

# Corrosion

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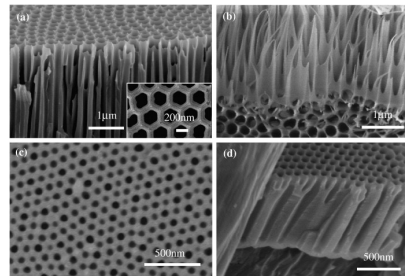
- 1. Main concepts**
- 2. Corrosion reactions**
- 3. The electrode potential**
- 4. Forms of corrosion**
- 5. Determination of corrosion rate**





# Definition of corrosion

- Corrosion is the disintegration of a material into its constituent atoms due to chemical reactions with its surroundings. (Wikipedia)
- Corrosion is an irreversible interfacial reaction of a material with its environment, resulting in the loss of the material or in the dissolving of one of the constituents of the environment into the material. (ISO Standard)



# Economic importance of corrosion

- Direct losses: replacement of corroded materials and of equipment ruined by corrosion
  - 5 tones of steel lost by corrosion every second
- Indirect losses: cost of repair and loss of production
- Cost of corrosion protection : Use of more expensive corrosion-resistant materials, application of surface coatings, cathodic protection systems
- Cost of corrosion prevention : maintenance, inspections, corrosion prevention by design

# Corrosion as a system property

Corrosion depends on the combination of:

- - Material  
composition, structure, surface
- - Environment  
oxidizing agents, aggressive ions, ions, adsorbing species,  
complexing species
- - Physical parameters  
temperature, flow conditions, stresses, contact with other metals

1. Main concepts

## 2. Corrosion reactions

**Corrosion systems**

**Cathodic and anodic reactions**

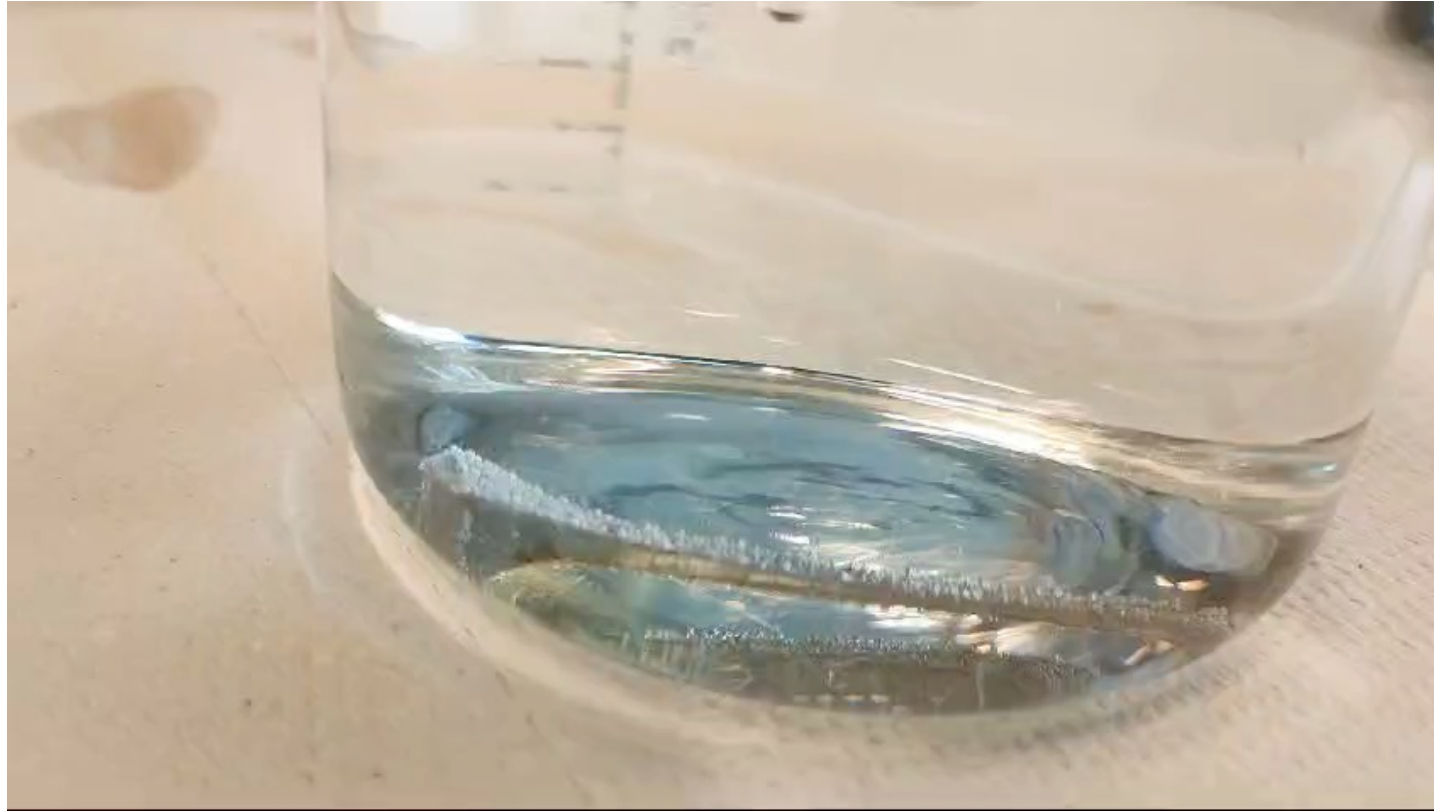
**Corrosion products**

3. The electrode potential

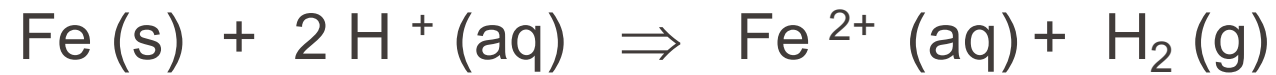
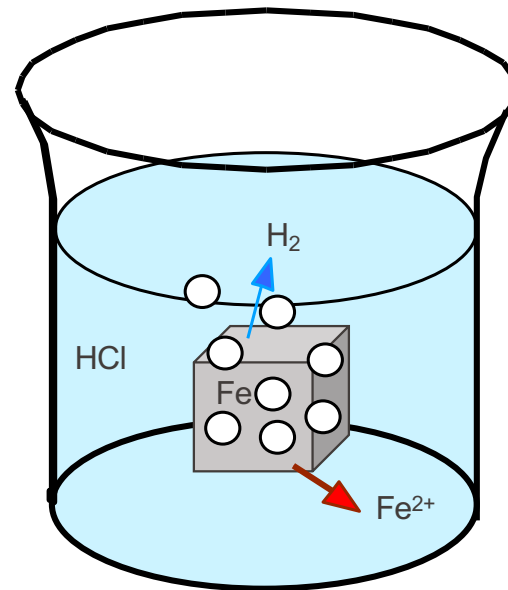
4. Forms of corrosion

5. Determination of corrosion rate

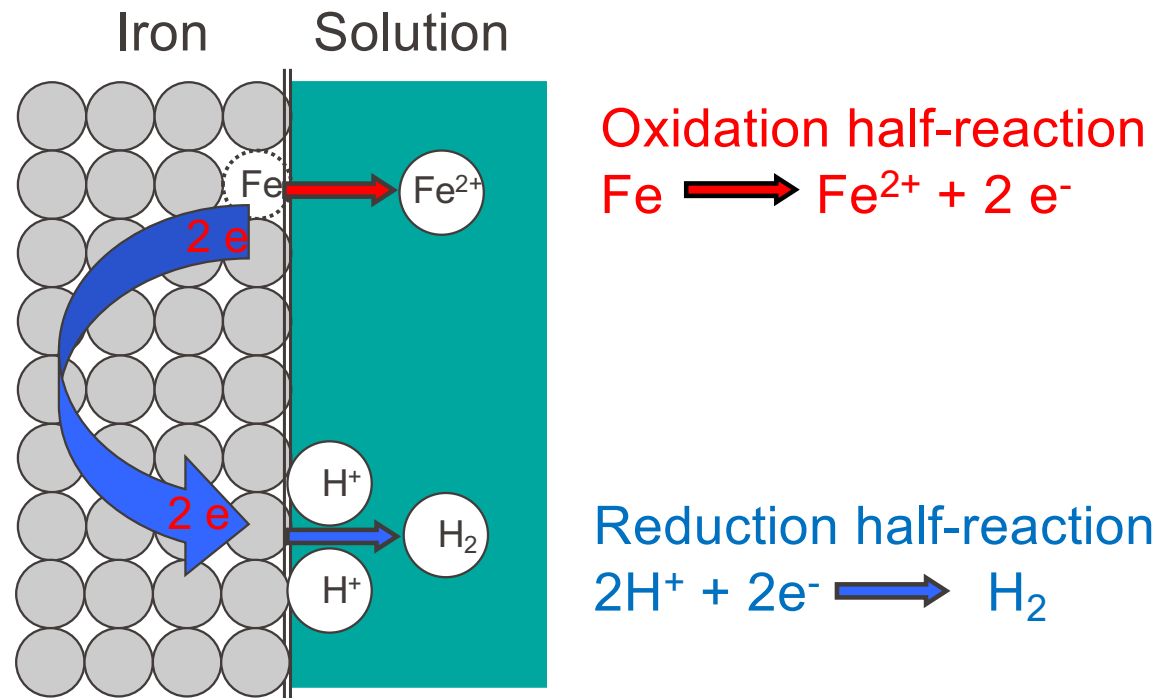
# Nail (iron) immerse in an hydrochloric acid solution



