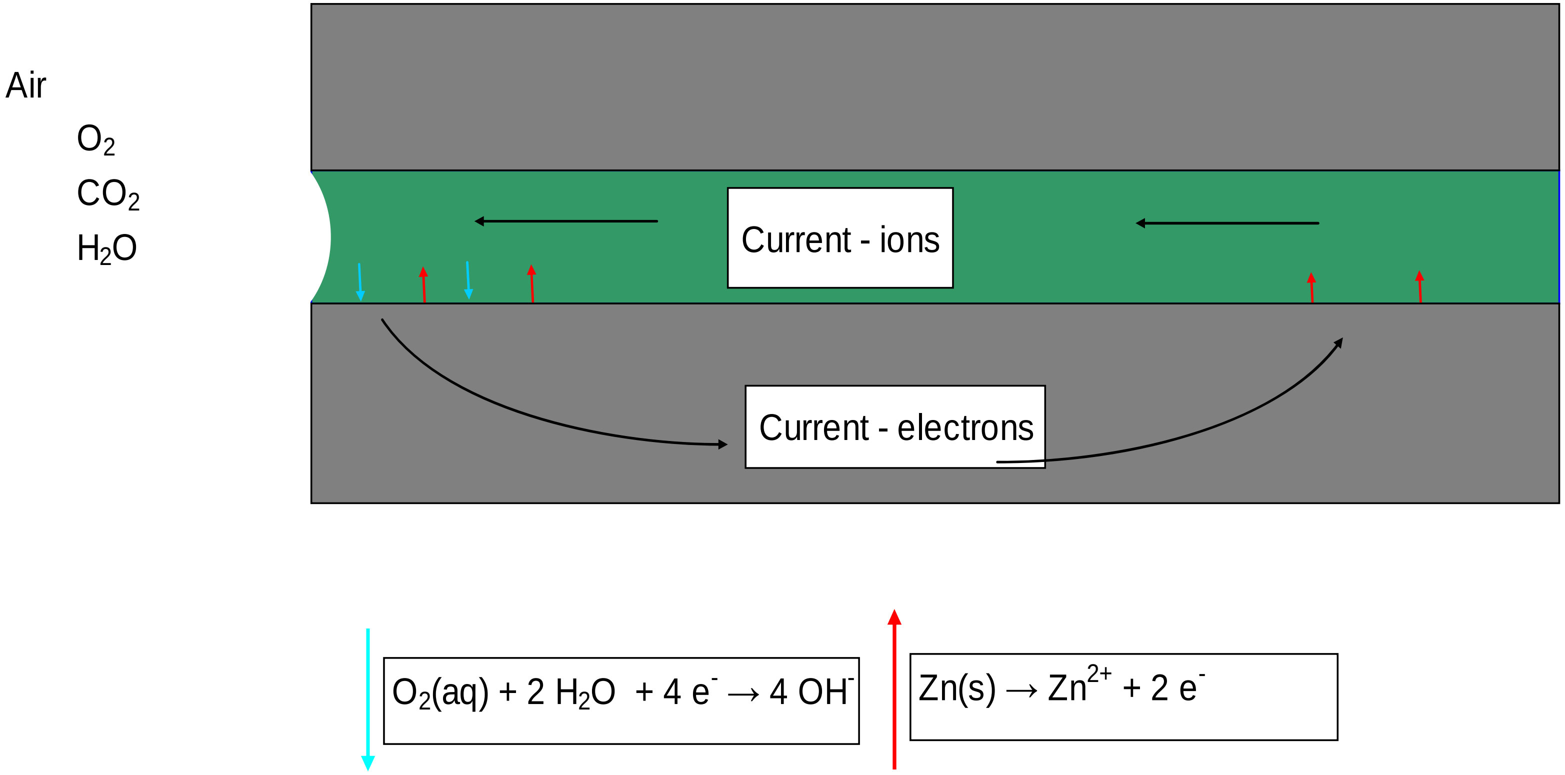
Water with NaCl and O_2

Zinc metal

$O_2(aq) + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^-$

$Zn(s) \rightarrow Zn^{2+} + 2\,e^-$

Confined zone (2)

