Introduction to corrosion
physical · chemical

Corrosion: reaction between metal and ext. environment, which promotes a degradation of the material
ceramics, metals, polymers

NB Different type of material -> different type of corrosion

For metals: corrosion -> degradation of metal -> degradation of properties (es resistance)

NB Corrosion is the cause of an important economic loss on GDP

Corrosion is an anti metallurgic process: in nature, metals are mixed with Ox in a stable form we must give energy to separate metal and ox (metallurgic process: endothermic process); when metal are in an env., they show a termodinamic tendence to recombine with ox, forming a more stable form -> rust (metal oxides) with electrochemical reactions

Def morphology: how corrosion appear to human eye or

- uniform corrosion
- galvanic corrosion: when we have two materials in contact, only the weakest material is corroded
- localized: corrosion is localized in specif point (pitting, crevice, ...)
- cracking corrosion: corrosion is combined with tensile ~~forces~~ stress

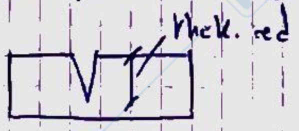
Recap: morphology
- uniform
- localized
- enviromental induced cracking (env + ext. stress)

mechanical stresses

NB e.i.c. is very dangerous because we can't see corrosion propagation until the failure

How to express corrosion rate: (intensity of corrosion process)

- mass loss per unit area and unit time [$g/m^2 s$]: good for uniform corrosion
- corrosion current density [A/m^2] electrical parameter
- thickness reduction per unit time [mm/year] good for local corrosion, where mass loss is very low



. Mass loss $V_m = \frac{\Delta M}{S t}$ mass loss   unit of measure $\left[\frac{mg}{dm^2 \, day}\right]$ practical unit of measure

. Thickness $V_p = \frac{\Delta M}{\rho S t} = \frac{V_m}{\rho}$ u of m $\left[\frac{mm}{year}\right]$

range $[0{,}1 - 10] \frac{mm}{y}$ depending on metal and env condition

Corrosion mechanism

- Wet corrosion: take place with water; electrochemical process (involves e^-)
- Dry corrosion: corrosion at high temperature in presence of dry gas

~~Corr reaction: between metal, O_2, H_2O rust~~

Corrosion reaction: metal + O_2 + H_2O / metal + acid pH → rust

Corrosion reaction can be split in 4 processes (theoretical approach)

- anodic reaction: $Me \rightarrow Me^{z+} + \textcircled{z}e^-$: metal dissolution (metal ions formation)
  - es: $Fe \rightarrow Fe^{2+} + 2e^-$
  - $Zn \rightarrow Zn^{2+} + 2e^-$
  - valence: number of e^- involved in process; metal as a tendence to provide e^-
  - → Metal provide e^- and forms the ions
  - diffuse into H_2O
- cathodic reaction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
  - $2H^+ + 2e^- \rightarrow H_2$

~~corrosion~~ corrosion is a sponteneous process in which a cathodic reaction goes on the metal and ask e^-; metal has a natural tendence to provide e^-

↓

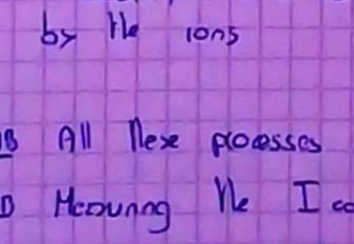
e^- produced at the AN and consumed at CAT

NB To have corrosion, this two reactions takes place simultaneously

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

NB Metal mass consumed is proportional to the ~~corrosion~~ e^- produced → current

- current in electrolyte (ions)
- current in metal (e^-)



in electrolyte I is moved by the ions

metal produced by AN (metal) and consumed by cat (O_2) — This e^- flow produces a I which has the opposite direction (C → A)

NB e^- moves only in the metal

NB All these processes take place at the same time

NB Measuring the I corr, we can find the amount of mass corroded

To stop corrosion, is sufficient to stop only one of this 4 process

In most of case, we can't observe a separation between anodic and cathodic reaction → MIXED POTENTIAL THEORY

There are also some case in which these processes are separated (as galvanic corrosion)

Recap. electrochemical reaction involves e^- / produced by AN (Me) \ consumed by CAT (O_2) | I_{corr} is generated

The amount of mass corroded depends by I_{corr}

→ Faraday law: $\boxed{\Delta M = \frac{M_m}{z F} I_{corr} \cdot t}$ $\quad A = \frac{C}{s}$

z: $\left[\frac{mol\,e^-}{mol_{Me}}\right]$ $\quad F$: $96{,}485 \left[\frac{C}{mol\,e^-}\right]$

$$\left|\begin{array}{l} \Delta M = \frac{M_m}{zF} I_{corr} \cdot t \\ V_p = \frac{\Delta M}{A t \rho} \end{array}\right. \rightarrow \boxed{V_p = \frac{M_m}{zF} i \cancel{A t} \frac{1}{\cancel{A t} \rho} = i \frac{M_m}{z F \rho}}$$

i: corrosion current density $\left[\frac{mA}{m^2}\right]$; $\frac{M_m}{zF\rho}$: depends by the metal

es Steel, $V_p \left[\frac{\mu m}{y}\right] = 1{,}17 \cdot i \left[\frac{mA}{m^2}\right]$

Fe $\quad M_m = 56 \frac{g}{mol}$ $\quad \rho = 8000 \frac{kg}{m^3}$

Thermodynamic of corrosion

Thermodynamic explains if a metal in a certain environment corrode

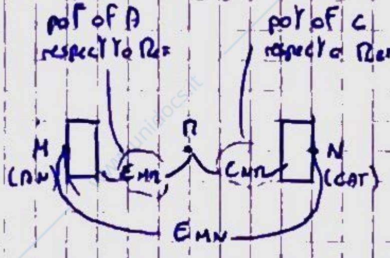
We are corrosion if $\boxed{\Delta G_{rx} < 0}$ (spontaneous reaction)

NB For a chemical reaction (no e^-): $aA + bB \rightarrow cC + dD \rightarrow \Delta G = \Delta G^\circ + RT \ln \frac{a_C^c \, a_D^d}{a_A^a \, a_B^b}$

For an electrochemical $\boxed{\Delta G = z F E^{MN}}$ — pot difference between anodic and catodic reaction

$\left[\frac{C}{mol_{Me}}\right] \cdot [V] = \left[\frac{1}{mol_{Me}} A V s\right] = \left[\frac{J}{mol_e}\right]$

defined respect to a reference one



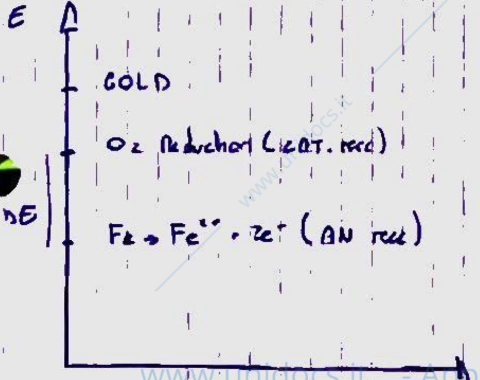
$E_{eq}^{MN} = E_{eq}^{MR} - E_{eq}^{NR} = E_{eq}^{A} - E_{eq}^{C} = -\Delta E$

$\boxed{\Delta E = E_{eq}^{C} - E_{eq}^{A} = -E_{eq}^{MN}}$ driving voltage

$\rightarrow \Delta G = -zF\Delta E \rightarrow \boxed{\Delta E = -\frac{\Delta G}{zF}}$

Spontaneous reaction: $\Delta G < 0 \rightarrow \Delta E > 0 \rightarrow \boxed{E_C > E_A}$ NECESSARY CONDITIONS TO HAVE CORROSION

E_C: cat reaction ; E_A: ANODIC reaction



$\Delta E > 0$ → CAT reaction requires e^- from metal → CORROSION

NB Most of metal has E_{AN} < than E_{O_2} → they corrode

<u>NB</u> E_{eq} can only be calculated (isn't the one measured on field)

$$\rightarrow \Delta E = -\frac{\Delta G^0}{zF} - \frac{RT}{zF}\ln\frac{\Pi a_{P,i}^{\nu_i}}{\Pi a_{R,i}^{\nu_i}}$$

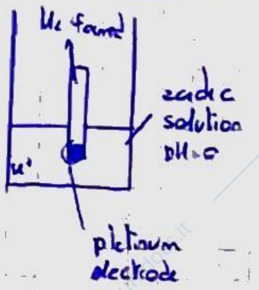
$$\rightarrow \boxed{E_{eq} = E^0 + \frac{RT}{zF}\ln\frac{[ox]}{[red]}}$$

the one which is with e⁻

$$\underbrace{aA + bB + ze^-}_{\text{oxidation}} \rightarrow \underbrace{cC + dD}_{\text{reduction}}$$

<u>Def</u>: reference electrode: potential of ~~H~~ hydrogen evolution in acidic solution (pH = 0)

$\rightarrow \boxed{2H^+ + 2e^- \rightarrow H_2 \uparrow}$ gas at 1 atm



To this reaction, we give the potential $E = 0$

<u>STD condition</u>: $pH = 0 \rightarrow \log(a_{H^+}) = 0 \rightarrow a_{H^+} = 1$

$p_{H_2} = 1\,atm$

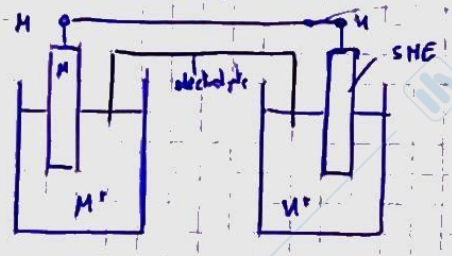
$$\rightarrow E_{H^+/H_2} = E^0_{H^+/H_2} + \frac{RT}{zF}\ln\frac{a_{H^+}^2}{p_{H_2}} = 0$$

SHE (standard hydrogen electrode)

SHE has a potential = 0, and it's the potential of the reaction $2H^+ + 2e^- \rightarrow H_2$ with $pH = 0$ and $p_{H_2} = 1\,atm$

<u>NB</u> ~~An~~ This reference electrode isn't used in practice

<u>es</u>



$E_{MH} = E_{M/M^{z+}} - \cancel{E_{SHE}} = E^0$ → respect to SHE

If: $T = 25\,C$, $a_{M^{z+}} = 1$, $a_M = 1$

<u>NB</u> O_2 RED $E_0 = 1.23\,V$ SHE Ⓒ

Fe DISS $E_0 = -0.44$ SHE Ⓐ

Ti DISS $E_0 = -1.63$ SHE Ⓐ

In both case, $E_C > E_A$ → corrode

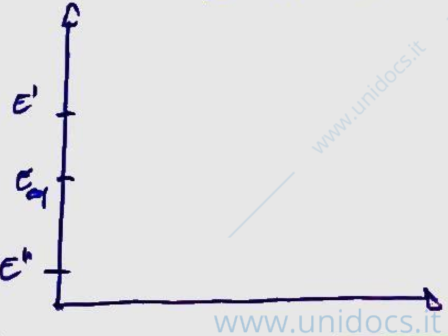
<u>NB</u> For Ti, ΔE ↑↑ : on the thermodynamic point of view, corrosion of Ti is very strong, but the kinetic is very low → ~~also~~ Ti corrosion is negligeable

For metal. $\boxed{M \rightarrow M^{z+} + ze^-}$ Hp: $a_M \sim 1$, $\ln = 2,3\log 10$, $T = 25\,C$

$$\rightarrow \boxed{E_{eq\,M/M^{z+}} = E^0_{M/M^{z+}} + \frac{0,059}{z}\log[a_{M^{z+}}]}$$

→ metal corrosion
← metal dissolution

<u>NB</u> Pot for [illegible] metal dissolution is in <u>equilibrium</u> $M_s \rightleftharpoons M^{z+} + ze^-$



Suppose that metal is force to work at $E' > E_{eq}$

→ reaction is moved to product → corrosion ↑

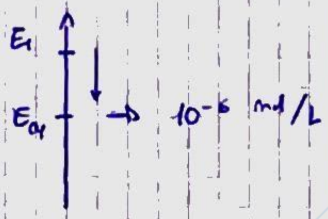
$E'' < E_{eq}$

→ reaction is moved to reactant → deposition ↓ (corrosion stops)

- $E > E_{eq} \rightarrow [a_{M^+}] \uparrow \rightarrow$ corrosion
- $E < E_{eq} \rightarrow [a_{M^+}] \downarrow \rightarrow$ deposition

Pourbaix definition

Def E_{eq} can be seen as the medium between corrosion and immunity zone → E_{eq} can be defined as that E for which concentration of metal ions is lower than 10^{-6} mol/L



The fact is that usually we don't [know] ions concentration → assuming 10^{-6} is a good rule if we don't know Me^{2+} conc.