# Corrosion of iron in hydrochloric acid



# Electrochemical reactions



# Typical oxidizing agents encountered in corrosion

- Acidic solutions (pH < 7):

Oxidizing agent: proton H<sup>+</sup>



- Solutions in contact with air:

Oxidizing agent: oxygen molecules O<sub>2</sub> dissolved in the solution



# Example: corrosion of pillars

- Steel (Fe) pillars



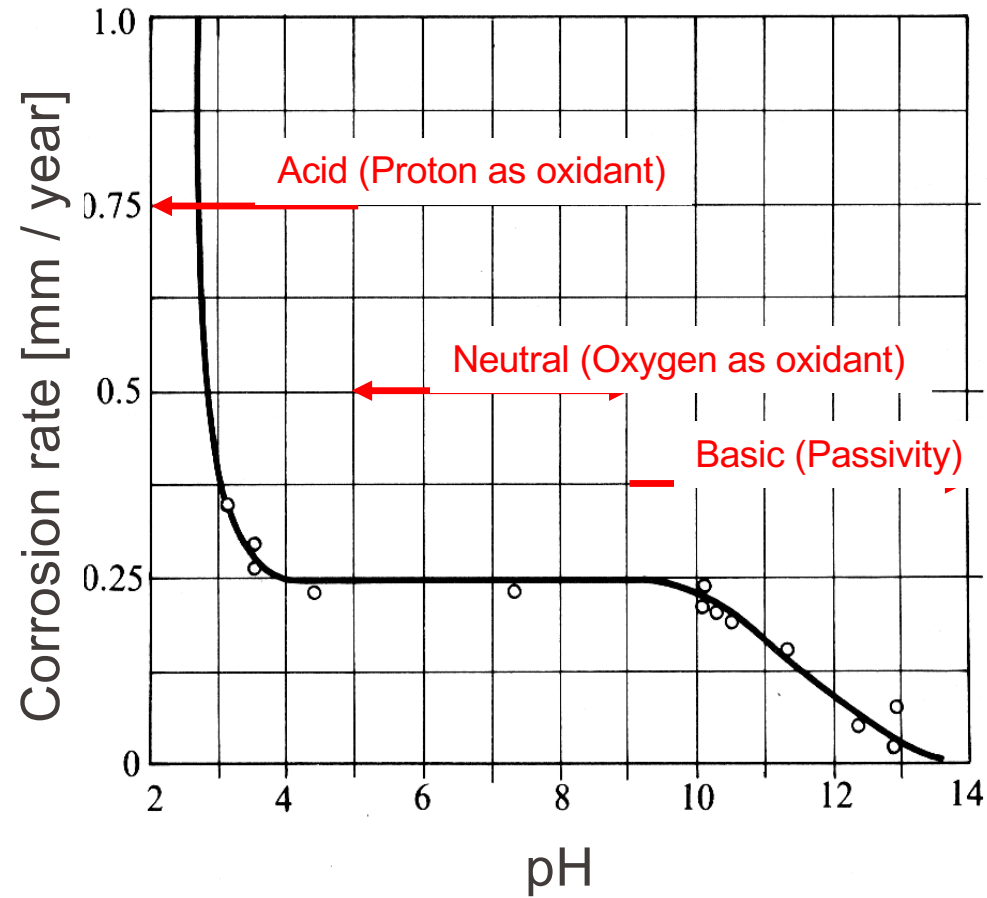
- Natural water:



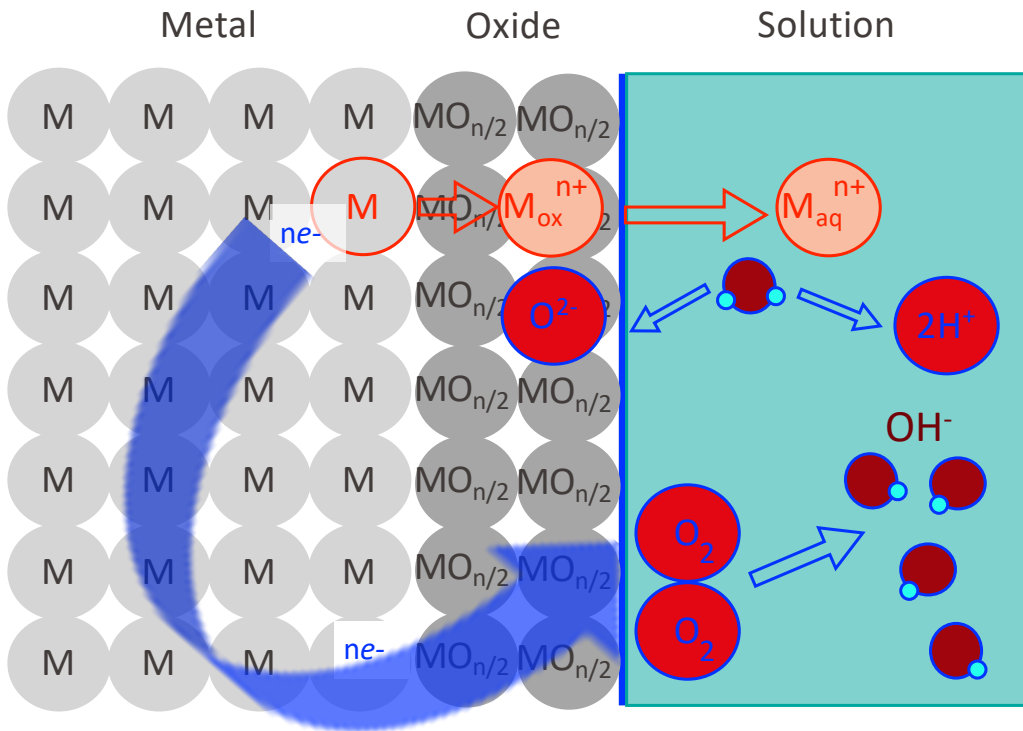
- Global reaction:  $2\text{Fe} + \text{O}_2 + 2\text{H}_2\text{O} \Rightarrow 2\text{Fe}^{2+} + 4\text{OH}^-$



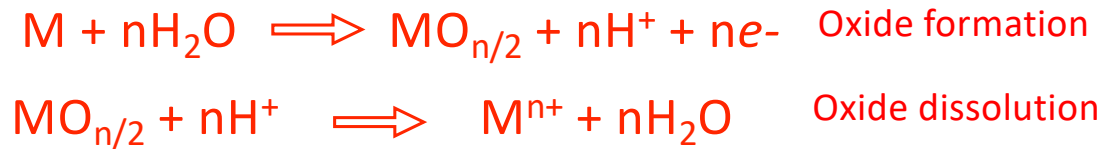
# Corrosion rate of iron changes with solution acidity



# Electrochemical reactions in an actively and passively corroding metal



## 2-step oxidation reaction:



## Reduction reaction:



# Corrosion products

- Dissolved ions

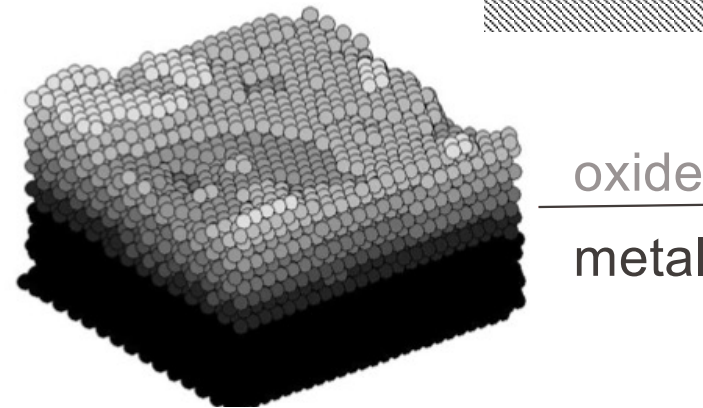
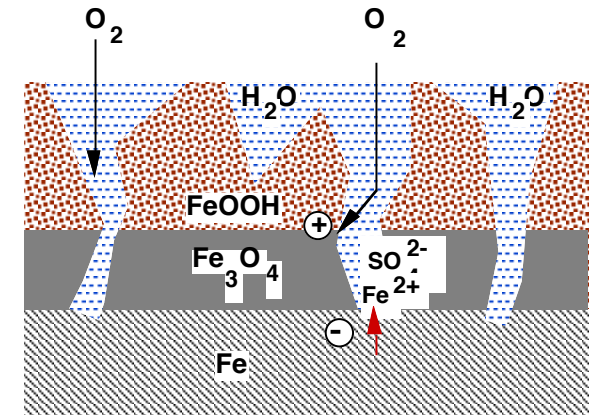
Example: acid corrosion of iron:  $\text{Fe} \Rightarrow \text{Fe}^{2+} + 2\text{e}^-$

- Non compact films

Examples: rust, copper patina

- Compact thin films

Example: passive film on aluminium



# Consequences of the electrochemical nature of corrosion: Faraday's law and corrosion rate



$$v_{\text{cor}} = i_{\text{oxidation, metal}} / n F$$

$v_{\text{cor}}$  = corrosion rate in (mol/cm<sup>2</sup>s)  $F$  = Faraday constant (96500 C/mol)