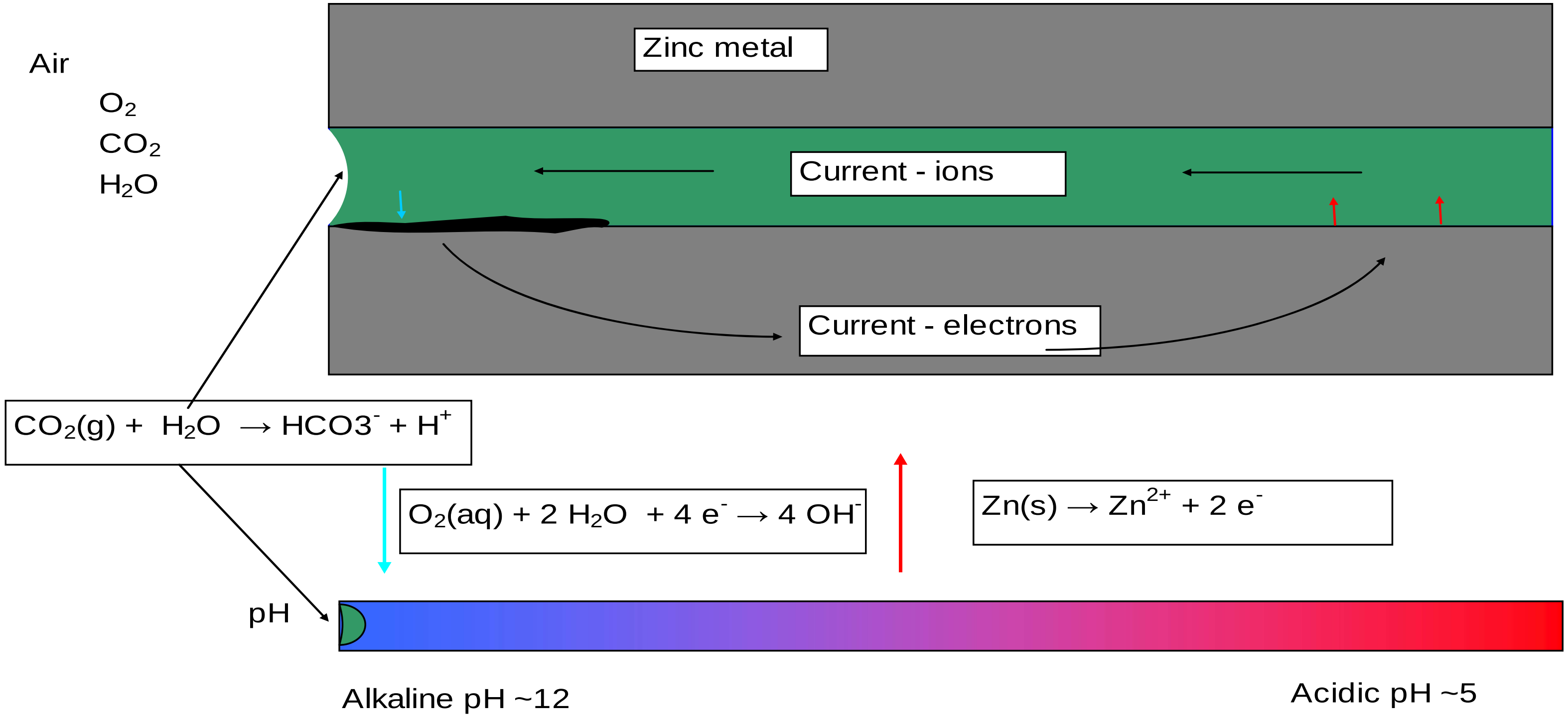


$O_2(aq) + 2\ H_2O\ + 4\ e^- \rightarrow 4\ OH^-$

$Zn(s) \rightarrow Zn^{2+} + 2\ e^-$

Differential aeration cell

Confined zone (3)



Air

O_2

CO_2

H_2O

Zinc metal

Current - ions

Current - electrons

$CO_2(g) + H_2O \rightarrow HCO3^- + H^+$

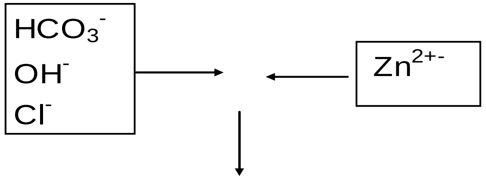
$O_2(aq) + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$