NB Different form of H_2 evolution

a) $2H^+ + 2e^- \rightarrow H_2$ (acid solution)
b) $2H_2O + 2e^- \rightarrow 2OH^- + H_2$ (neutral solution)
c) $2H^+ + 2OH^- \rightleftharpoons 2H_2O$ (eq of water)

} pH ↑ in both cases

$\rightarrow b + c)\ \cancel{2H_2O} + 2H^+ + 2e^- + \cancel{2OH^-} \rightarrow \cancel{2OH^-} + H_2 + \cancel{2H_2O} = a)$

$\rightarrow \Delta G_a = \Delta G_b + \cancel{\Delta G_c}$ → a) e b) are equivalent from energetic point of view

We consider now a): $E_{eq} = E^0_{H_2/H^+} + \frac{0{,}059}{2\cancel{F}} \log_{10}\left[\frac{a^2_{H^+}}{a_{H_2}}\right]$

⇒ STD ~~pot~~ condition

Assuming $p_{H_2} \sim 1 \rightarrow E_{eq} = 0 + \frac{0.059}{\cancel{2}\cancel{F}} \log_{10}[a^{\cancel{2}}_{H^+}]$

Def $pH = -\cancel{lg} - \log_{10}[a_{H^+}]$

eq potential for H_2 evolution is every condition (at equilibrium

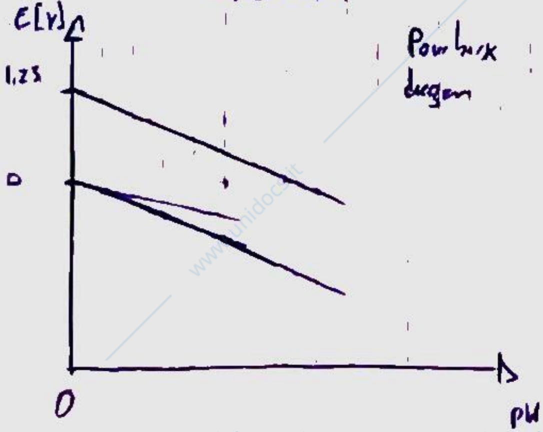
$$\boxed{E_{eq\,H^+/H_2} = -0{,}059\ pH}$$

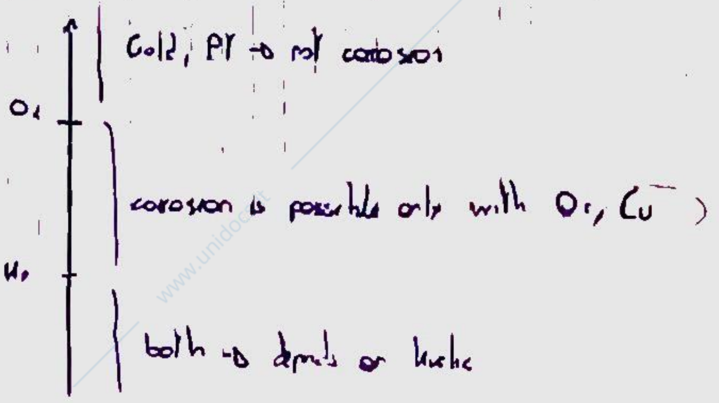
NB if $pH = 0 \rightarrow a_{H^+} = 1 \rightarrow$ STD condition $\rightarrow E_{eq\,H_2/H^+} = 0$

Oxygen reduction: $\frac{2}{4} O_2 + 2H^+ + 2e^- \rightarrow \frac{2}{2} H_2O$

$$E_{eq} = E_0 + \frac{0.059}{\cancel{2}} \log_{10} \frac{[a_{H^+}]^{\cancel{2}}[\cancel{p_{O_2}}]^{2/4}}{[\cancel{a_{H_2O}}]^{2/2}} = E^\circ + 0{,}059 \log_{10}[pH\, a_{H^+}]$$

$$\rightarrow \boxed{E_{eq} = \underbrace{E_0}_{1{,}229\ (STD)}\ \cancel{+} - 0.059\ pH}$$

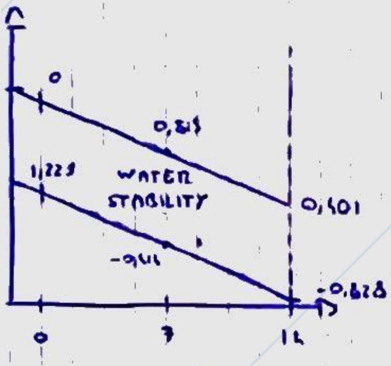




Recap: CAT: $E_{eq\ H_2/H^+} = -\frac{0.059}{2}\ pH$

AN $E_{eq\ O_2} = 1.229 - \frac{0.059}{2}\ pH$

Pourbaix diagram water / O_2 / H_2



- $H_2 \rightleftharpoons 2H^+ + 2e^-$ / $E > E_{eq}$ → H^+ prod → H_2 dissolution (→)
  \ $E < E_{eq}$ → H_2 prod → H_2 evolution (←)

- $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ / $E > E_{eq}$ → H^+ prod → O_2 evolution (←)
  \ $E < E_{eq}$ → H^+ ↓ → H_2O_2 dissolution (→)

<u>es</u>: de-aerated solution, pH = 4 $[Fe^+] \sim 10^{-6}$

Ⓐ $Fe \rightarrow Fe^{2+} + 2e^-$ $E_{eq} = -0{,}44 + \frac{0{,}059}{2} \ln[10^{-6}] = -0{,}44 - \frac{6 \cdot 0{,}059}{2} = -0{,}62$ V SHE

Ⓒ $2H^+ + 2e^- \rightarrow H_2$ $E_{eq} = -0{,}059\ pH = -0{,}059 \cdot 4 = -0{,}236$ V SHE

→ $E_{eq_C} > E_{eq_A}$ → corrosion ✓ $\Delta V = -0{,}236 + 0{,}62 = 0{,}384$ V driving voltage

Ⓐ $Cu \rightarrow Cu^{2+} + 2e^-$ $E_{eq} = 0{,}34 - \frac{6\ 0{,}059}{2} = 0{,}163$ V SHE

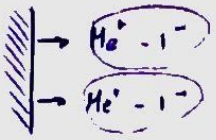
→ $E_{eq_C} < E_{eq_A}$ → corrosion × → $\Delta V < 0$

Consider now aerated solution

Ⓒ $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E_{eq_C} = 1{,}229 - 0{,}059\ pH = 0{,}993$ V SHE

$E_{eq_C} > E_{eq_A}$ → Cu corrodes in aerated solution

NB In some cases, we can consider $[Me^+] \sim 10^{-6}$: <u>es</u> in some cases, ions produced are taken by negative ions presence in solution → they form some insoluble products



→ concentration of free Me^{z+} ↓↓

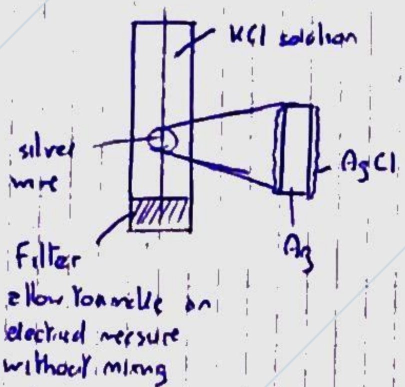
→ $E_{eq} = E_0 + \frac{0{,}059}{z} \log[M^{z+}]$ ↓↓ (es Cu, Si)

Different types of reference electrode

NB E of the ref electrode must be constant

In the practice, we don't use SHE

- Silver chloride reference electrode



Inside we have eq. between metal, ions and salt (Ag, Cl, $AgCl$)

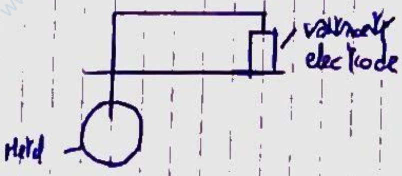
This eq. is electrochemical

$$E_{eq} = E_0 + 0{,}059 \log\left(\frac{a_{AgCl}}{a_{Ag}\, a_{Cl^-}}\right)$$

We suppose $a[\text{solid}] = 1$

$$\rightarrow E_{eq} = 0{,}222 - 0{,}059 \log[a_{Cl^-}]$$

We put an amount of KCl in order to have a saturated solution → $[a_{Cl}]$ const → const E_{eq} → a solution is saturated when we can see the deposition



NB This electrode is used in sea water → KCl solution is sea water; [Cl] is known

- Standard calomel electrode

Based on an electrochem. eq between Hg_2Cl_2, Hg, Cl, ...

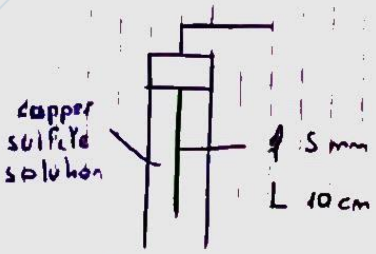
$$E_{eq} = E^\circ + 0{,}059/2 \log\left(\frac{a_{Hg_2Cl_2}}{a_{Hg}\, a_{Cl}^2}\right)$$

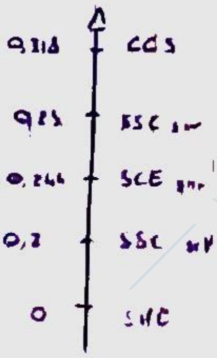
$E_{SCE,\,KCl} = 0{,}244$ V SHE

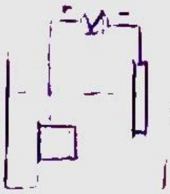
- Copper - Copper sulfate

Used in soil

$E_{CSE,\,CuSO_4} = 0{,}318$ V SHE







Pourbaix diagrams

Termodynamic diagrams which says if metal, metal ions are stable; it doesn't say nothing on corrosion rate

Three region
- immunity: metallic phase is stable
- corrosion: metallic ion is stable
- passivation & passivity: oxides and hydroxides are stable
  - passivation: formation of oxides and hydrox.
  - passivity: oxides forms a layer which stops corrosion

- Metal dissolution $Me \rightleftharpoons M^{z+} + ze^-$ eq between metal and metal ions

a) $\boxed{E_{eq} = E^0_{M/M^{z+}} + \frac{0.059}{z}\log a_{M^{z+}}}$ NB const with pH

- Passivation $Me + zH_2O \rightleftharpoons Me(OH)_z + zH^+ + ze^-$

b) $\boxed{E_{eq} = E_0 + \frac{0.059}{z}\log\frac{\overset{=1}{a_{M(OH)_z}}\, a^z_{H^+}}{\underset{=1}{a_{Me}}\,\underset{=1}{a^z_{H_2O}}} = E^0 - 0.059\,pH}$ // to catodic lines

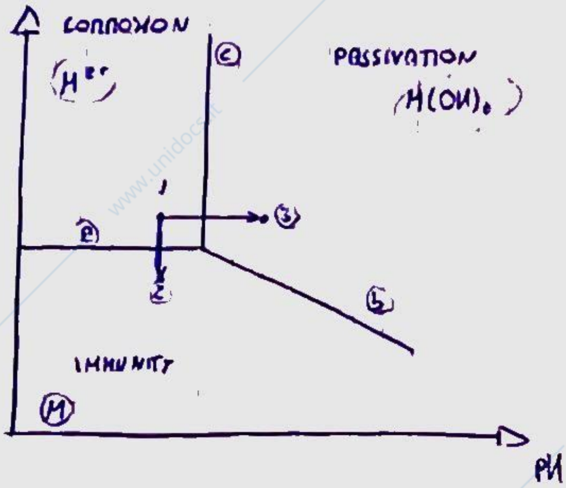
- Eq $M^{z+}/M(OH)_z$ $M^{z+} + zH_2O \rightarrow M(OH)_z + zH^+$ → chemical reaction

$$K(T,P) = \frac{a^z_{H^+}\,\overset{1}{a_{M(OH)_z}}}{a_{M^{z+}}\,\underset{1}{a^z_{H_2O}}} = \frac{a^z_{H^+}}{a_{M^{z+}}}$$

$$\rightarrow \log K = \log\frac{(a_{H^+})^z}{a_{M^{z+}}} \xrightarrow{c)} \boxed{pH = \frac{A - \log a_{M^{z+}}}{z}}$$

pH > pH$_{eq}$ $M(OH)_z$ stable

pH < pH$_{eq}$ M^{z+} stable

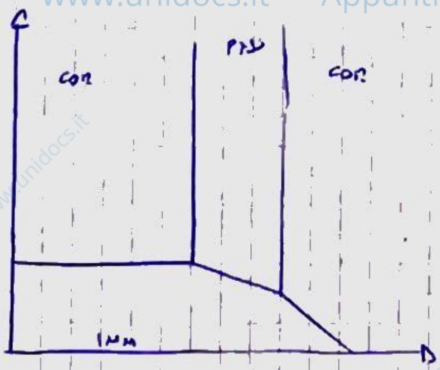


NB We can pass from corrosion to immunity given decreasing E using a current (1 → 2) → galvanic protection