- Conversion to engineering units:

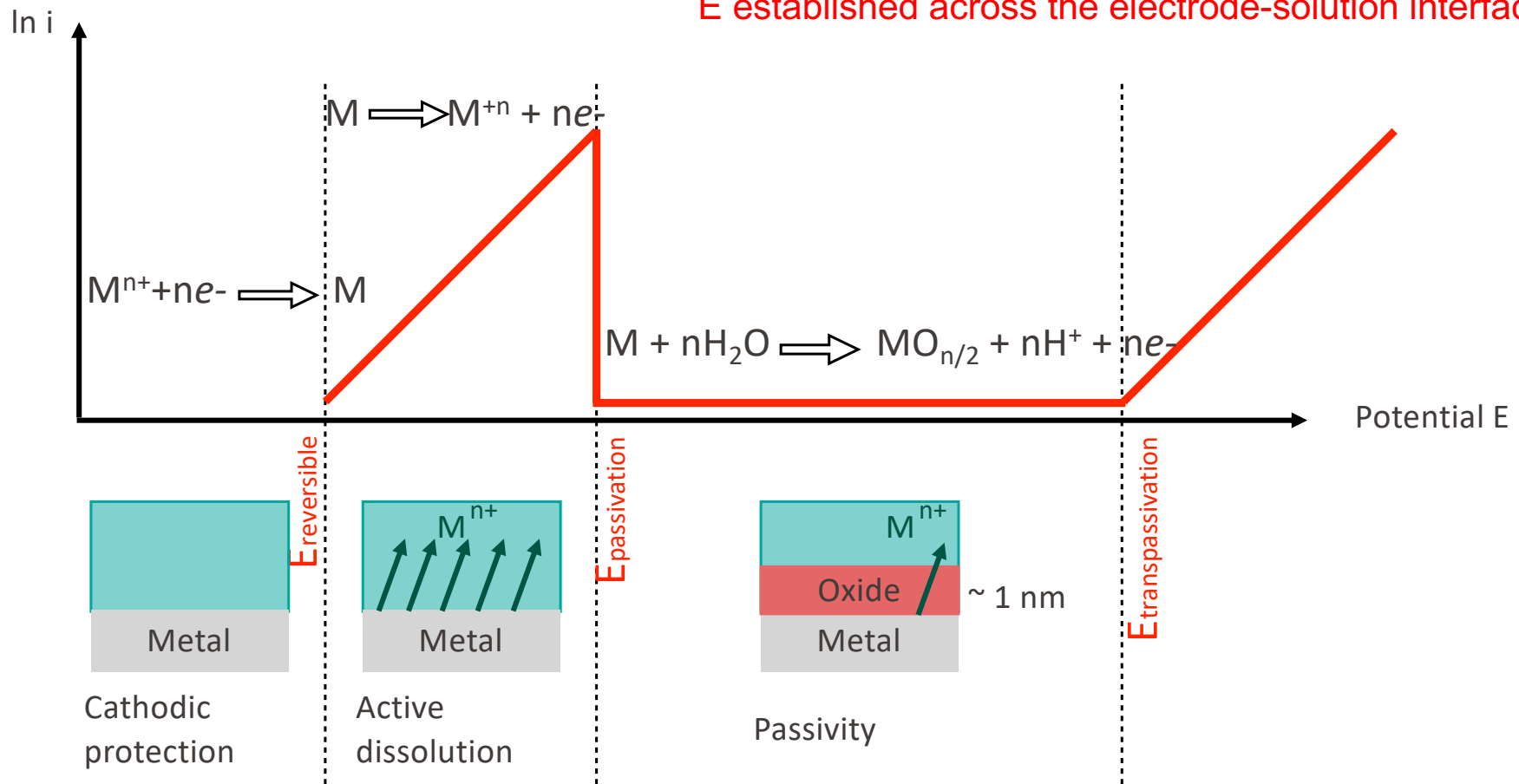
$$v_{\text{cor,m}} = \text{corrosion rate in (g cm}^{-2}\text{s}^{-1}) = M v_{\text{cor}}$$

$$v_{\text{cor,l}} = \text{corrosion rate in (cm s}^{-1}) = M \rho^{-1} v_{\text{cor}}$$

$M$  = molar mass of metal (g/mol)  $\rho$  = density of metal (g/cm<sup>3</sup>)

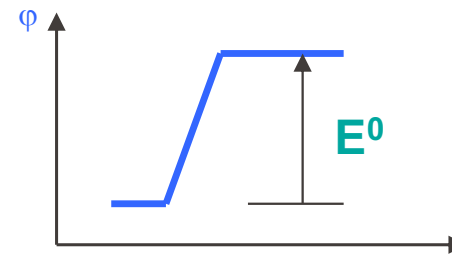
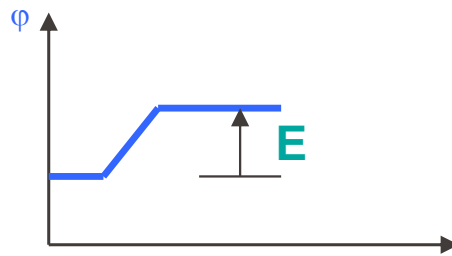
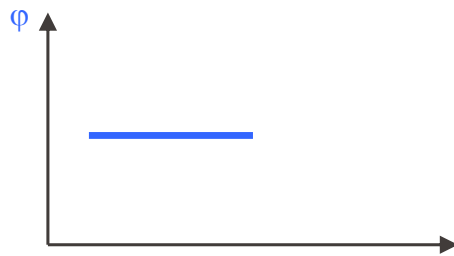
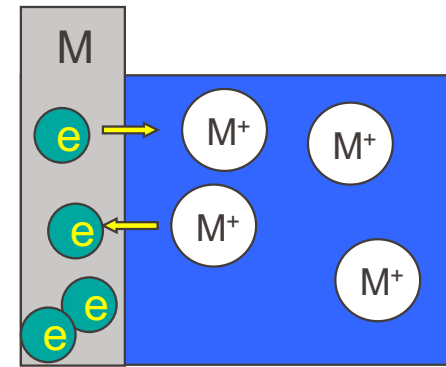
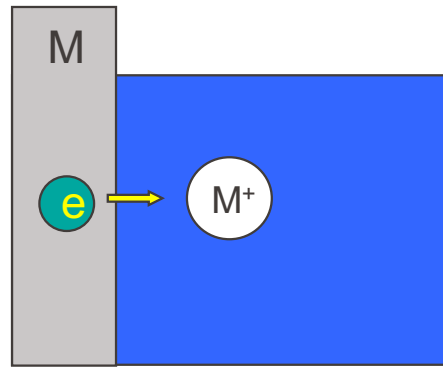
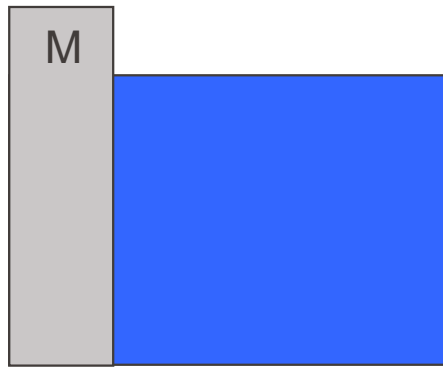
# Consequences of the electrochemical nature of corrosion: corrosion versus electrode potential

Corrosion reactions are driven by the electrode potential  $E$  established across the electrode-solution interface



1. Main concepts
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# Electrode potential



Non equilibrium

Equilibrium: reversible potential  $E_{rev}$

# Standard equilibrium potentials $E^0$ of electrode reactions

Electrode reaction	$E^0$ (V)
$\text{Mg}^{2+} + 2\text{e}^- \leftrightarrow \text{Mg}$	-3.045
$\text{Al}^{3+} + 3\text{e}^- \leftrightarrow \text{Al}$	-1.670
$\text{Ti}^{2+} + 2\text{e}^- \leftrightarrow \text{Ti}$	-1.630
$\text{Cr}^{3+} + 3\text{e}^- \leftrightarrow \text{Cr}$	-0.900
$\text{Zn}^{2+} + 2\text{e}^- \leftrightarrow \text{Zn}$	-0.760
$\text{Fe}^{2+} + 2\text{e}^- \leftrightarrow \text{Fe}$	-0.440
$\text{Ni}^{2+} + 2\text{e}^- \leftrightarrow \text{Ni}$	-0.257
$2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$	0.000
$\text{Cu}^{2+} + 2\text{e}^- \leftrightarrow \text{Cu}$	0.340
$\text{Ag}^+ + \text{e}^- \leftrightarrow \text{Ag}$	0.799