$Zn(s) \rightarrow Zn^{2+} + 2\ e^-$

pH

Alkaline pH ~12

Acidic pH ~5



HCO_3^-

OH^-

Cl^-

Zn^{2+-}

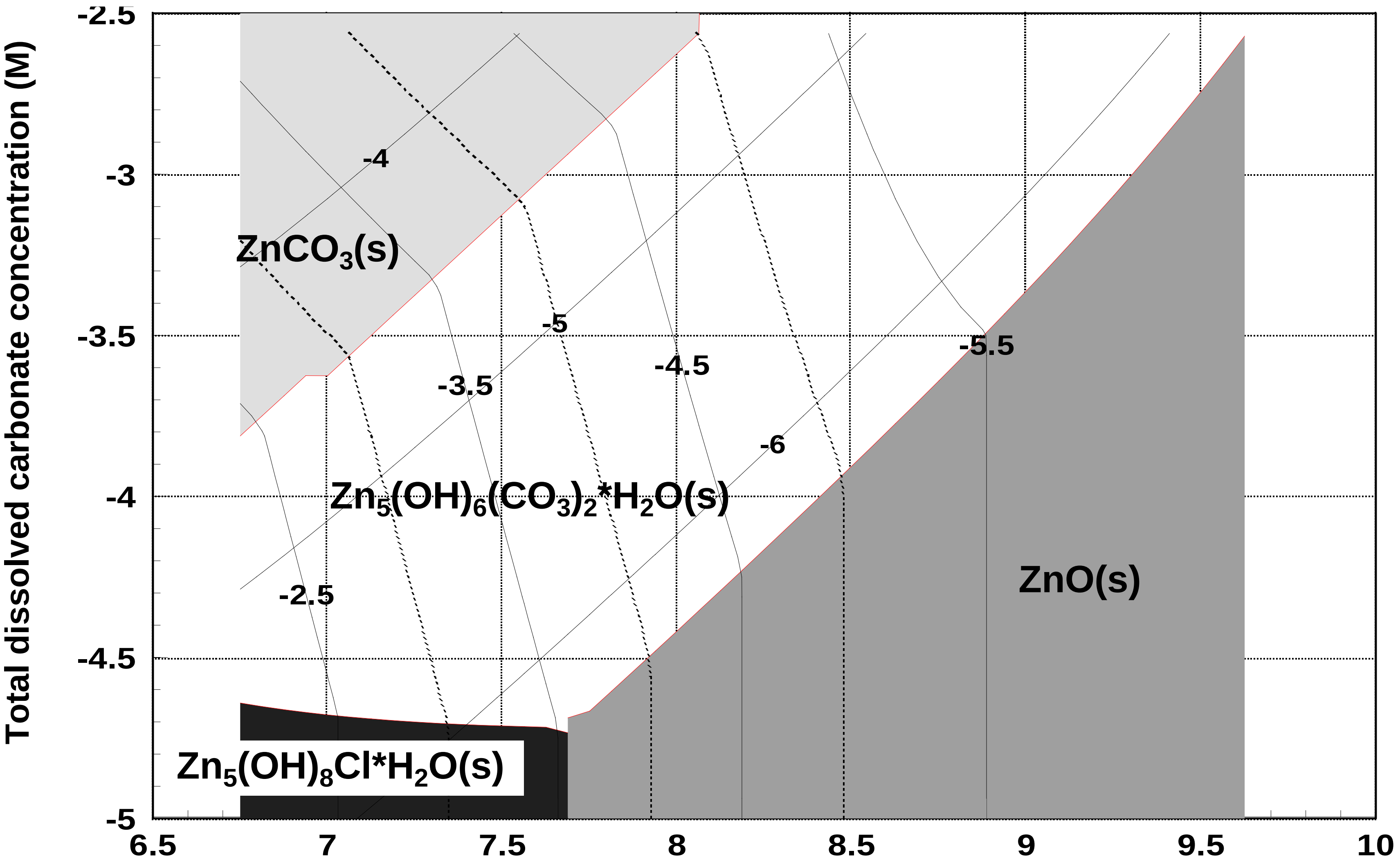
Precipitations at the zinc surface

$Zn^{2+} + OH^- \rightarrow 2\ ZnO_2(s)$