NB We can avoid corrosion also increasing pH (only in small volume)

NB In passivation corrosion is very low, but isn't 0; in immunity, corrosion is 0

NB Amphoteric metals - metals in which corrosion is possible at low and high pH es Zn, Al, high pH corrosion region has an equilibrium between immunity and passive zone



Kinetics of corrosion

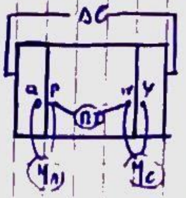
Kinetic says how much is the corrosion rate → if is very low, corrosion is negligible

$$\Delta E = E_{eq\,C} - E_{eq\,A} = \eta_A + \eta_C + RI$$

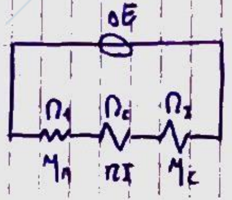
anodic overvol. catod. overv. ohmic drop

→ ΔE (driving force) is dissipated in 3 contribution

- η_A: dissipation of energy in anodic reaction
- η_C: ~~catod~~ dissipation in catodic reaction
- ohmic drop in electrolyte



→



$$\Rightarrow I = \frac{\Delta V}{\Sigma R_i}$$

In order to decrease I, is sufficient have only 1 of resistor very high → serve to stop corrosion

Overvoltage related to reaction / <u>activation overvoltage</u>: depends on energy required to activate reaction
\ <u>concentration polarization</u>: due to a variation in demand composition (different conc.)

– ACTIVATION OVERVOLTAGE - ANODIC : $\boxed{E_{ap} = \eta_A}$ $\eta_A = E - E_{eq}$

we suppose to put ~~ref~~ ref. electrode very close to metal surface → we measure only contribution of anodic process (Q - P are very closed → no ohmic drop)

(IP) ref electrode in P is a isoelectronic electrode (made by same metal of Q)

When anod is linked to catod, we have I → we measure a potential

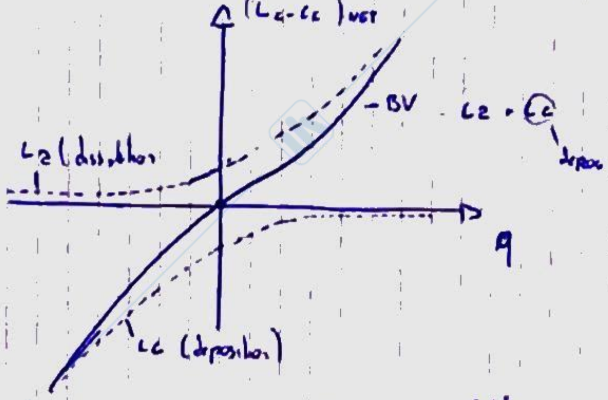
Consider now a reaction $\boxed{M \rightleftharpoons M^{z+} + ze^-}$

- $E = E_{eq}$ → $i_a = i_c = i_0$ <u>exchange current density</u> (con metal oxidation = ions deposition rate)
- $E > E_{eq}$ → $\eta = E - E_{eq} > 0$ → Ⓡ is moved to products → $\boxed{i_a > i_c}$
  → net anodic current $\boxed{i = i_a - i_c}$
- $E < E_{eq}$ → $\eta = E - E_{eq} < 0$ → Ⓡ is moved to reactant → $i_a < i_c$
  → net anodic current $i = i_a - i_c < 0$

Def BV $\boxed{i = i_0\left[e^{\left[\frac{\alpha zF}{RT}\underbrace{(E-E_{eq})}_{\eta}\right]} - e^{\left[-\frac{(1-\alpha)zF}{RT}\underbrace{(E-E_{eq})}_{\eta}\right]}\right]}$ Butler Volmer
- $\eta > 0$ AN
- $\eta < 0$ CAT

↳ how i change when $E \neq E_{eq}$ $\qquad = i_a - i_c$ $\qquad$ $\alpha = 0.5$ symmetry in fraction between the 2 reaction

We apply B-V to anodic partial process $\rightarrow i = i_0 e^{\left[\frac{\alpha zF}{RT}\eta\right]} - i_0 e^{\left[-\frac{(1-\alpha)zF}{RT}\eta\right]}$



- $E = E_{eq} \rightarrow \eta = 0 \rightarrow i_a = i_c \rightarrow i_{net} = 0$
- $E \gg E_{eq}$ $\quad i_c \rightarrow 0$
- $E \ll E_{eq}$ $\quad i_a \rightarrow 0$
- $E \sim E_{eq}$ $\quad (e^x = 1 + x)$

$\rightarrow i = i_0\left[\cancel{1} + \frac{\alpha F z}{\cancel{RT}}\eta - \cancel{1} + \frac{(1-\alpha)zF}{RT}\eta\right]$

$\rightarrow \boxed{i = \eta \frac{zFi_0}{RT}}$ linear dependence on η

Tafel law $|\eta| \gg 10$ mV $\rightarrow i \approx i_0 e^{\left[\frac{\alpha zF}{RT}\eta\right]} \rightarrow \ln i = \ln i_0 + \frac{\alpha zF}{RT}\eta$

$\rightarrow \eta = \frac{RT}{\alpha zF}\ln i - \underbrace{\left(\frac{RT}{\alpha zF}\ln i_0\right)}_{\text{cost}} \rightarrow \boxed{\eta = a + b \log i}$

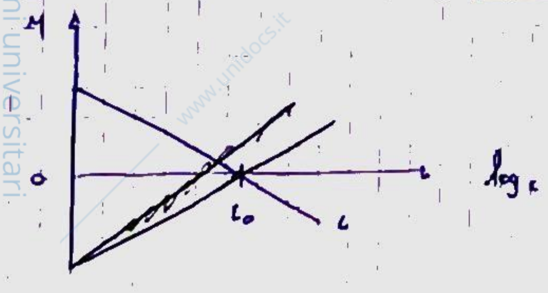
z = 1	120	mV
z = 2	60	

→ Fe, Cu, Zn

Recap $|\eta| \ll 10$ mV $\rightarrow \boxed{i = \eta\frac{zFi_0}{RT}}$

$\eta_a \gg 10$ mV $\rightarrow \boxed{\eta_a = -\frac{2.3\,RT}{\alpha zF}\log i_0 + \frac{2.3\,RT}{\alpha zF}\log i}$

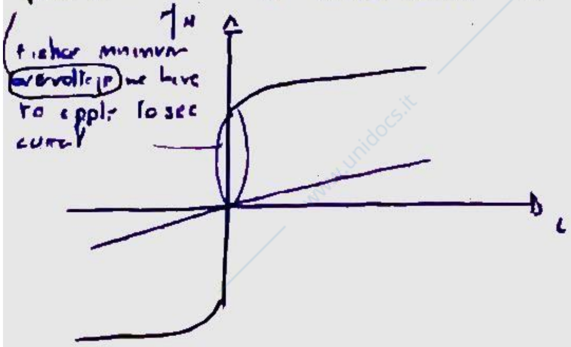
$\eta_c \ll -10$ mV $\rightarrow \boxed{\eta_c = \frac{2.3\,RT}{\alpha zF}\log i_0 - \frac{2.3\,RT}{\alpha zF}\log i}$



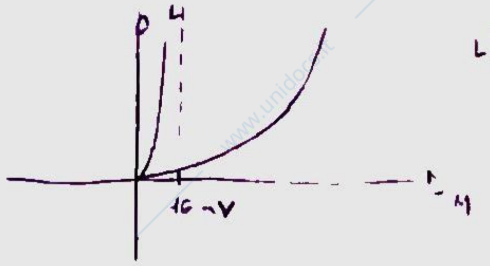
Piorelli class:
- normal metals: $\eta\downarrow < 10$ mV (Hg, Al, Zn)
- inert metals $\eta\uparrow > 100$ mV (Fe, Cr, Ni, Co)
- intermediate metal

polarization

(higher minimum overvoltage we have to apply to see current

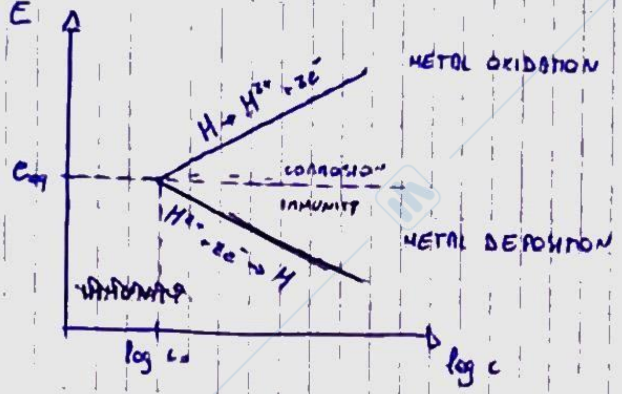


normal $\eta\downarrow\downarrow$ even at high i → low η → fast kinetics

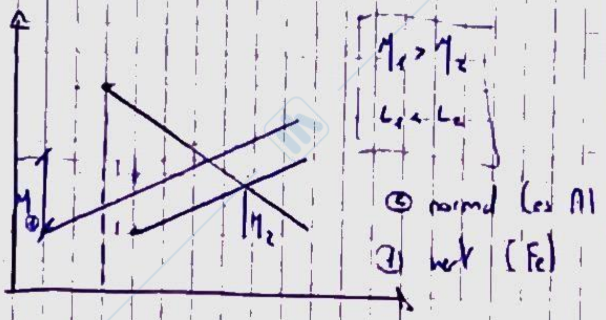


$i_0^{N} > i_0^{IN}$

NB To measure η_A (PA) we don't use an isoelectrodic reference: so when at $i = 0$, we measure $\eta \neq 0$, which is the difference ~~[illegible]~~ between eq pot of the electrode and of the reference electrode

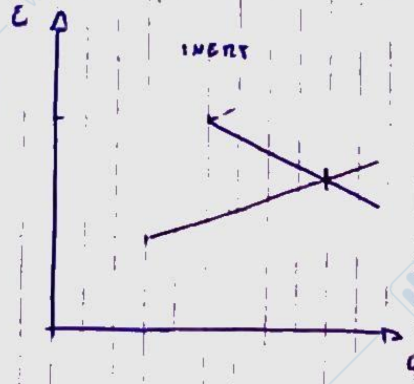


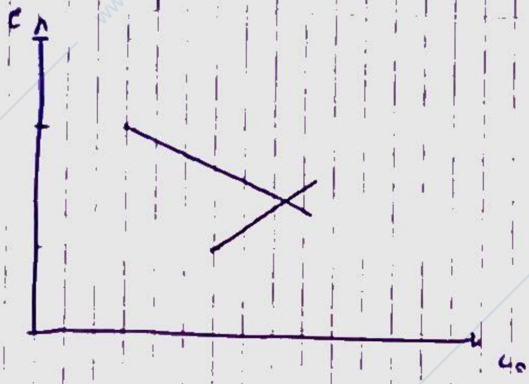
NB ANTI CORROSION



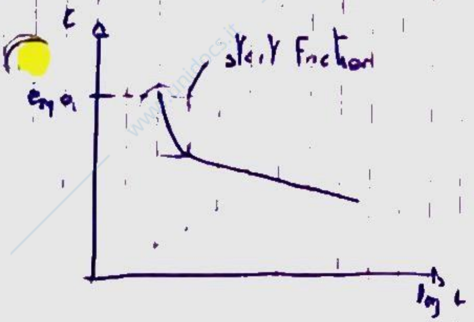
- CATHODIC OVERVOLTAGE : $\boxed{E_{NW} = \eta_c}$

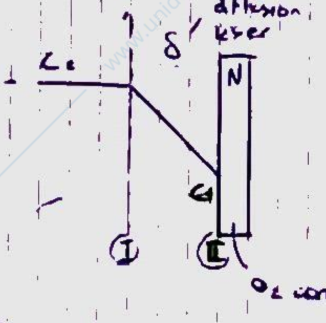
$2H^+ + 2e^- \to H_2$ NB [illegible] 2:1 b = 120