$$E^0 = - \Delta G^0 / n F$$

*Conditions:*

25°C

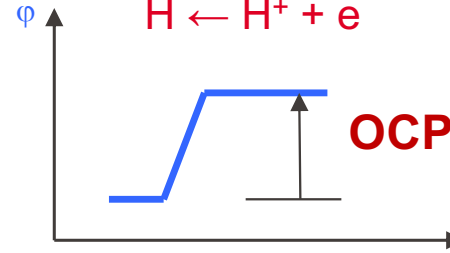
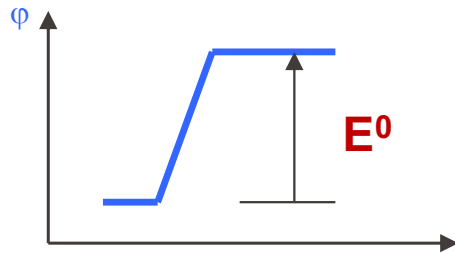
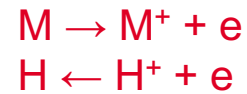
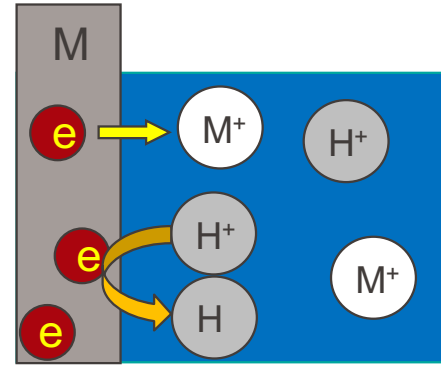
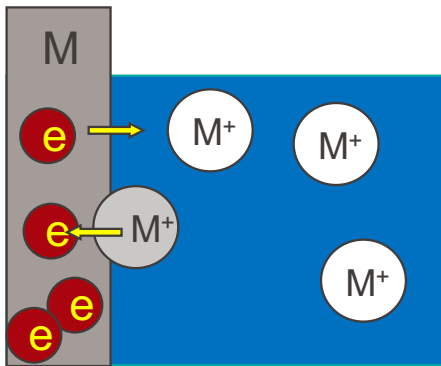
1 M activity of soluble species

1 atm activity of gaseous species

# OCP vs Equilibrium potential

One reaction occurring on the electrode: **simple electrode**

Two or more reactions occurring on the electrode: **mixed electrode**

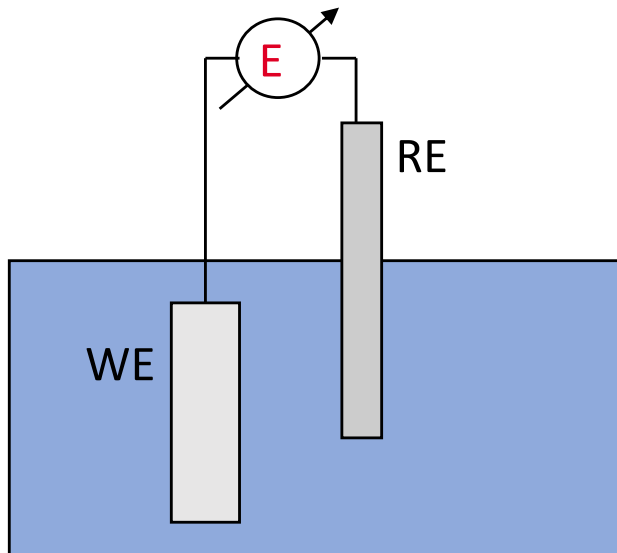


Equilibrium potential  $E^0$

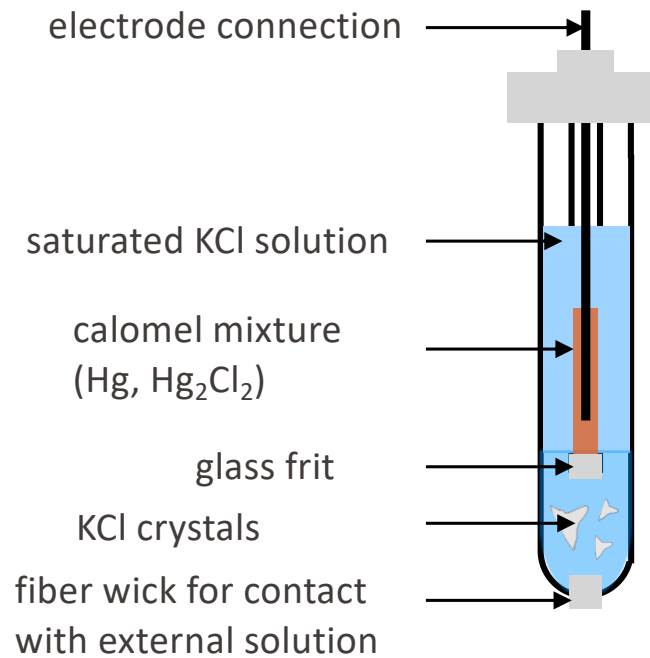
Open Circuit Potential OCP

# Open circuit potential (OCP)

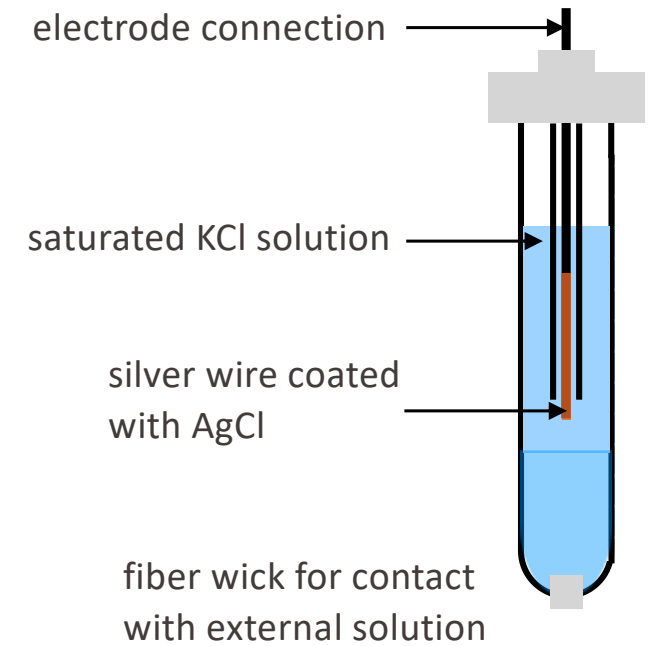
High impedance voltmeter



## Calomel electrode (SCE)



## Ag/AgCl (SSE)



# Equilibrium and OCP potentials

Standard (reversible) potential

Corrosion potential in flowing aerated seawater (average)