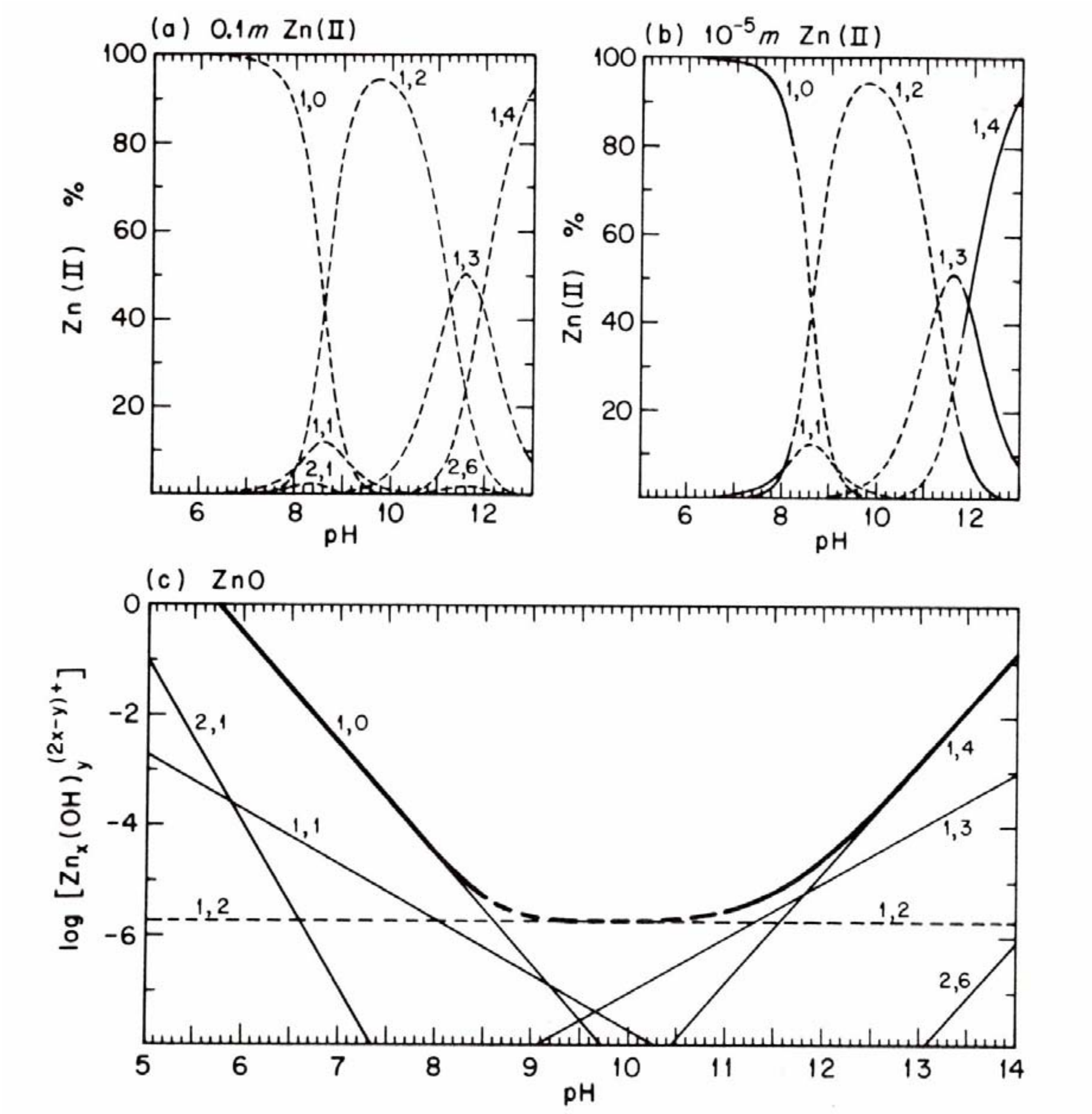
$5\ Zn^{2+} + HCO_3^- + 9OH^- \rightarrow Zn_5CO_3OH_8(s) + H_2O$

$5\ Zn^{2+} + 2\ Cl^- + 2OH^- \rightarrow Zn_5Cl_2OH_8(s)$

Zinc(II)-Equilibrium Properties(1) 0.5M NaCl



Zinc(II)-Equilibrium Properties(2)