For ox reduction, there is another contribution due to <u>concentration polarization</u>: O_2 must diffuse into the liquid solution





- c_2 O_2 in bulk
- c_1: O_2 at electrode
- Δc depends on velocity of diffusion

O_2 consumed by reaction

CORROSION RATE IS INFLUENCED BY THE VELOCITY OF THE DIFFUSION RATE OF O_2 THROUGH THE SOLUTION

$$\to E_{eq,O_2} = E^0_{O_2} + \frac{0.059}{2}\log\frac{a^2_{H^+}P_{O_2}}{a_{H_2O}\cdot 1} = 1.229 - 0.059\,pH + \frac{0.059}{2}\log(P_{O_2})$$

P_{O_2} change between ① and ②

$$\boxed{\Delta E_{diff} = E_{II} - E_I = \underbrace{\frac{0.059}{2}\log\frac{c_1}{c_2} < 0}_{c_1 < c_2}}$$

↓ capacity of cathode to acquire e^- depends on the capacity of O_2 to reach the metal surface → corrosion rate depends on diffusion layer

We can define $\boxed{V_D = D\frac{C_2 - C_1}{\delta}}$ $\left[\frac{mol\,O_2}{m^2\,s}\right]$ velocity of O_2 diffusion

$\Delta M = \frac{M_m}{zF}\underbrace{i\,S\,t}_{F}$ → $\boxed{\frac{\Delta M}{S\,t\,M_m} = \frac{i}{zF} = V_c}$ consumption rate

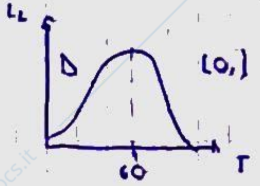
→ $V_D = V_c$ → $\boxed{i = \frac{zFD(C_2 - C_1)}{\delta}}$ → relation between i and gradient in ~~concentration~~ diffusion of O_2

NB $C_1 = 0$ (O_2 completely consumed on surface) → $\boxed{i_L = \frac{zFDC_2}{\delta}}$ LIMITING CURRENT DENISTY

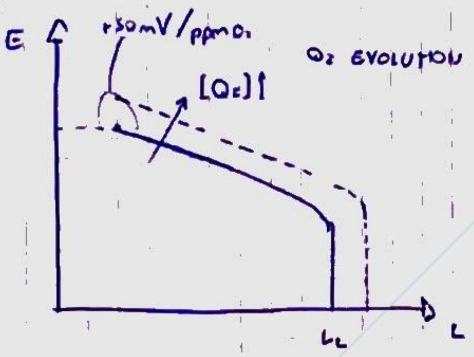
max possible reduction rate due to O_2

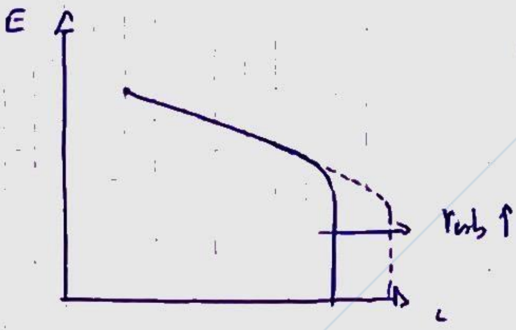
NB If I know i_L, I know max corrosion rate

- T ↑ → O_2 ↓ but D ↑ { i_L ↑ till 60 C; i_L ↓ T > 60 C



- salinity ↑ → $[O_2]$ ↓ → i_L ↓
- turbulence ↑ → $[O_2]$ ↑ → i_L ↑

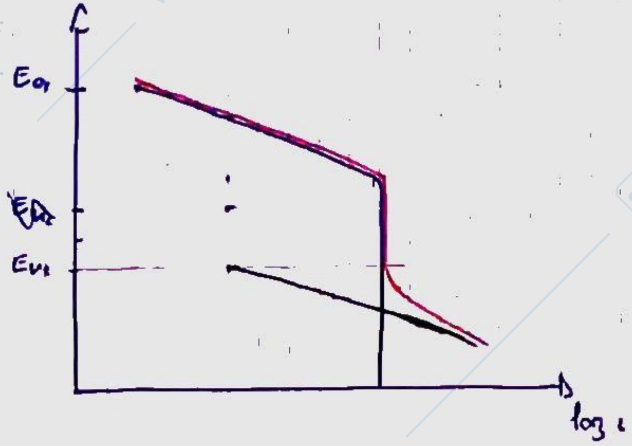




NB $i_L = \frac{4FD}{\delta}[O_2]$ → 10 For
- stagnant solution
- ambient T

~10

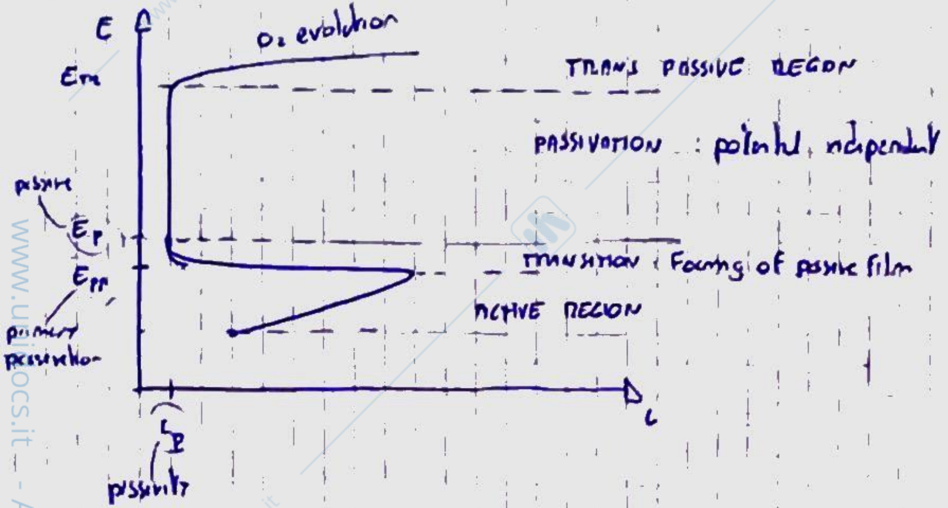
ppm $\left[\frac{mg}{ug}\right]$



- IF $E_M < E_{H_2}$, it provides e^- for both H_2 and O_2
- IF $E_M > E_{H_2}$, it provides e^- only to O_2 dissolution

Passivation and Passivity

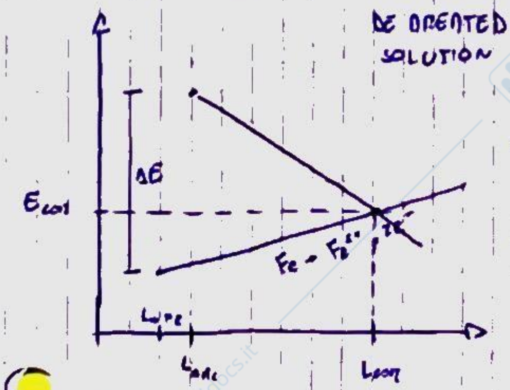
Passivity: Formation of passive film which block corrosion



NB $pH \downarrow \rightarrow E_{pp} \uparrow$

NB E_m is so high that $E > E_{O_2,eq} \rightarrow 4OH^- \rightarrow O_2 + 2H_2O + 4e^-$
→ we're producing O_2 increasing acidity $(OH^- \downarrow)$ → acidity breaks passive Film
~~[illegible] corrosion~~

Evans diagram



- $i_0^{H} > i_0^{Fe}$ → Fe is not noble (at. corrosion)
- Tafel slope of Fe is 60 mV (bivalent), H b = 120 (monovalent)
  → H is steeper

NB Steel is forced by cat. process, to give e^- to H^+
→ is forced to work anodically

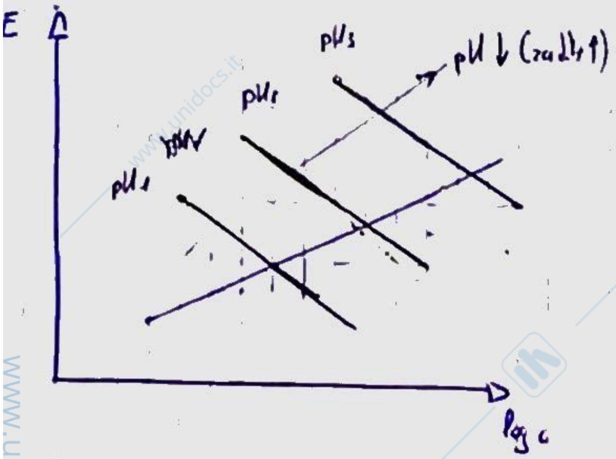
$$\Delta E = E_c - E_a = E_c - E_{corr} - (E_a - E_{corr}) = \eta_c + \eta_a + \cancel{RI}$$

$\boxed{i_a = i_c = i_{corr}}$ → amount of e^- required by catod is equal to e produced by anod

$$\left.\begin{array}{l} \eta_c = -b_c \log \dfrac{i_{corr}}{i_{0,c}} \\ \eta_a = b_a \log \dfrac{i_{corr}}{i_{0,a}} \end{array}\right\} i_{corr} = i_{0,c} \cdot 10^{\left[-\frac{E_{corr} - E_c}{b_c}\right]} = i_{0,a}\, 10^{\left[\frac{E_{corr} - E_a}{b_a}\right]}$$

NB E_{corr} is measured on Field

EFFECTED OF ACIDITY



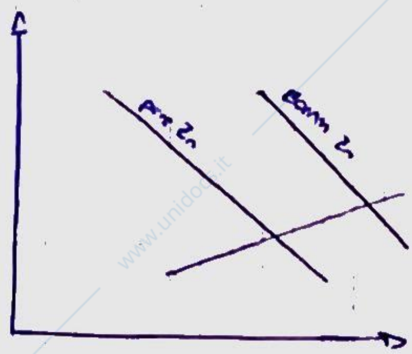
$E_{eq}^{H_2} = -0.059\ pH \rightarrow pH\downarrow \rightarrow E_{eq}^{H_2}\uparrow$

$\rightarrow$ acidity ↑ (pH↓) → i_{corr} ↑

NB pH ↓ → H^+ ↑ → rate of reaction ↑ → $i_0^{H_2}$ ↑

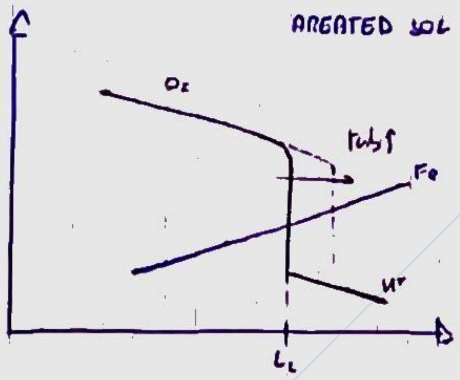
es pH=3 i_0 = 10

pH: 2 i_0 = 1



Normal metal

impurity ce effect starting point



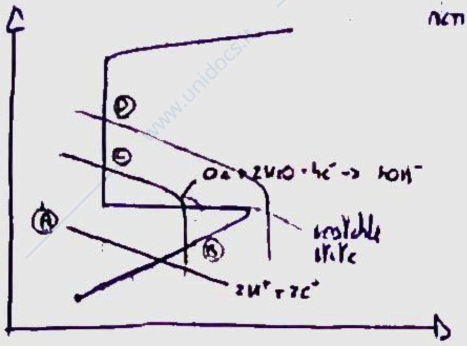
Steel works in diffusion control region

→ $\boxed{i_{corr} = i_L}$

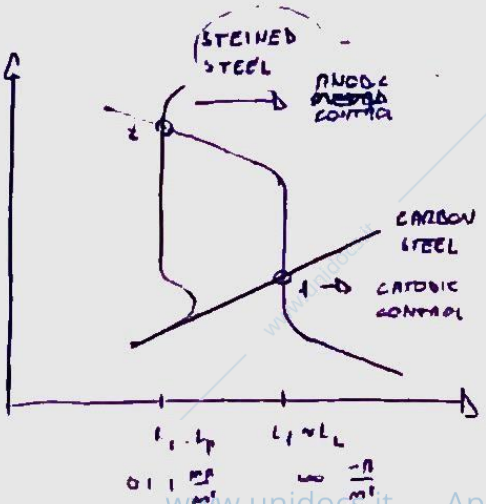
NB $i_a \ll i_{o_2} \rightarrow i_{corr} = i_L$