Magnesium -3.045 V

Magnesium -1.35 V

Aluminium -1.67 V

Zinc -0.75 V

Titanium -1.63 V

Aluminum -0.65 V

Chromium -0.90 V

Iron -0.40 V

Zinc -0.760 V

Copper -0.1 V

Iron -0.440 V

Nickel 0.1 V

Nickel -0.257 V

Silver 0.1 V

Copper 0.340 V

Titanium 0.25 V

Silver 0.799 V

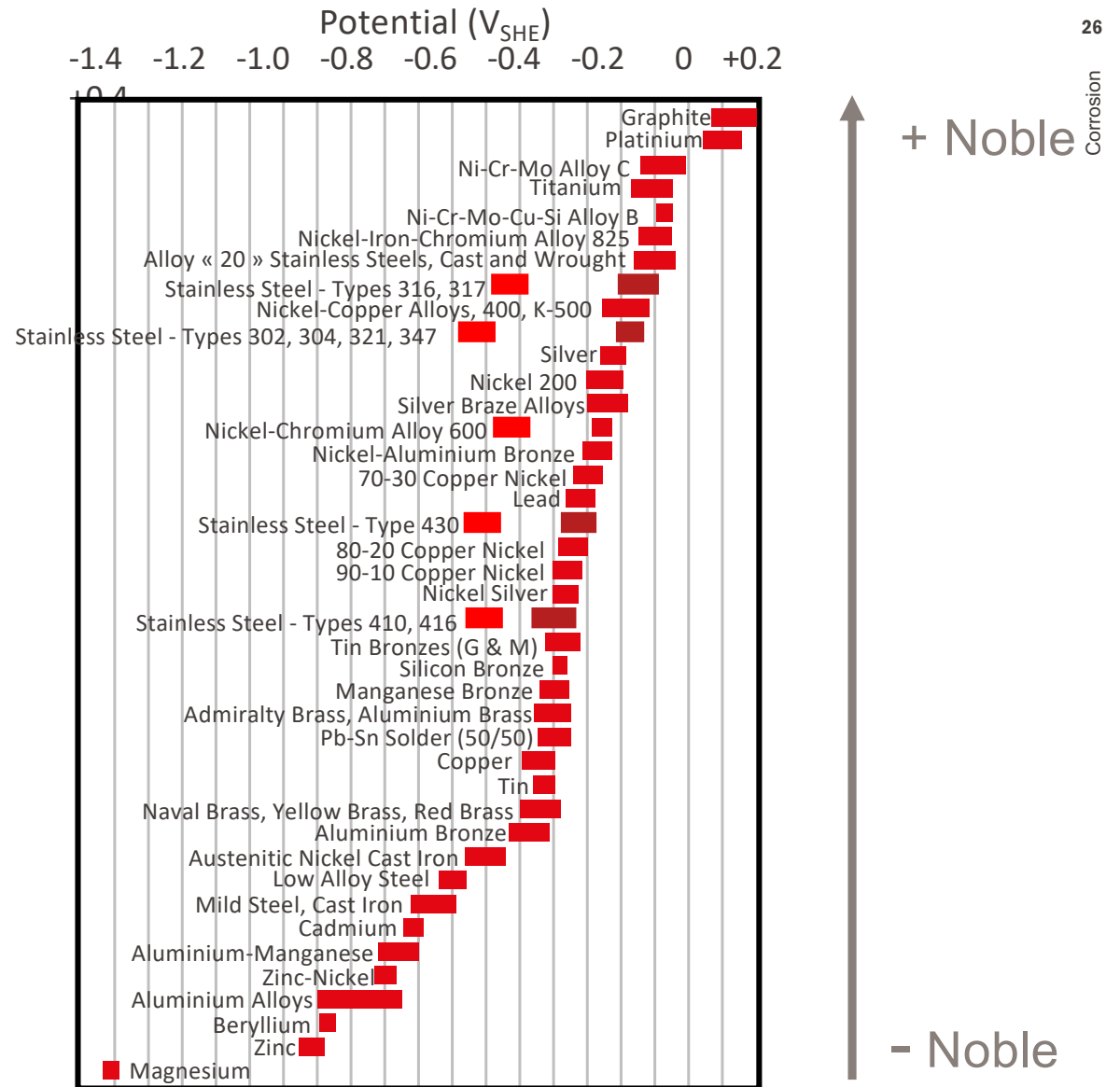
Chromium 0.35 V

# OCP of titanium and its alloys

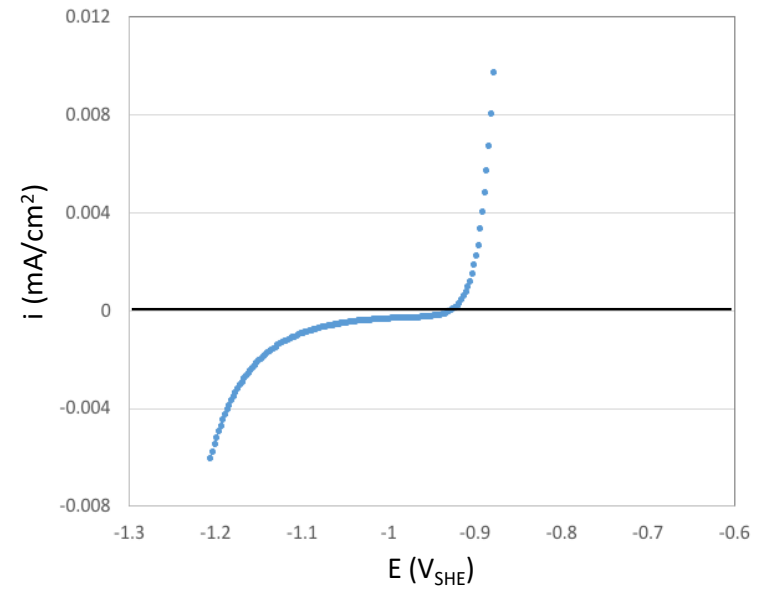
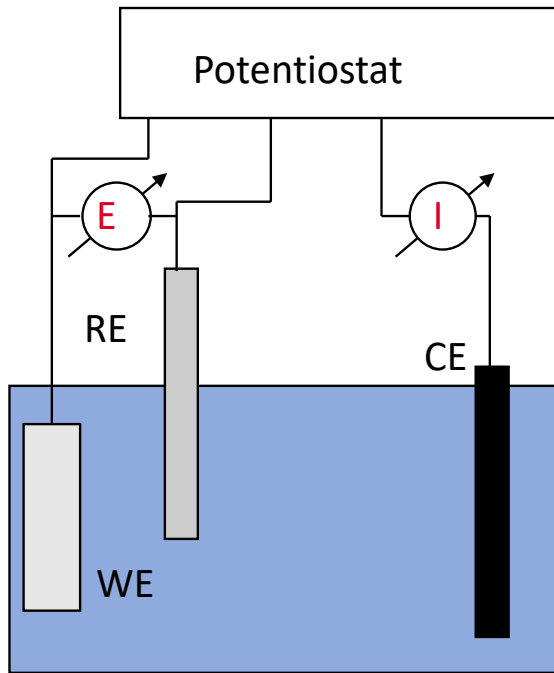
Influence of	Material	Environment	OCP ( $V_{SHE}$ )
Acidity	Ti CP	H <sub>2</sub> SO <sub>4</sub> 0.05 M H <sub>2</sub> SO <sub>4</sub> 0.5 M	-0.35 -0.69
Chemistry	Ti6Al4V	PBS* PBS + albumin PBS + collagen	-0.18 -0.32 -0.41
Oxidising agents	Ti6Al4V	Calf serum Calf serum + 0.1% H <sub>2</sub> O <sub>2</sub>	+0.19 +0.3
Alloying elements	Ti Ti 0.05% Pd	NaCl 4.3M	-0.51 -0.03

# Galvanic series in seawater

■ Active state  
 ■ Passive state

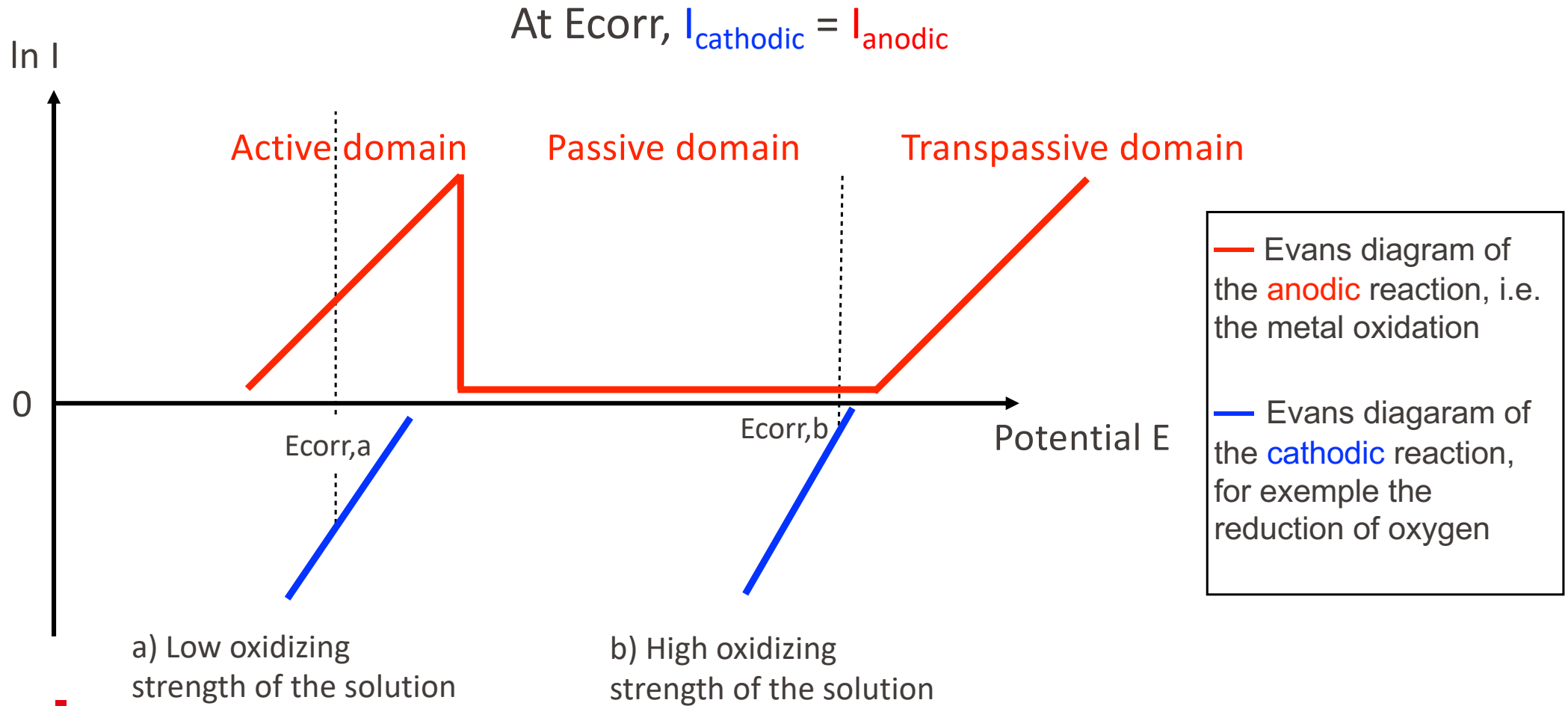


# Corrosion potential ( $E_{\text{corr}}$ )



Polarization curve E-i of Sn in citrate buffer, pH 4.5

# Corrosion potential

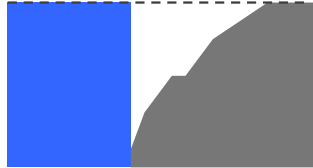


1. Main concepts
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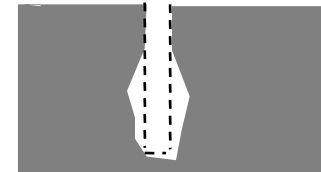
# Eight types of corrosion: Fontana and Green



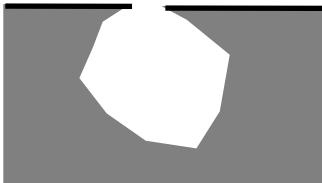
*uniform corrosion*



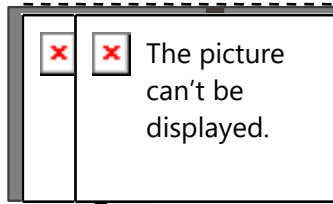
*galvanic corrosion*



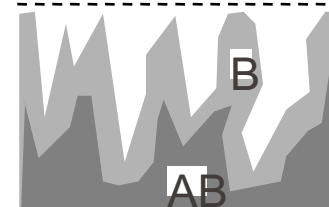
*crevice corrosion*



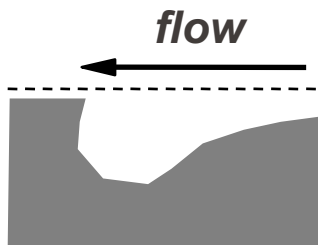
*pitting corrosion*



*intergranular corrosion*



*selective leaching*



*erosion corrosion*



*stress corrosion cracking*

can't be displayed.