Baes&Mesmer:*'The Hydrolysis of Cations'*

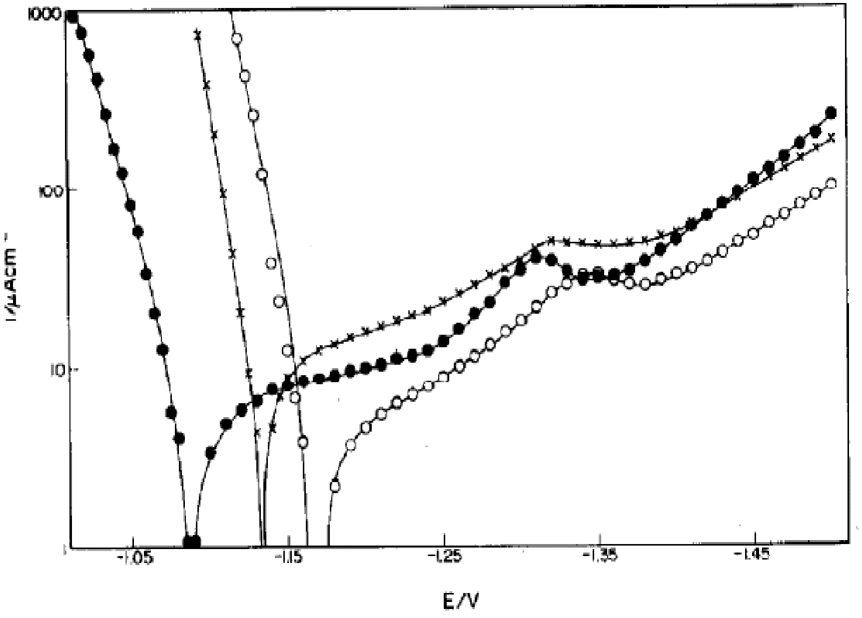
pH>8.75: $[Zn(OH)_2(aq)]>[Zn^{2+}]$

pH>11.2 :$[Zn(OH)_3^-]>[Zn(OH)_2aq]$

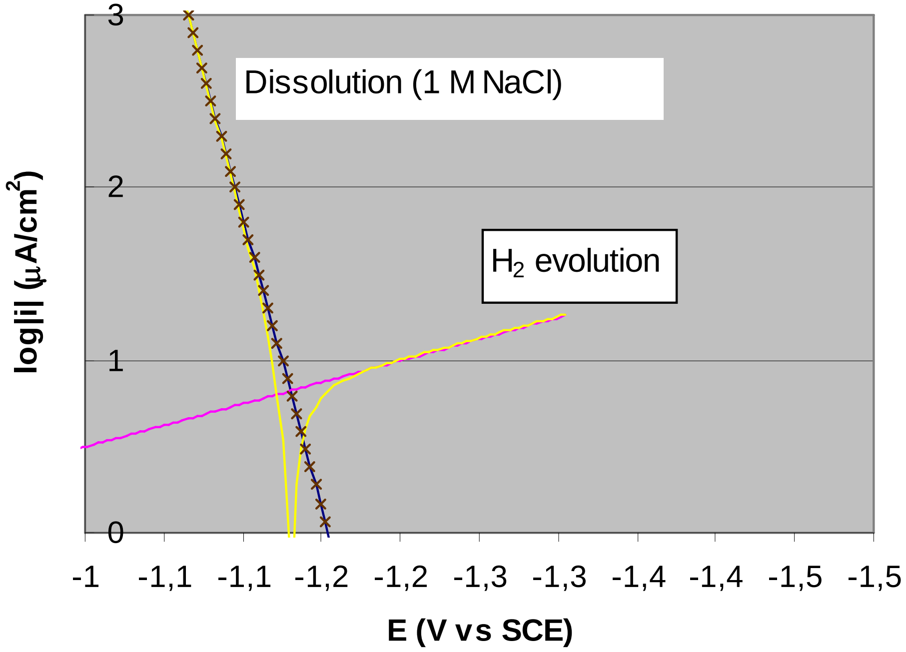
The chemical system

	lg k		H+	Cl-	CO2(aq)	Zn2+	Na+	
H+		1	1	0	0	0	0	
Cl-		-1	0	1	0	0	0	
CO2(aq)		0	0	0	1	0	0	
Zn2+		2	0	0	0	1	0	
Na+		1	0	0	0	0	1	
OH-	-14,00	-1	-1	0	0	0	0	
NaOH(aq)	-14,22	0	-1	0	0	0	1	Neglected
NaCl(aq)	-0,78	0	0	1	0	0	1	Neglected
CO32-	-16,68	-2	-2	0	1	0	0	
HCO3-	-6,35	-1	-1	0	1	0	0	
NaCO3-	-16,14	-1	-2	0	1	0	1	Neglected
NaHCO3(aq)	-6,52	0	-1	0	1	0	1	Neglected
ZnOH+	-8,96	1	-1	0	0	1	0	
Zn(OH)2(aq)	-16,90	0	-2	0	0	1	0	
Zn(OH)3-	-28,40	-1	-3	0	0	1	0	
Zn(OH)4-2	-41,20	-2	-4	0	0	1	0	
ZnCl+	-0,19	1	0	1	0	1	0	
ZnCl2(aq)	0,18	0	0	2	0	1	0	Neglected
ZnCl3-	-1,40	-1	0	3	0	1	0	Neglected
ZnCl4-2	-1,52	-2	0	4	0	1	0	Neglected
Zn2(OH)+3	-9,00	3	-1	0	0	2	0	Neglected
Zn2(OH)6-2	-57,80	-2	-6	0	0	2	0	Neglected
Zn5(OH)6(CO3)2*H2	-43,10	0	-10	0	2	5	0	
Zn5(OH)8Cl2*H2O	-39,35	0	-8	2	0	5	0	
Zn5(OH)9Cl*H2O	-47,65	0	-9	1	0	5	0	Neglected
ZnO(s)	-11,14	0	-2	0	0	1	0	
ZnCl2(s)	-7,05	0	0	2	0	1	0	Neglected
ZnCO3(s)	-5,89	0	-2	0	1	1	0	Neglected

Zinc corrosion, Kinetic parameters - Zinc dissolution



. Effect of anions on the polarization curves for zinc in molar solutions at pH 5.8, (●) $NaClO_4$, (○) Na_2SO_4, (×) NaCl.