- turb : i_L ↑ → i_{corr} ↑

ACTIVE PASSIVE METAL



- Ⓐ corrosion takes place, no contribution of passivation
- Ⓑ if metal is active when immersed in solution, corrosion
- Ⓒ if passive film already form → corrosion (NB if passive film is broken, the metal works in Ⓑ)
- Ⓓ passive film is stable if it is broken, it's able to reform → good working condition

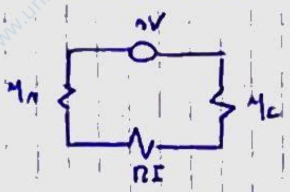


- ACTIVE METAL : i_{corr} is decided by catodic process
- PASSIVE : it's metal which set the corrosion rate

with Cr 18%

NB E_{corr} is the potential which is measured in field

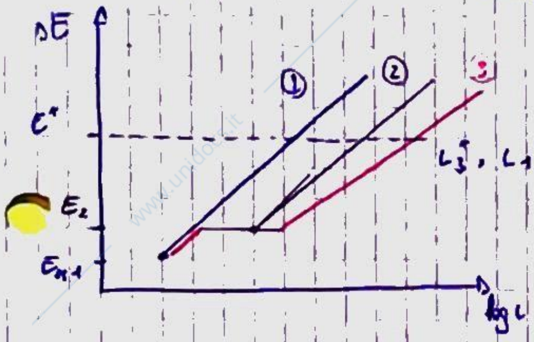
NB Electric circuit analogy (hp: no ohmic loss for ε current, because of high cond of the el)



hp $\Omega I \rightarrow 0$ $\rightarrow$ $\Delta V =$ $\quad I = \dfrac{\Delta V}{\eta_a + \eta_c}$

- $\eta_a \ll \eta_c$ $\rightarrow$ CATHODIC OVERVOLTAGE CONTROL (as O_2 diffusion zone)
- $\eta_a \gg \eta_c$ $\rightarrow$ ANODIC OVERVOLTAGE CONTROL (as passivation film)

Consider the case of multiple anodic reaction



③ global curve

$i_3^* = i_1(E^*) + i_2(E^*)$

Generalized corrosion form

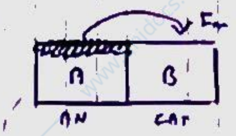
Def when all the surface is affected by corrosion, it's easy to see and easy to stop

es carbon steel in natural env. or in acid solution

CR [$\mu m/y \sim 10^2\ \mu m/y$] depends on ambient condition (different $[O_2]$, different T, ecc)

Galvanic coupling

Corrosion due to the contact between two metal with different electrochemi properties



$\rightarrow$ They have different practical nobility

Ⓐ corrosion rate increase

Ⓑ corrosion rate decrease (or also stop)

Def practical nobility: metals don't have different corrosion potential (free corrosion C)

NB Ranking of E_{eq} is different by ranking of corrosion po

$\checkmark$ $E_{corr,A} < E_{corr,B}$ $\rightarrow$ B is more noble

When metals are put in contact, we have a $\Delta E = E_B - E_A$ due to diff pot of metals $\rightarrow$ we have the generation of a new current (I_m MACRO CIRCULATE

I_m perturbate the process on A & B, increasing corrosion on A and decreasing on B

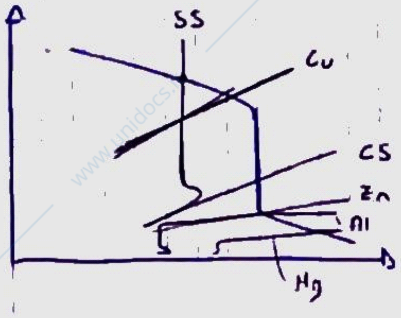
Depends on

- practical nobility of the metals ΔE_p set the size of perturbation
- cat - to - an surface ratio
- overvoltage of cathodic reaction on more noble metal
- electrolyte conductivity

- Practical nobility : poor metal : Hg, ~~Zn, Al, Mn~~ noble metal :

Hg	-1,6 - -1,7 V CSE	Fe -0,3 - -0,6
Zn, Al	-0,9 - -1,1 V CSE	Ti , ST steel

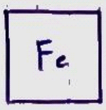
NB ΔE_p depends not only by the metals, but also by cathodic process and electrolyte



- SS - Cu ΔE no → I_m no → contact isn't a problem
- Cu - CS ΔE ↑ → I_m↑ → problem for CS

NB galvanic ~~cathodic~~ protection is based on coupling my system with a less noble metal which corrodes working as an anode

- Cathodic to anodic surface ratio .

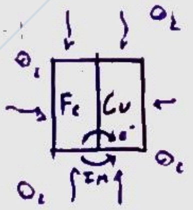


1 m² Fe seawater

i_L , 100 mA/m²

V_{corr} , 120 μm/y

ΔM = 912 g



0,5 m² Cu 0,5 m² Fe

i_L , 100 mA/m²

V_{corr} = 240 μm/y

ΔM = 912 g

In 2nd case, $E^{Cu}_{corr} > E^{Fe}_{corr}$ → Cu works as cathode → I_m that provokes an increase of Fe corrosion rate , O_2 is moving on all the surface (O_2 and takes place anyway) → O_2 corrodes Fe ∀ according to limiting current density

Also Cu is corroded by O_2, but e⁻ given by Cu are taken by Fe ~~CO~~

→ Fe is working for its O_2 and Cu's O_2

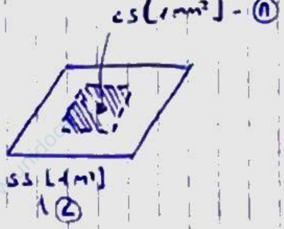
→ ΔM is the same , but Fe A is half → $cr^{②} = 2\, cr^{①}$

$$\boxed{i_A = i_{A,corr} + \frac{I_M}{S_A}} = i_{A,corr} + \frac{i_L S_C}{S_A} = i_L\left(1 + \frac{S_C}{S_A}\right) = \boxed{i_L\left(\frac{S_A + S_C}{S_A}\right)}$$

i_A ↓ after coupling; $i_{A,corr}$ ↓ before coupling

NB galvanic corrosion is always due cathodic process → no O_2 , no galv corrosion

Def throwing power we don't have to consider geom surf , but surface of the electrode which exchange a current this surface is defined by throwing power



$i_s = i_c \frac{1m}{1mm^2}$ ⊗

We should consider only the area which exchange current → depends on the ability of the current to reach a certain distance from anode → Lmax (throwing power)

This is due to ohmic drop effect

- ELECTROLYTE WITH HIGH Ω (soil)

  $\frac{S_a + S_c}{S_a} \sim 2 \to i_a \sim 2 i_c$

- ELECTROLYTE WITH LOW Ω (es sea water)

  $\frac{S_a + S_c}{S_a} \uparrow\uparrow$

→ For anod, coupling corrosion is less severe in high Ω ↑ (soil, air)

→ galvanic protection is more effective in Ω ↓

Ω ↑ Lmax ↓
Ω ↓ Lmax ↑

es

In soil, Lmax ↓ → anod spacing ↓ → n° sacr anod ↑ → cost ↑

In sea water, Ω ↓ → Lmax ↑ → spacing distance ↑

$$\boxed{\Delta V} = RI = iA\frac{\rho L}{A} = \boxed{i \rho L_{max}} \begin{cases} \Delta V \uparrow \to L_{max} \uparrow \\ i, \rho \uparrow \to L_{max} \downarrow \end{cases}$$

electrolyte

- Catalytic properties of the cathode

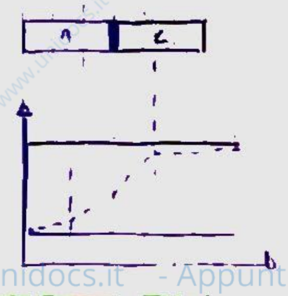
1) Cu / Fe ΔV = 0,5 V CR_{cs} ↑ Cu active

2) SS / Fe ΔV = 0,5 V CR_{cs} ↓ SS PASSIVE → oxides layer inhibites ox RED

Prevention

- avoid dangerous coupling
- using insulating flanges to avoid electric contact
- avoid $S_c \gg S_a$
- painting coating (we cover all or only cathode → if I cover only an → Icorr !! to increa

$i_{corr} = i_c\left(1 + \frac{S_c}{S_a}\right)$



region interested by current exchange shows a variation in potential

Pitting corrosion

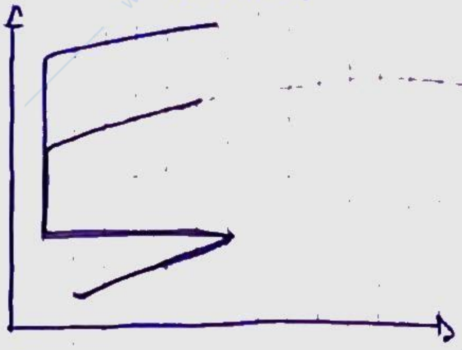
Localized form, attacks typical of passive metal (as in concrete, ss in seawater)
Due to localized breakdown of the passive metal
We don't have a great mass loss → difficult to detect, mass loss ↓, but penetration ↑↑

- Pitting initiation: initial period where metal remain in passive condition, but chloride (Cl^-) needs time to break the passive film (incubation period); passive metal isn't able to reform
- Corrosion propagation: corrosion starts to penetrate

When pitting start, is very difficult to stop. It's important the prevention: metal bar must be selected in order to avoid that it's affected by pitting

Def critical chloride threshold Cl_{th}: minimum value which provokes corrosion, depends on metal and environment

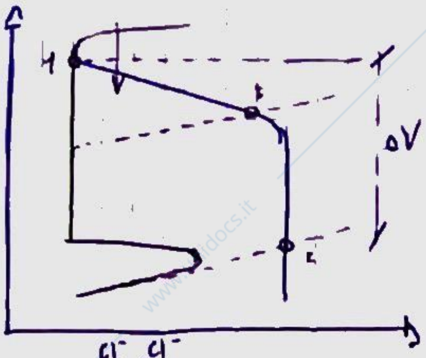
Def pitting potential E_{pit}: minimum E for which we have a pit corrosion, depends on metal and environment



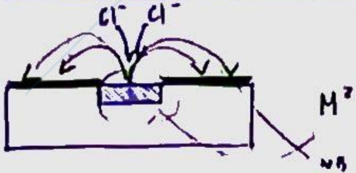
chloride decrease passive range

NB incubation time and pit localization are based on a stochastic approach → difficult to predict

PITTING PROPAGATION IS THE RESULT OF MACROCELL MECHANISM
↓



NB if passive film is broken, inside the metal (pit), the corrosion pot is E_2 (we have no more passive film, metal works as an active metal) → i_{corr} inside the pit is very high
E_3 is a medium value between passive zone (cathodic) and the pit (ANODIC) → we have the generation of a macrocell current between pit and passive film → Im protects passive zone and corrode the pit



$M^{2+} + 2H_2O \rightarrow M(OH)_2 + 2H^+$

NB in the cathodic region, we have O_2 reduction → pH ↑ → this increase of alkalinity protect the cathodic region from corrosion → we don't have other pit in the region interested by the I_M

[illegible] Im forces pit to provide e^- for passive (CAT) zone
Cl^- move in opposite direction of Im → conc of Cl^- inside the pit
(moved by electric field)
} PASSIVE FILM ISN'T ABLE TO REFORM

NB Only the way to stop corrosion is using galvanic protection in order to neutralize I_M

NB In seawater, bacteria form a biofilm which [illegible] decrease cathodic reaction on metal
(catalyses the cathodic reaction and increase ΔV by [illegible] mV

Pitting pot E_{pit} depends on both { metal / environment → not easy to calculate

- A stagnant condition very good for pitting initiation (stag → pit in ↑)
- bacteria pitting E ↑ → E > E_{pit} → risk of pit initiation
- time to start pitting is about lot of hours (cleaning operation resets initiation time)
- surface orientation higer risk on horizontal surface
- inclusions put at risk the efficacy of passive film
- metal composition PREN = %Cr + 3,3% Mo + 16% N → summarize positive effect

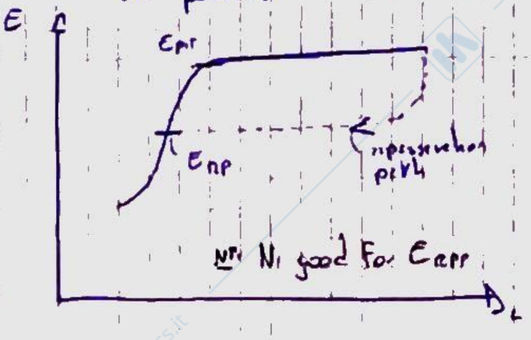
  PREN ↑ → Pit resistance ↑ NB S ↑, Mn ↑ → pit resistance ↓
- chloride $[Cl^-]$ $E_{pit} = A - B \log[Cl^-]$ $\boxed{Cl^- \text{ sea water}: 20000\,ppm}$