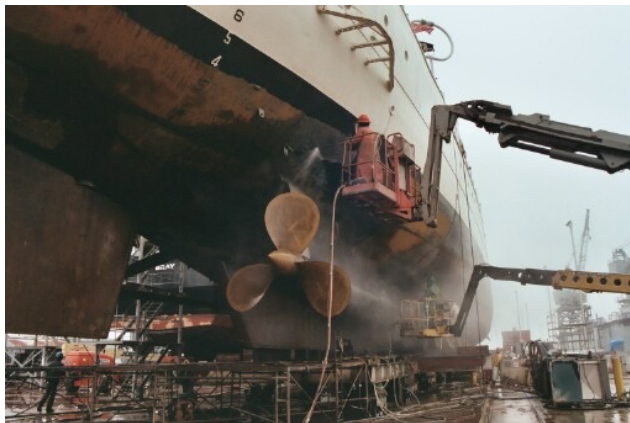
# Eight types of corrosion: uniform corrosion



Material thinning due to chemical reaction between the metal and the environment.

*uniform corrosion*

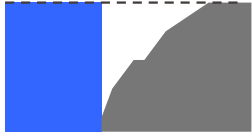
**Wet corrosion**  
(immersion in the corrosive fluid)



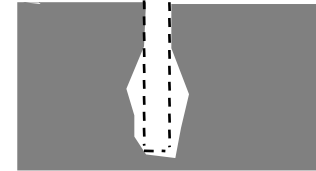
**Atmospheric corrosion**  
(water condensation film)



# Eight types of corrosion: localized corrosion



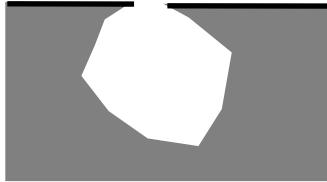
*galvanic corrosion*



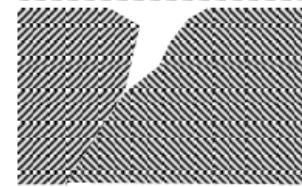
*crevice corrosion*



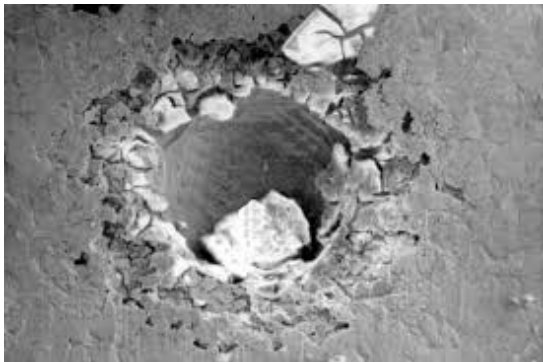
# Eight types of corrosion: localized corrosion



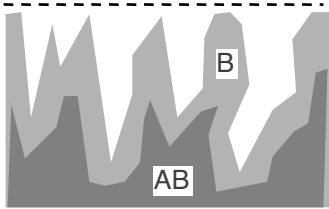
*pitting corrosion*



*Intergranular corrosion*



# Eight types of corrosion: selective



*selective leaching*

In an alloy, selective dissolution of the less noble (lowest corrosion potential) component. It generates porosity (loss of mechanical strength) and changes in colour.

*Examples:*

- *Dezincification of brass (Cu-Zn) alloy*
- *Loss of copper in carat gold alloys and thus of aesthetic properties*



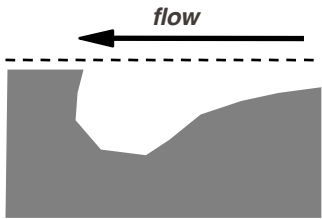
*Brass propeller*

*Zone weakened by selective dissolution of Zn (red colour of copper)*



*Fracture of the blade*

# Eight types of corrosion: corrosion under mechanical stresses



*erosion corrosion*



*stress corrosion cracking*



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# Simple immersion tests

Samples of defined weight are kept immersed for a certain time. Corrosion is measured by weight loss or by dimensional changes.

- + *Simple*
- + *Close to reality*
- *Changes of electrolyte (evaporation, accumulation of corrosion products) not controlled.*
- *Requires removal of the corrosion products*
- *No real time measurement*

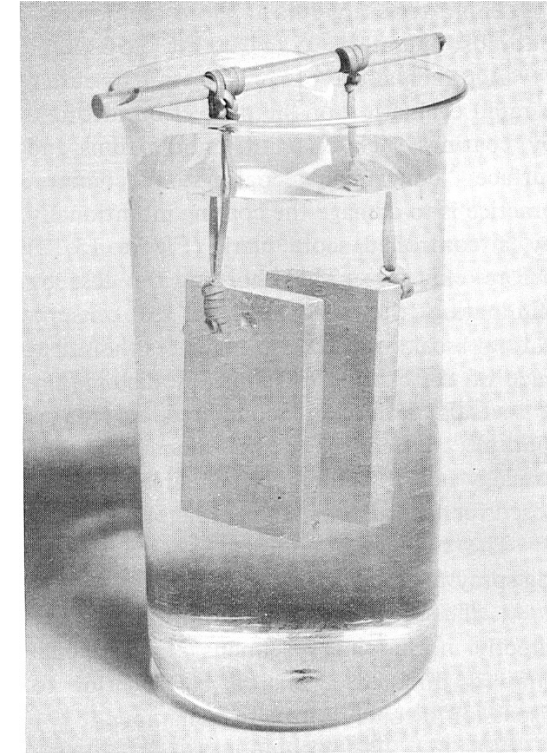
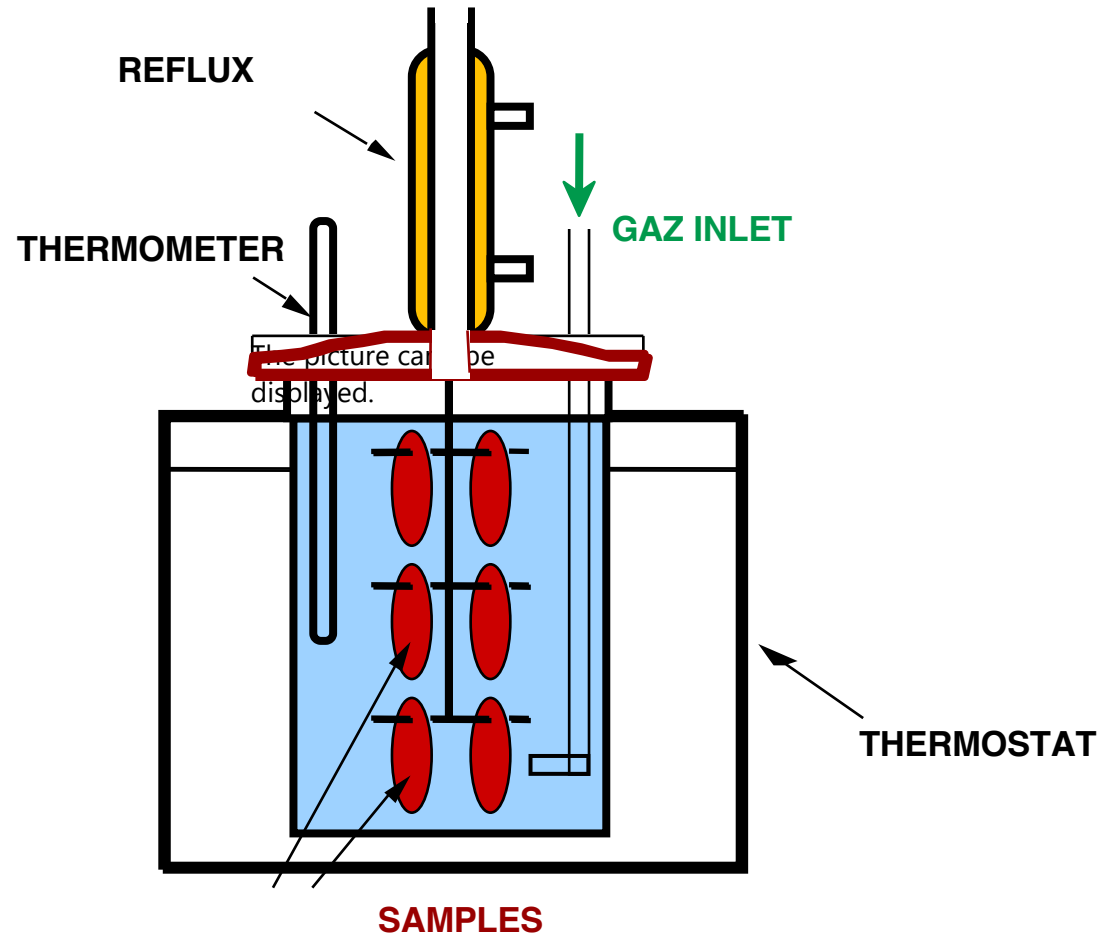