L. M. Baugh

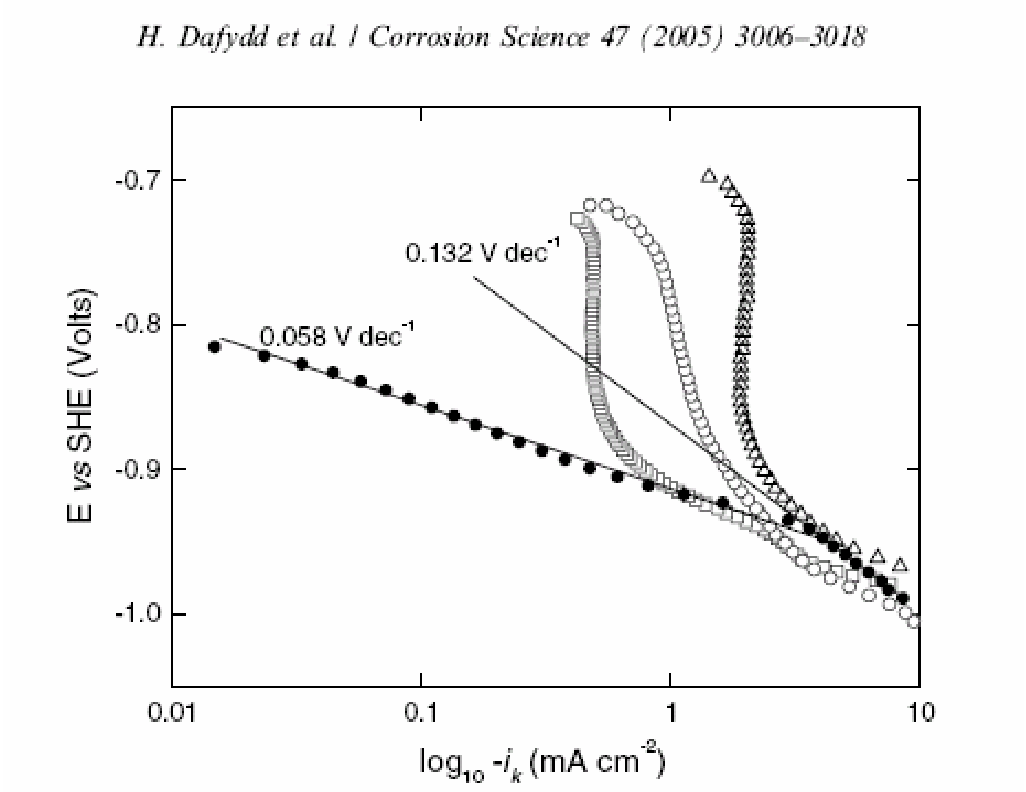
Corrosion and polarization characteristics of zinc in neutral-acid media - I. Pure zinc in solutions of various sodium salts

Electrochim Acta. Vol. 24, pp. 657-467.(1979)

i_0=20+[Cl-]*1000 (A/m^2) konc in M

(E_0=-763 mV vs. NHE)

Zinc corrosion, Kinetic parameters – O_2 reduction



$i=i_0*10$^$(-(E-E_0)/bc)$
E_0=-0,8 V(SCE),
i_0= 0.01 mA/cm^2
E_0=-0,558 V(NHE),
i_0= 0.1 A/m^2

In 0.86 M NaCl [O_2] eq~0.203 mole/m^3.
i_0= 4*F*k0*cO_2 yields
k_0=1.276E-6 m/s

Tafel plots of kinetic current density (ik) for cathodic O_2 reduction in aerated 0.86 MNaCl at pH 9.6 calculated from anodic-going polarization curves at ω = 320 rad/s. **Filled symbol:Zinc**, open symbols: zinc alloys

H. Dafydd, D.A. Worsle and H.N. McMurray. The kinetics and mechanism of cathodic oxygen reduction on zinc and zinc–aluminium alloy galvanized coatings. Corr. Sci. 47 (2005) 3006–3018

Zinc corrosion - passivation

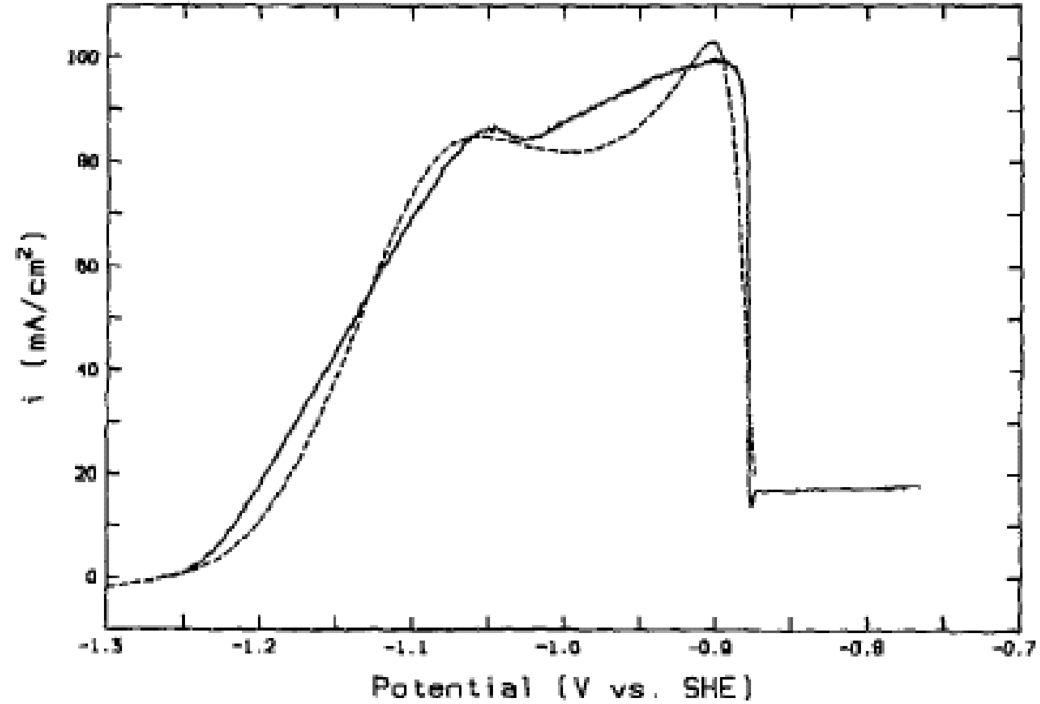


Fig. 1. Current density vs. potential for a zinc electrode in alkaline electrolyte. Base case conditions are specified in Table II. Solid line represents experimental values and dashed line is simulated result.