NB These effects aren't independent one each other. To define corrosion, we use a probability technique to caracterize ~~for~~ pitting initiation
probabilistic

NB Most important param (T, pH, PREN) → ~~Log Chart~~ $\log[Cl_{cr}] = f(PREN, T, pH)$
easy to calculate
pH ↑ → E_{pit} ↑

NB Tipicall driving voltage for pit is $\boxed{\Delta E = 0,5\ V}$

Def Repassivation potential: applying an an I opposite to I_m, we can decrease the potential



NB Ni good for E_{rep}

To stop pitting, is not enough to move E < E_{pit} but we ve to go ~~[illegible]~~ < E_{rep}

$E_{rp} < E < E_{pit}$: pitting cannot start, but can't stop if it's already initiated → imperfect passivity

Crevice corrosion

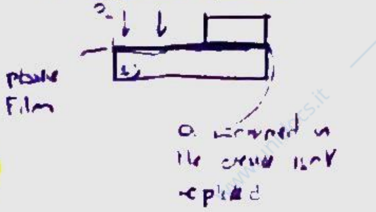
Morphology similar to pitt.: break of passive film isn't aleatory but is localized

Local breakdown on discontinuity ~~[illegible]~~ (crevice) — sub millimetric interstices on surface of metal

- ~~crevice~~ oxigen depletion stage
- macrocell formation
- propagation

(first two: incubation)

- ox depletion



$M + 2H_2O \rightarrow M(OH)_2 + 2H^+ + 2e^-$

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

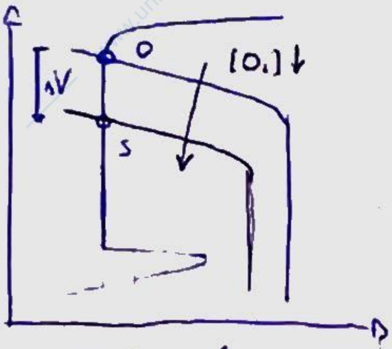
when metal works in passive ~~[illegible]~~ region, passive film increase because of ~~cathodic~~ ~~current~~ oxidation process → lower dependence with i_p very small

e^- made available by passive film are taken by ~~[illegible]~~ O_2

→ i_p measured anodic rate of O_2 → O_2 is consumed

NB incubation time depends on i_p (PREN, T, pH) and crevice volume inside the crevice, O_2 isn't replaced -> variation of $[O_2]$

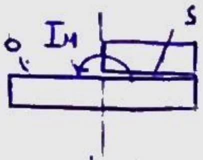
- macrocell formation



— inside crevice

O: catode
S: anod | ΔVos produce I_M

I_M is due to a difference in concentration



- propagation: inside the crevice, $[O_2]$↓ -> $[Cl^-]$↑ (Cl^- is ~~att~~ moved to positive pole -> crevice) -> Cl^- brokes passive film

NB No Cl^- -> no corrosion

NB inside the crevice, condition become more and more bad (acidity increase) -> passive film doesn't reform

NB Fixing T, $[Cl^-]$ which provokes crevice is lower than pitting -> crevice is a stronger form of pitting -> crevice is more aggressive of pitting (we have I_m generated by crevice)

Environmental induced cracking

Corrosion mechanism based on combination between environmental and mech. stress

-> effect production of cracks (no mass loss) -> plastic material fails like brittle material

- Stress corrosion cracking - depends on | metal
  environment
  tensile stress

as pitting for SS at T>20°C

crack can be: - intergranular: along grain boundary
- transgranular ~~transgrain~~ across grain

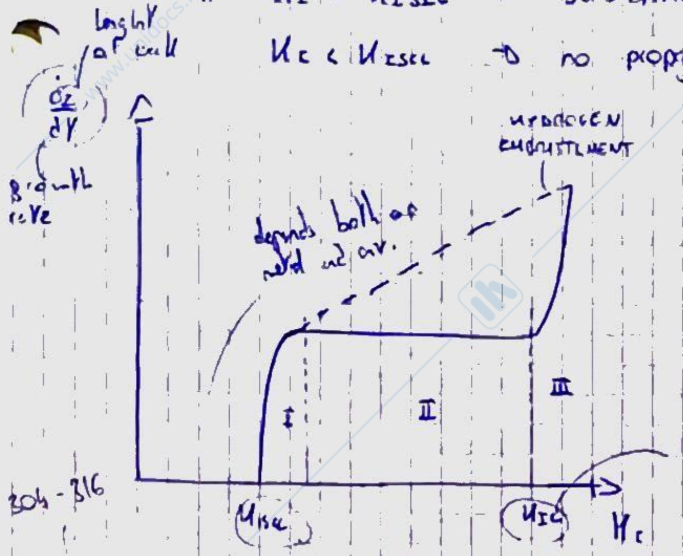
- incubation: time to form small crack on the surface
- propagation: subcritical (high propagation rate, but small crack)
  critical (we have the component mechanical failure

- INCUBATION (NUCLEATION) negligible if we have pits, deformation or small defect on surface -> incub time depends on material conditions
- SUBCRITICAL subcritical until a critical length of crack depends on coupling
- CRITICAL material isn't able to resist to the external load -> propagation unstable -> istantaneous failure toughness ↑↑ -> a before failure ↑↑ , σ↑ -> a↓

Def stress intensification factor measure intensification of the overall stress applied, to the defect

K_I [MPa $\sqrt{m}$]

NB if $K_I > K_{ICR}$ → unstable propagation
if $K_I > K_{ISCC}$ → subcritical growth
$K_I < K_{ISCC}$ → no propagation



$K_I < K_{ISCC}$ no propagation

grow rate depends both on corrosion and stress
Ⓘ effect of mech. factor
Ⓘⓘ depends only on corrosion effect

depends on metal

NB increasing mechanical strength (graph)
thoughness ↓ → K_{ISCC} ↓

NB Low strain rate (deformation rate) is most critical

NB Ni 10% provokes a low time to failure → typical condition for SS
→ SS aren't very resistant to env. induced crack

NB SCC is favorited at T ↑ (> 70 C)

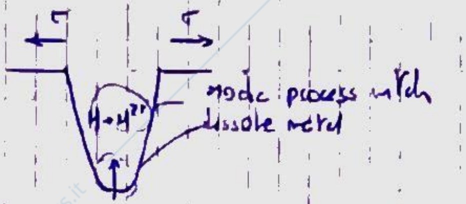
NB [Cl^-] ↓ Tcr ↑ [60 ÷ 80 C]
SCC water / potable water
Tcr is related to Cl^- content

NB Face Centered Cubic → H diffusion ↓ — more resistant (more compact)
Body Centered Cubic → H diffusion ↑
~~[illegible]~~

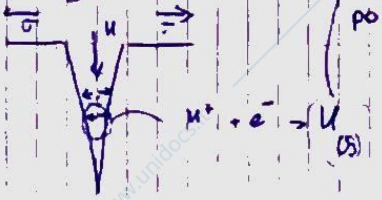
~~→ Hydrogen embrittlement~~

SCC

Anodic dissolution



Hydrogen embrittlement



$H + H \to H_2$ this reaction is inhibited by catalyst poisoning (es S components)

stress generates a crack on the passive layer, crack surface which is now expose to aggressive environment → if passivation rate is slower than sliding rate, → anodic propagation (crack tip remaining active)

H_2 diffusion in crack tip → H stops movement of dislocation → the evolution generates H with increase tip size K_{ISCC} ↓
- block dislocation → no more plastic behaviour
- gas inside metal cracks stress inside → H_2 formation inside crack → internal stress

NB Cathodic polarization stops anodic dissolution, but increases H_2 embr
E ↓ — anodic dissolution stop
— H embr increase propagation (increase H production)

Embrittlement
- without stress (blistering) — wh external stress
- with stress : SULFIDE STRESS CRACKING (SSC) → stress ↑ → H embr ↑
σ < 700MPa → H embr not important

Source of H
- catodic process at low pH (H^+ ↑)
- pickling acid solution used to clean the metal

H recombination could be even stopped by poisoning

In field, we don't measure stress, but hardness -> no corr. if $\boxed{hard < 22\ RC}$

Def hard spot: local points with high hardness -> risk of crack (es weld point)

Flow induced corrosion

Stress is generated by fluid motion -> mechanical action on fluid in the metal

- erosion: without particles
- abrasion: erosion + particles
- cavitation: stress due to formation of bubble
  es P variation, bend
- erosion corrosion: reached where turbulence is reached
  max fluid velocity Uc depends on metal and fluid $\boxed{U_c = \textcircled{c}/\sqrt{\rho_{fluid}}}$
  Morphology of corrosion follows flow direction -> it's easy to understand if we are flow corr.

- local geometry
- strongness of passive film
- ability to reform passive film

depends on metal

es SS resist (1)
Cu resist (2)

- monophase fluid
- no solid particles

- cavitation: due to P variation -> bubble formation -> bubble implosion -> stress on metal surface which can remove passive film

Protection: choose of proper metal or proper fluid (or fluid velocity); also, proper design or coating

Intergranular corrosion

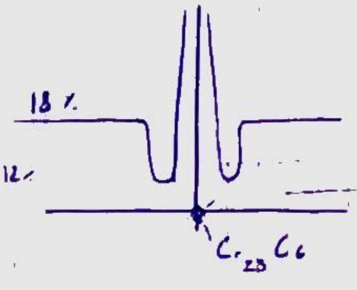
Takes place on grain grain boundary -> weak point for corrosion resistance because of segregation of secondary phases

- presence of impurity on g.b.
- formation of intermetallic with low nobility

Most important case is for austenitic ss: precipitation of Cr components in g b

In order to increase formation of alloy, we move to T↑↑, in order to dissolve all species in the metrix, then fast cooling (solubilization) due to fast cooling, elements can't able to recombine again

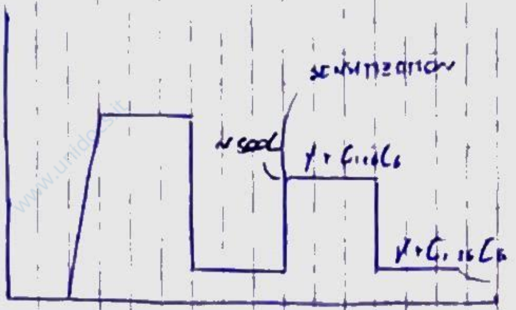
If we put T at 500-850 C, we have peak precipitation of chromium carbides $Cr_{23}C_6$ close to g.b., we have decrease of Cr content (it moved into g b combined with C) -> passive film formation is inhibited (Cr < 12% min value to have passive film)



Different Cr concentration -> different passive film
-> corrosion where passive film is weaker

precipitation of cromium carbides into the grain boundary

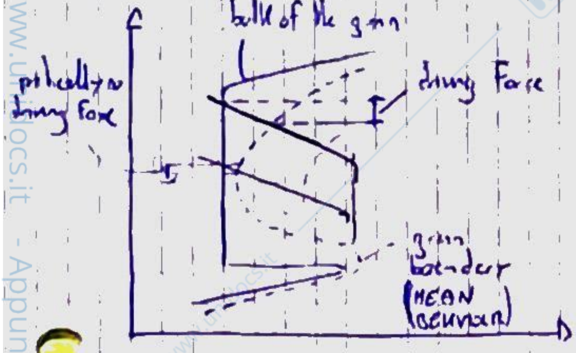
NB segregation increases mechanical resistance



SENSITIZATION FOR FERRITIC SS: carbides, separation of nitrides T > 900 C

T is too small to promote diffusion of carbide

Def sensitization time: time required to have carbide formation $\Delta t \downarrow$ if $T \uparrow$ or $C \uparrow$



Intergranular corrosion takes place only if we've thermodynamically condition

NB $\Delta t_{sens} \uparrow$ → curves are shifted to right
→ $\Delta C \uparrow$

time at which the metal is taken at T ~ sensitization

solubilization

Prevention:
- T ↑ > 1000 C → carbide dissolution → not practical solution
- reduction of C < 0.03 % AISI 304 L - 316 L (L means low carbon)
- use elements which have a greater affinity with carbon and form carbides instead of Cr (es Ti, Nb) AISI 321 (Ti) 347 (Nb)

austenitic

STABILIZED METAL

5·%C 10·%C

even in this case, we can't stop corrosion when it started → material selection

NB risk for zone near to to a weld, which is heated by welding (HEAT AFFECTING ZONE)