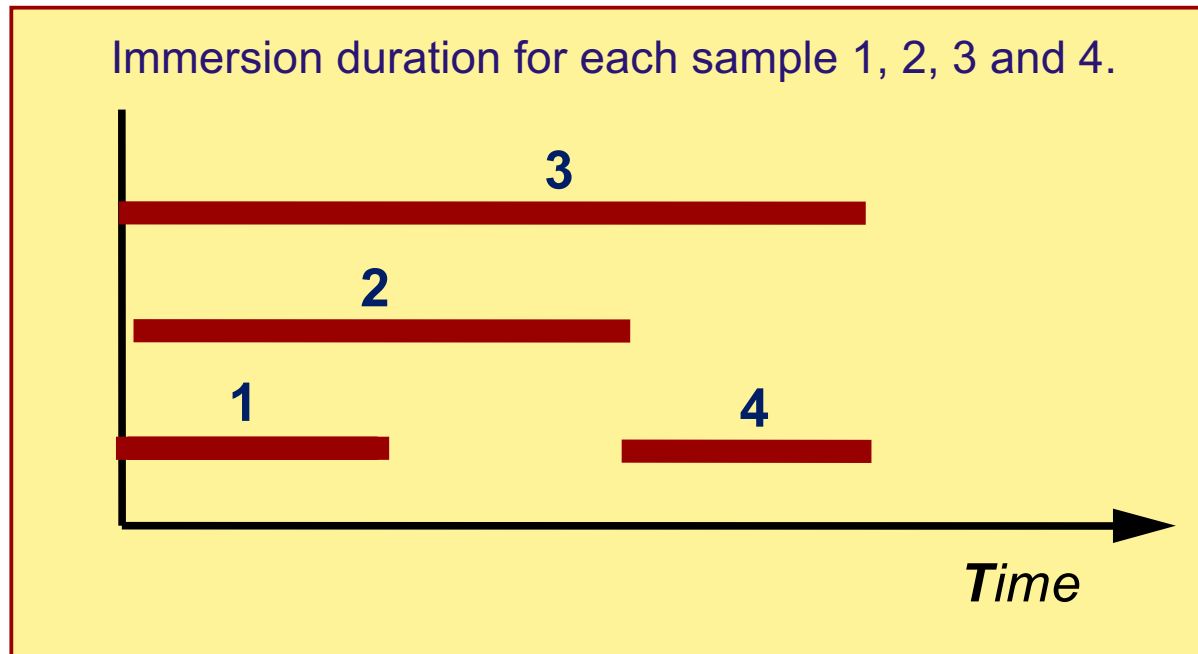
FIGURE 15-10 – Beaker test exposing two specimens. Note specimens are electrically insulated from each other and that supporting rod is suspended from a nonconductor.

*NACE Basic Corrosion course,  
A. deS. Brasunas Ed, NACE Houston 1970*

# Controlled immersion tests



# 4 sample immersion test sequence



Samples 1,2 and 3 for assessing corrosion rate evolution during time.  
Comparison Sample 1 vs 4 for assessing effect of solution ageing.

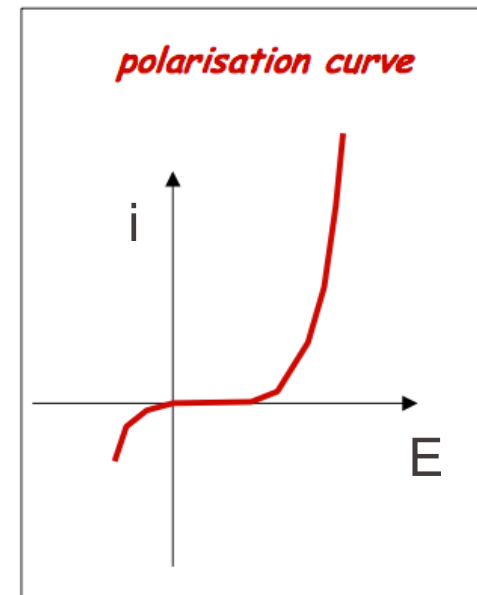
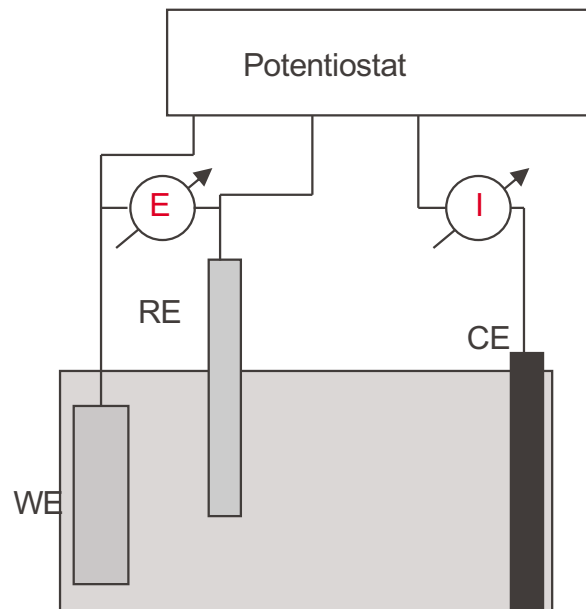
# Real scale atmospheric corrosion tests



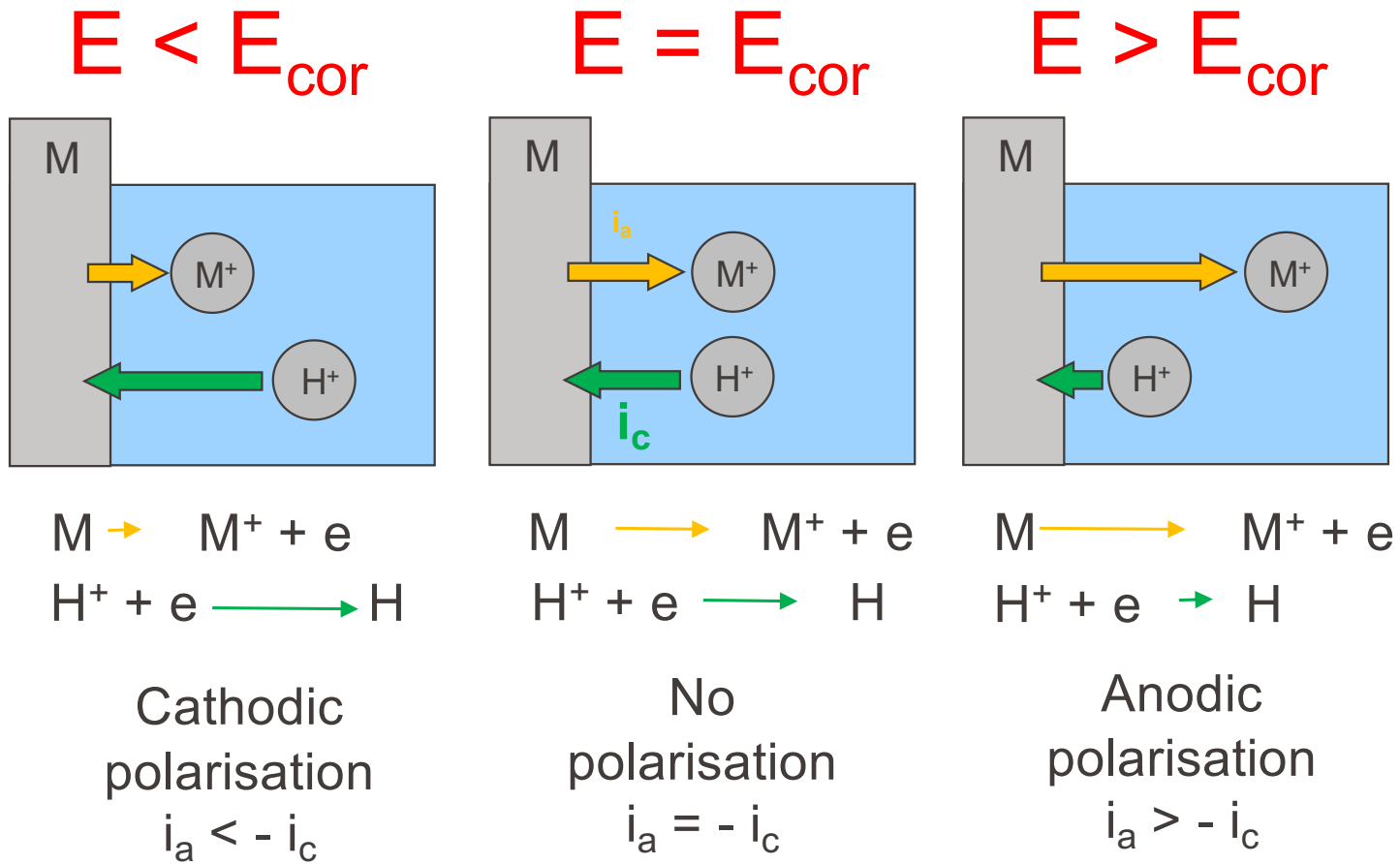
# Potentiostatic method for measurement of polarisation curves

POTENTIOSTAT: electronic device that maintains a selected potential  $E$  between RE and WE by passing an appropriate current  $I$  between WE and CE.