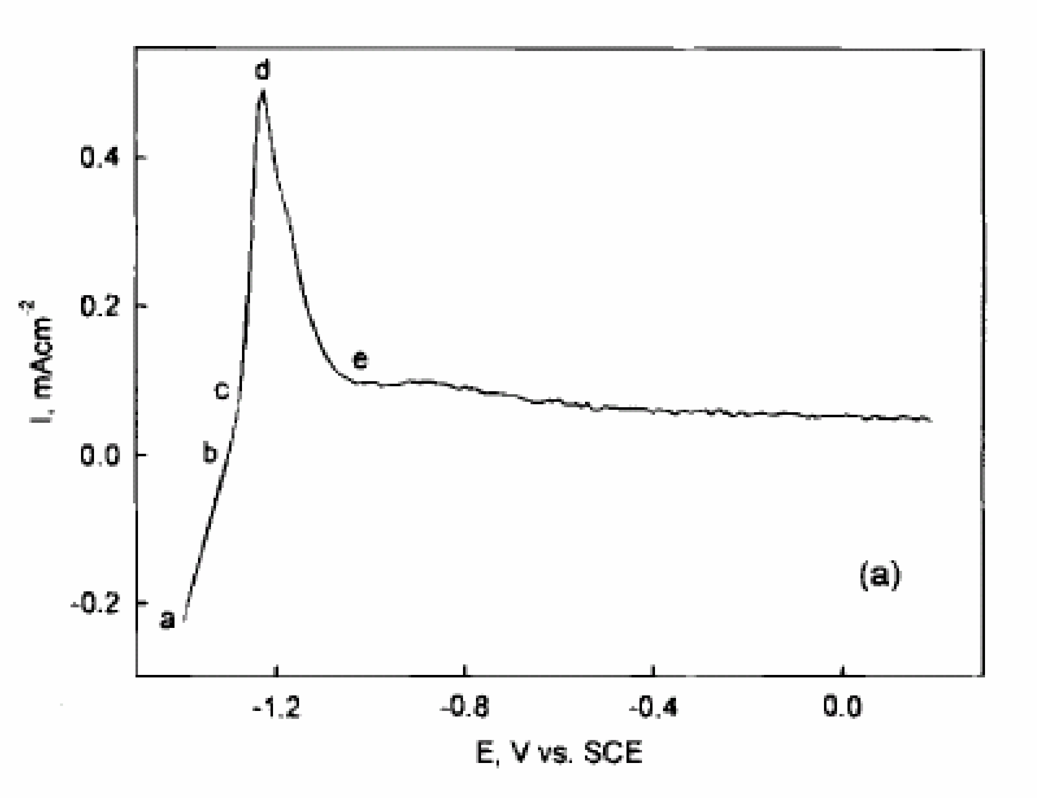
pH 14

Ipass ~20 mA/cm^2

Geoffrey Prentice, Yu-Chi Chang, and Xuning Shah. A Model for the Passivation of the Zinc_Electrode in Alkaline Electrolyte

J. Electrochem. Soc., VoL 138, No. 4, April 1991 p 890

Zinc corrosion - passivation



pH 10.5

Ipass ~0.1mA/cm^2

Anodic polarization curve for zinc quiescent 0.1 M sodium borate/1.0 M sodium hydroxide (pH 10.5) solution at 22 1°C. Sweep rate 10 mV/s.