Cathodic protection

Electrochemical technique: ext current which change equilibrium condition

$2Fe \rightarrow 2Fe^{2+} + 4e^-$

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

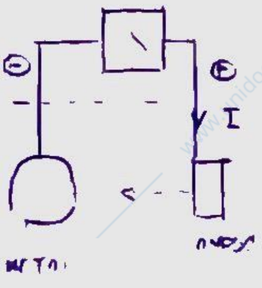
} CP provides e^- to O_2 → steel isn't forced work in corrosion

NB CP can be obtained using a galvanic anode → ~~[illegible]~~ provides a current which protect my metal (for ex, Mg, Zn, Al) $E_m > E_{anode}$

CP with galvanic protection works good in seawater (low resistivity) [0.2 Ωm]
→ throwing power ↑ → L_{max} ↑, it isn't so good in soil

Critical point of CP with galvanic is that it works with a fixed ~~threshold~~ driving voltage (max ~ 1 V)

Other system CP with impressed current system DC feeder with flexible ΔV applied (max 30 V)



Anode is a metal which by the current isn't necessary use a low noble metal, because ΔV is imposed by the feeder

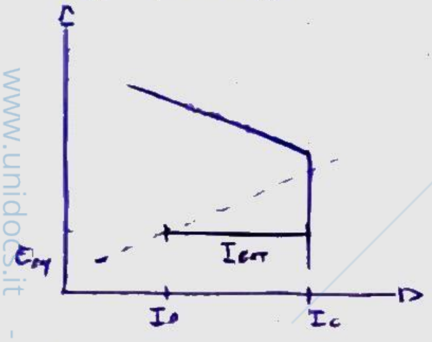
→ AUXILIARY ELECTRODE

Sufficient condition to stop corrosion

- ACTIVE $E_{prot} \leq E_{NERNST}$ → immunity (or quasi immunity)
- PASSIVE $E_{prot} < E_{pit}$

  $E < E_{pp}$ → we reform passive film (perfect passivation zone)

- CP immunity



Applying ex c, $E < E_{eq}$ → metal works in immunity zone

NB In most of case is acceptable $c_{corr} \sim 10 \mu m/y$

→ $E_{prot} > E_{eq}$ → QUASI IMMUNITY

in soil
| - 0.95 V CSE IMMUNITY
| - 0.85 V CSE Q IMMUNITY
| works in Q.I instead of IMM is an economical reason

NB I_{prot} depends by the surface of the metal. S↑ → I_{prot}↑ → cost ↑

→ cathodic protection is used in combination with coating protection

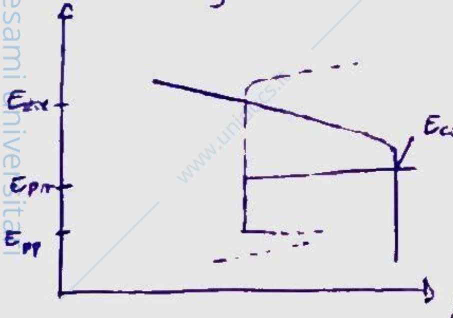
→ $\boxed{I_{prot} = i_{L,O_2}\ S\ (1 - \varepsilon_{coat})}$ → coating reduces exposed surface

NB ε changes in time because of degradation

- CP passivity (as SS in Cl^- or CS in concrete)

  (Cl⁻ contaminated)

Used to stop pitting when it's already started → I want metal works again in passive range → $E_{pp} < E_{prot} < E_{pr}$



main reaction become H_2 evolution

- i_{corr} ↑↑ (around 10 c.c., according to H_2 Tafel law → cost ↑↑)
- H_2 Formation
  - cathodic disbonding (delamination of coating)
  - H_2 embrittlement (only for high strength metal)

due to different pot distribution along the pipe

(green) OVER PROTECTION

cathodic current is the i required by cathodic process at $E = E_{prot}$ → i we have to provide to our system

NB Problem if E_{prot} ↓↓: we may have ~~degradation~~ delamination of the coating → E ↓↓ → H_2 evolution with formation of large bubbles → disbonding of the coating

→ η_{coat} ↓ → I ↑

NB For ex Al, no immunity pot → vs E_{eq} ↓↓↓ → i_{cat} ↑↑ → pH ↑↑ → we more to corrosion region (amphoteric metal) → only passivity potential

→ CATODIC PROTECTION INCREASE ALCALINITY (pH) → PROBLEM FOR AMPHOTERIC METAL

good for CS

NB CP increases (locally) pH > 9 → calcareous deposit that works as a natural coating
↳ i_{prot} for CS in sea water ↓ with time

in ~ -0.85 V CSE |
-1.2 V CSE | → over protection condition → E_{cp} ↓↓ → problems due to HE

NB CP is more difficult in acid env., because it will need more e^- → IS NOT EASY TO POLARIZE METAL WITH HYDROGEN EVOLUTION

CP by galvanic anode

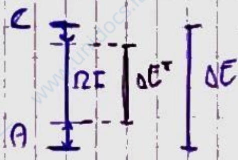
Condition: $E_{corr-AN} < E_{corr-MET}$, For basic metal (CS) → Zn, Al, Mg

NB CS is an anode for SS

es η_{Mg} ~ 50% very low, because Mg has a very high self corrosion (E_{Mg} ↓↓)

Theo cons → mass consumed
practical cons

$\eta < 1$ { impurities, which can lead to passivation of the anode / self corrosion of the anode



$$I = \frac{\Delta E}{\Delta R} = \frac{E_{corr-c} - E_{corr-A}}{R_E + R_{cable} + \eta_a + \eta_c} = \frac{E_c^* - E_a^*}{R_E}$$

important only for long cable

→ ΔE^* consider η_a, η_c effect

→ E_c, E_a working potential $E_c = E_{corr-c} - \eta_c$

$E_A = E_{corr-A} + \eta_A$

ρ↑ → R_A↑

S_A↓ → R_A↑

Driving voltage of the anode: $\Delta E = E_{prot} - E_A$

In order to calculate I, we need to know resistance of the electrolyte

$R_E = \boxed{R_A} + R_C$

↳ $R_C \ll R_A$ because anode surface is lower

We use different relations to calculate R_A based on anode geometry and resistivity

To locally reduce R_A, we used a backfill

- IR drop ↓ → clay effect (absorbes moisture and sodium sulphate)
- risk of passivation ↓ : if the anode passivate, the anode isn't able anymore to provide high current (sulfate ions effect) - sulfate reduces passivation - es. gypsum (Ca-sulfate))
  ↳ in sea water, no need of b.f. because Cl^- break the passive film

NB Minimum number of anode
- pot distribution $N_P = L_{pipe} / L_a$ — throwing power
- current demand $N_I = I_{prot} / I_a$ — anode output ↳ $\frac{\Delta E}{R}$
- duration $N_W = W / W_a$

} max of this 3 number is the n of anode used

$$\boxed{\Delta M = \frac{M_m}{zF} \frac{I \, \Delta t}{\eta}}$$

consumption $\left[\frac{kg}{Ay}\right] = \frac{M_m}{zF}$

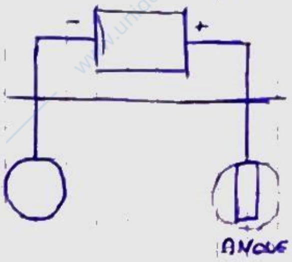
$$\left[\frac{kg}{\cancel{kmol}} \cdot \frac{\cancel{kmol}}{\cancel{mol\,e^-}} \cdot \frac{\cancel{mol\,e^-}}{\eta}\right]$$

in CS | $\Delta E_{Zn} = 0,2$
$\Delta E_{Mg} = 0,7$
protect' | $\Delta E_{Al} = 0,25$

ΔE ↑ Mg
Al
Zn

CP by impesed current

Very flexible, applied in env. with high resistivity, it can provide a lot of I



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

- SOLUBLE ANOD : scrap ~~diode~~ metal of ~~a~~ the pipe → cheap, but anod is consumed
- INERT ANOD . Ti - MIX METAL OXIDE (Ti cover by noble metal) or Si - Fe

$2H_2O \rightarrow O_2 + 4e^- + 4H^+$ anod provides current without corrosion

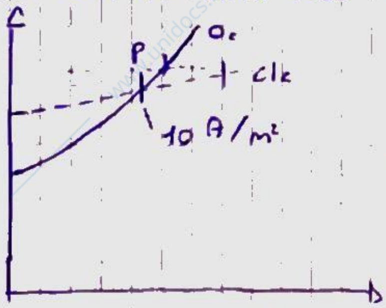
(anodic reaction, occurs at $E > E_{T.PASSIVE}$

→ not consumed, but expensive

NB By the way, ΔV is provided by generator, not by the anod

NB With inert anod, we have pH ↓ (H⁺ production) locally if we use SS, we have corrosion because pH ↓↓ dissolves passive film ; Ti - MMO is instead protected (can MMO corrosion resist that at low pH !!)

!!! If we have an INERT ANOD in seawater we have also Cl⁻ (20 % sw)



$E > E_P$ → highest contribution due to Cl_2 ev.

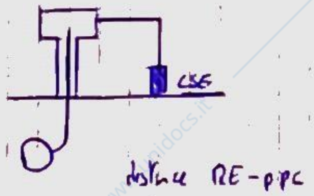
$2Cl^- \rightarrow Cl_2 + 2e^-$

NB Reaction at anod isn't spontaneous : it forced by dissifeeder

$$\boxed{V = \underset{\text{no for soluble}\atop \sim 2.3V \text{ for inert}}{\overset{\text{with anodic reaction + thermodynamic barrier}}{\boxed{\psi^*}}} + R I_{TOT}}$$

Cathodic protection monitoring

Def IR - Free potential : it must be lower than E_{prot} (-0.85 VCSE in soil)



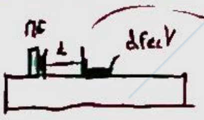
$$\boxed{\underset{\text{measured value}}{E_{on}} = E_{IR-free} + \overset{\text{ohmic drop in soil}}{IR}}$$

→ in the reading, we want to eliminate the ohmic drop

$$IR = \underset{\text{soil resistivity}}{\rho} \cdot i \cdot \overset{\text{distance RE-pipe}}{d}$$

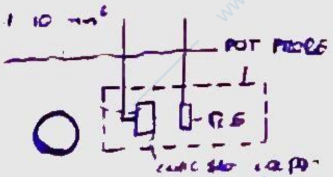
→ it must be eliminated or strongly reduced, ~~we can eliminated~~ we have to strongly reduced i or d

- ~~when~~ Fixed reference electrode - distance : electrode is put very close to the pipe → d ≈ 0
  electrode maintain is position during it's service life
  problem once electrode is installed, we have no more the possibility to control electrode
  → problem of duration ⊗
  → we don't know where the defect is located ⊗

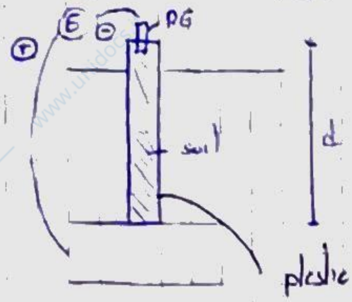


d ≠ 0 → R not negligible
→ very sensitive to interference current

- potential probe - distance : ~~we create a~~ ~~with fixed~~ corrosion coupon made of same steel of the pipe, connected to the pipe , coupon is representative of the coating defect we think to have on our pipe
  Problem of duration ⊗



- Luggin tube - distance [illegible] probe using a portable reference electrode



inside tube, no current circulation → it's like we take the measurement on the pipe
→ no ΔV in the tube

plastic tube: current cannot enter in the tube because there is no ΔV in the tube

- elimination of i (NB we can't eliminate stray current) — other current different from protection current

IE-I elimination: when I eliminated i_prot, metal needs some time to return at E = Ecorr (free corr) (~ hours day); if we take measure within n s after ~~[illegible]~~ current interruption, we measure E_prot

NB If we are in overprotection, when we stop ~~[illegible]~~ current, we block H2 evolution and we eliminated the anodic overvoltage related to H2 ev → E_OFF > E_real

(H2 eliminations is in the order of 10^{-3} s → problem to identify overprotection

- 100 mV decay criterion: ON-OFF meas. is taken once i is stopped and after one day

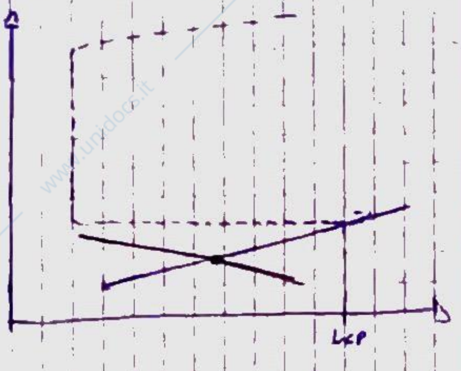
~~ONLY~~ $E_{1\,DAY} - E_{1\,second} > 100$ mV : used if we can't able to verify −0.85V criterion

means that our system is working at least a 100 mV lower than ~~[illegible]~~ E free corr
→ CR is at least 10 times lower than free corr. condition

used if we're not able to reach −0.85 V for ex in case of deterioration of the coating

Anodic protection

Used for active passive metal, anodic polarization increases E, anodic current is used to form passive film on an act. pas metal which works in anodic condition



ANODIC vs CATODIC criterion is the amount of i required by the protection mechanism

Coatings

Physical barrier, has a good efficiency if is not damaged

- Metallic - less noble: most used approach, coating is anodic respect to metal protected metal → if we have defect, defect doesn't corrode → ACTIVE PROTECTION (for the scratch)
- Metallic - more noble: risk of galvanic coupling is avoided or large resistance
- Non metallic: high thickness (> 1 mm) ORGANIC
  low thickness (< 1 mm)

only barrier effect

because of small i_corr (IN ~~[illegible]~~) ATMOSPHERE

ANODE CORRODES FORMING METAL OXIDES WHICH COVER THE SCRATCHES

ANODIZING: increases thickness by an anodic treatment

FINISHING → barrier and esthetic effect
INTERMEDIATE → barrier effect ≈ 100 μm
PRIMER (Zn)
METAL → microcell mechanism - active protection

Painting must be replaced every ~ 5 years because of degradation
Zn ~ 85% in a binder of resin

Change of environment

- Oxygen removal
  - stripping (physical): inert gas remove O_2 from our solution
  - oxygen scavenger: ammonium bisulphite (T_{room} ✓, pH ↑ 5) | chemical
  - hydrazine (pH not ✓, T 110 C ✗) | chemical
- Reduction of overvoltage

Def $\boxed{\varepsilon = \frac{CR_0 - CR_{inh}}{CR_0}}$ depends on the amount of inhibitors put into the electrolyte

Inhibitor changes the slope of det or and curve (changes the kinetic)
Inhibitors starts to works after a minimum consumption. If $C < C_{min}$, we can see an increase in corrosion rate (for active passive metal which work in active region)

Corrosion in soil

Soil: mix of solid particles, water and air
- aerobic: soil with O_2 (sand)
- anaerobic: soil without O_2 (clay)

it depends on diffusion, in correlation with H_2O content

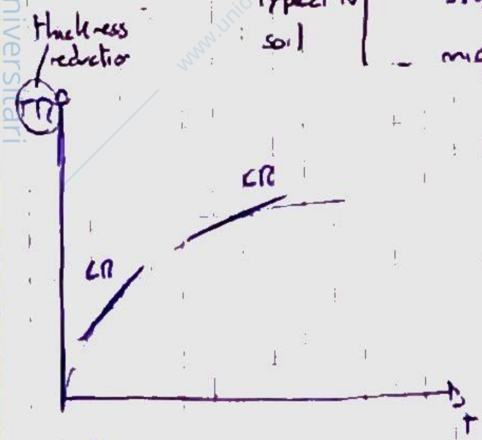
$[H_2O]\downarrow \rightarrow [O_2]\uparrow$
O_2 content, H_2O content → resistivity of the soil

NB to have corrosion we need both O_2 and H_2O (electrolyte)

NB $[O_2]$ depends also on the depth, it's higher near to surface

Type of corrosion:
- general corrosion | aerated soil
- localized | aerated soil

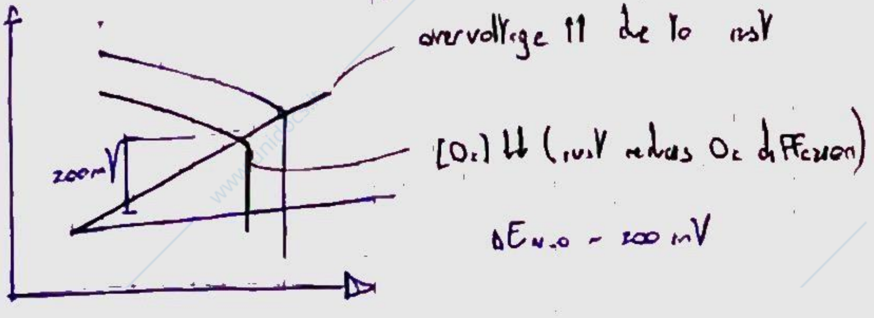
Typical for soil:
- stray current corrosion
- microbiological corrosion (deaerated soil)



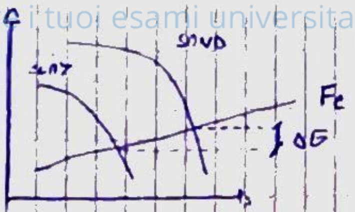
NB CR strongly decreases in time: presence of rust reduces O_2 diffusion to the metal surface (for generalized corrosion)

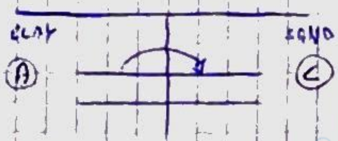
NB → CR < 10 μm/y

NB This layer isn't uniform, moreover, we have other types of corrosion → cathodic protection



In presence of Cl^- and S ions, rust layer is very porous → CR doesn't decrease ($Cl > 200$ ppm $S > 1000$ ppm)





soil with ~~different~~ differential aeration → corrosion is driven by macrocell mechanism

ΔE is due to different aeration

CS

CLAY	$E_{corr} = -0{,}6 / -0{,}7$	V CSE
SAND	$E_{corr} = -0{,}3 / -0{,}4$	V CSE

NB ΔE is not so high; moreover, L_{mk} is low → CR is not so high

region interested by current circulation is small

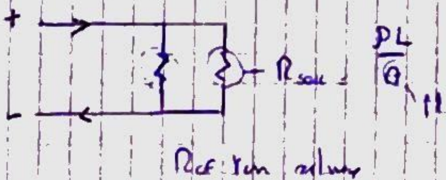
Solution: cathodic protection

Corrosion can be due by interference current in soil — extend curr that intercept the pipe producing corrosion

- stationary: current is constant (es other CP protection with DC feed)
- non stationary: electric field is variable (es tram) → current flow in soil because high A

important both intensity and duration

low in duration but high in intensity

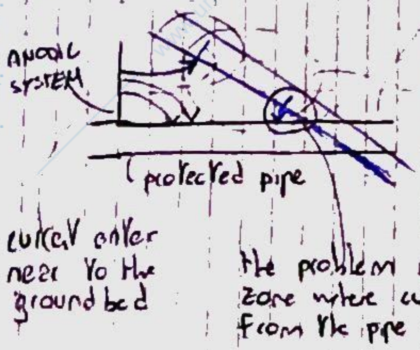


R_{DC}: tram railway

How to stop

- drainage: strong electrical connection to protect both structure (can be done if the pipe is already underground (NB we should pump more current) used for structure already existing
- use insulating joint: joint introduce an extra resistance (we need more than one joint) used for new structure

STATIONARY



NB not in contact (if they were in contact, our pipe, ~~other pipe~~ would be protected)

a part of current of the protection in the system enter in a point and exit from another

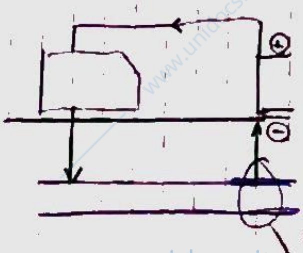
current enter near to the ground bed

the problem is the zone where curr exit from the pipe

NB I exits in correspondence of the coating defect

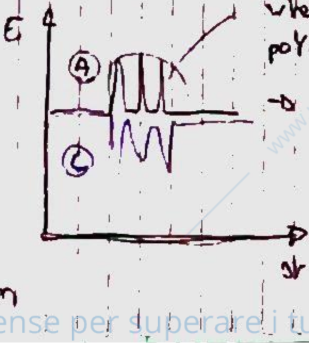
$$L = \frac{I_{int}}{A_{defect}}$$ if A_{defect} ↓↓ → L ↑↑ → CR ↑↑ (mm/y)

NO STATIONARY (DC current)



low distance

anodic zone → corrosion



when we see variation in potential, we have interference → we map potential for each

For prevention, we can combine both Bonds and drainage

Microbiological in soil is provoked by SRB in deaerated soil (anaerobic bacteria)

→ very severe localized corrosion

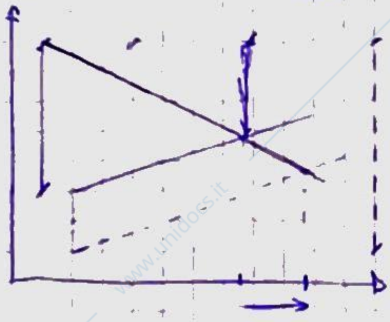
IF $S > 200$ ppm → MIC corrosion (bacteria catalized the corrosion, cat process is H_2 evolution)

Ⓐ $4Fe \to \boxed{4Fe^{2+}} + 8e^-$

Ⓒ $8H^+ + 8e^- \to 8H$

BAC $SO_4^{2-} + 8H \to \boxed{S^{2-}} + 4H_2O$ → the overvoltage of this reaction is reduced by bacteria

$Fe^{2+} + S^{2-} \to FeS$ ~ 10^{-20} → (Fe^{2+} ↓↓↓) → $E_{eq,Fe}$ ↓↓



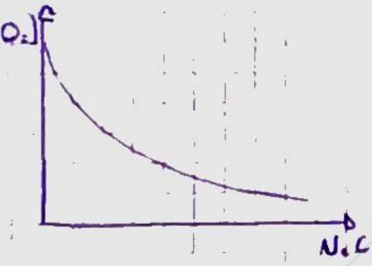
→ ΔE ↑ → CR ↑

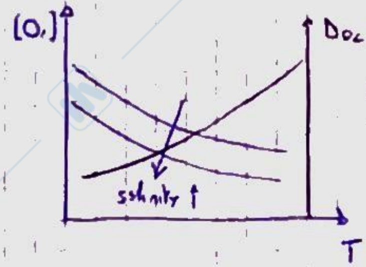
Cathodic protection in deaerated soil with bact

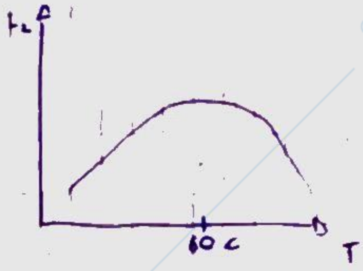
→ $\boxed{E_{prot} = -0{,}95 \text{ V CSE}}$ (for C.S)

Corrosion in water

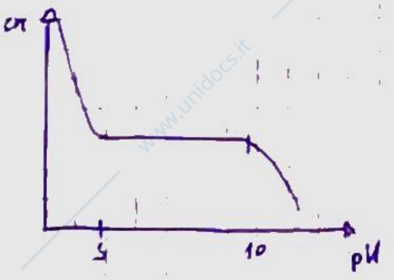
- CR is, for steel, i_{LIM} ; $i_L \in [10\ mA/m^2$ (stag) 2 A/m^2 (max turb)]







- pH



- low pH: acidic condition $H_{2,eq}$ ↑ → HE becomes main process
- neutral condition: i_L not depends on pH
- high pH = passivity of the metal

- Scaling tendency: precipitation of calcareous deposits (in sea water), Formation of calcareous deposit increases with pH (we need $[OH^-]$ ↑↑) pH > 9-10 → in cathodic protection

Def Langelier index: $pH - pH_{SAT} > 0$ → scal (< 0 → no scal)   Ryzn: $2pH_s - pH$

min PREN 40   salinity ~ 35 g/L (total of salts)   high Cl^-, bacteria } PREN ↑↑

Seawater: pH ∈ [8,1 - 8,3]   corrosion rate depends also on depth

Hardness: ability of the water to form scaling (depends on Ca^{2+} Mg^{2+} content)

→ measured in French degree [1°F = 10 ppm $CaCO_3$]

critical for Im rec. (ρ ↓↓)   sea ρ ~ 0.2 Ωm   fresh ρ ~ 20 Ωm

NB Sal ↑ → ρ ↓ (cond ↑)

NB $[O_2]$ changes with depth (due to diffusion)

→ high depth → anaerobic condition → bacteria corrosion (MIC)

NB oxidizing bacteria with catalize cathodic process (O_2 [illegible] reducing cathodic fraction → E_{corr} ↑ ~ 20 mV → risk of pitt (problem)