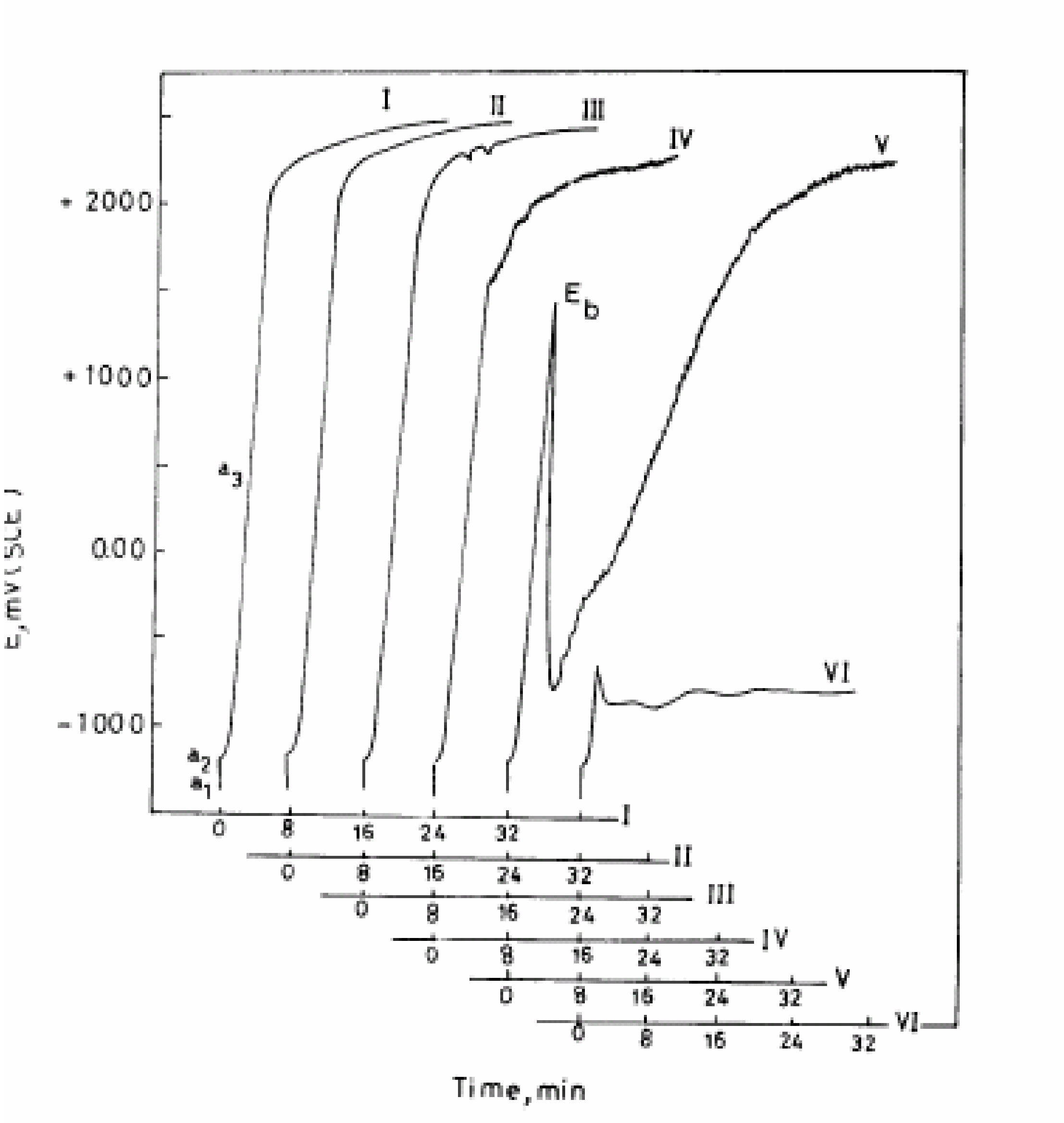
Digby D. Macdonald, Khaled M. Ismail, and Elzbieta Sikora. Characterization of the Passive State on Zinc J. Electrochern. Soc., Vol. 145, No. 9, September 1998 p.3141

Zinc corrosion - passivation

pH 9.2

Ipass ~0.07 mA/cm^2

Dep on [Cl$^-$]



Anodic polarization curves for zinc electrode in .05 Na2B4O7 at a current density 70 µA/ cm^2, in the absence and presence of various NaCl concentrations: (I) 0.0, (II) .001 M, (III) .002M, (IV) .0028M, (V) .003 and (VI) .005 M.

E.E. Abd El Aal. Effect of Cl- anions on zinc passivity in borate solution. Corr. Sci. 42 (2000) pp. 1-16

Zinc Corrosion- Passivity

- Passivity also by precipitated solids
- Passivity depends on amounts of solids on the surface
- A few monolayers gives some degree of passivity
  - (Kannagara & Conway)
- Relatively high passive currents ~100μA/cm^2
- $i = i_{act} * (1-\theta) + i_{pass} * \theta$
- I_{act} from Butler-Volmer equation
- θ approaches unity assymptotically with increasing amounts of corrosion products

$\Theta = 1 - \exp(-M_{solids}/(N_{monolayers} * M_{monolayer})$

Conditions-summary

- Troublesome geometry – long and thin
- Large aqueous equilibrium system
  - Diffusion and migration
- Fairly complicated corrosion reactions
  - Active-passive transition
  - Oxygen reduction distributed after [O_2] and local potential
  - Dissolution reaction distributed after local potential, zinc ion concentration and surface coverage

Comsol Multiphysics

- Diffusion in equilbrium systems OK
- Migration of charged species with electroneutrality OK
- BUT NOT THE TWO TOGETHER
  - Export from REL to Comsol Electrokinetic flow mode sticks to integration times of 10^{-8} s! (Ver 3.4)

- We have had to be innovative!