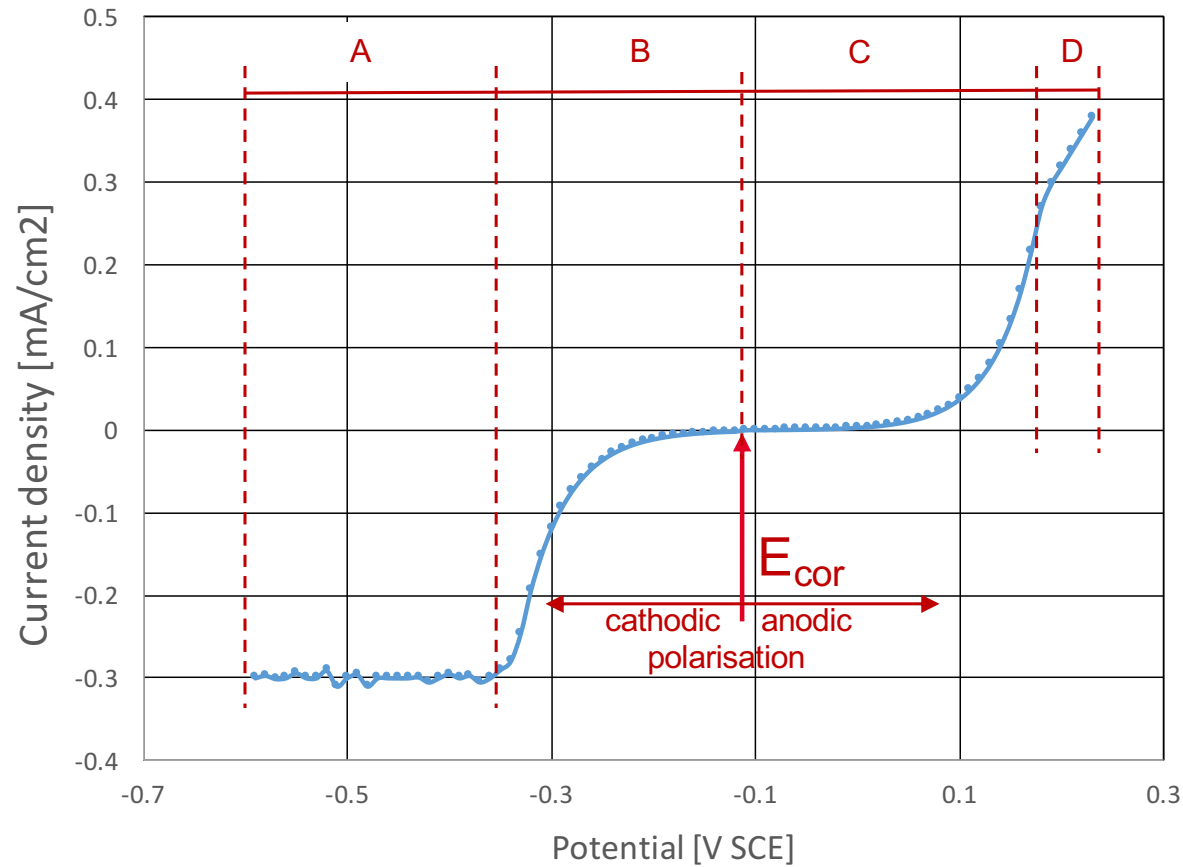
*RE: reference electrode, CE: counter electrode, WE: working electrode*



# Polarisation ( $E$ - $E_{cor}$ ) of a mixed electrode (corrosion of iron in acid)



# Polarisation curve of copper in NaCl solution



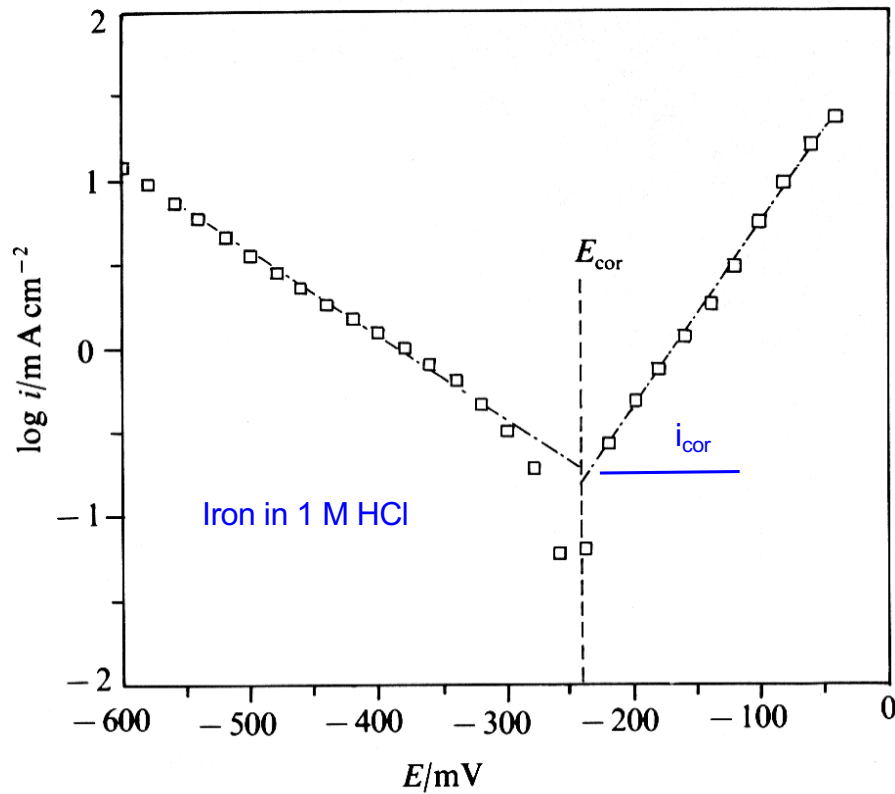
A: Constant current independent on potential.

B: Exponential increase in cathodic current.

C: Exponential increase in anodic current.

D: Linear increase in current.

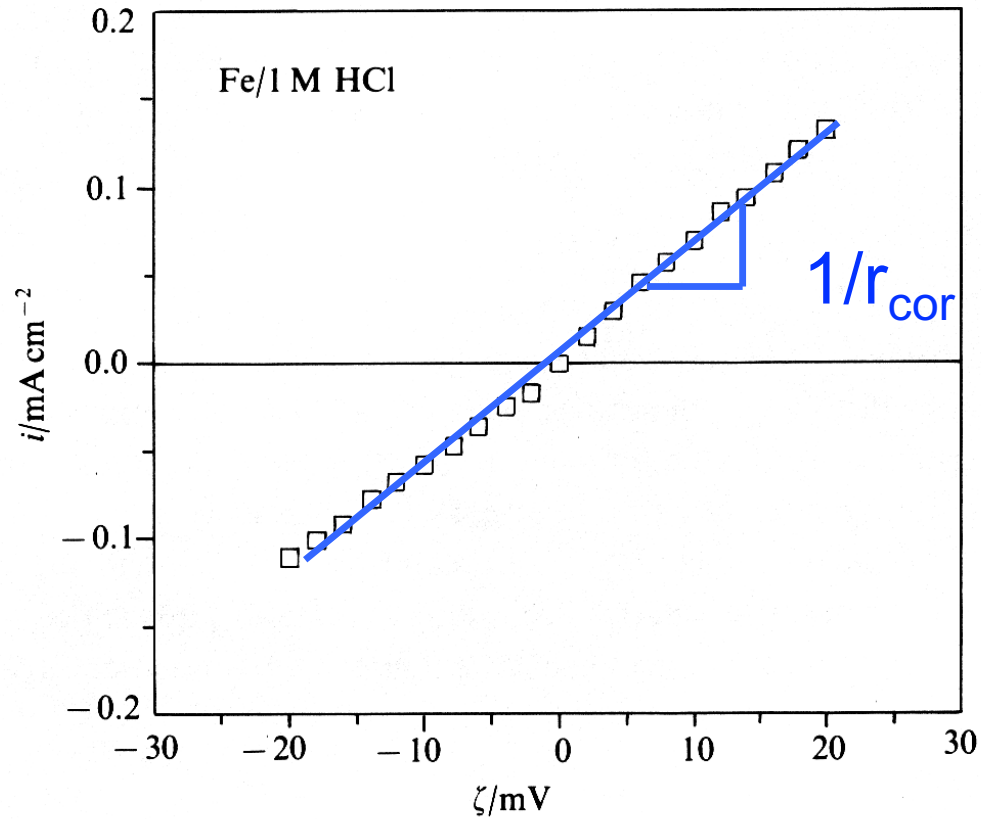
# Determination of corrosion rates from polarisation curves



$i_{\text{cor}}$  is determined by the extrapolation of the cathodic and anodic linear section of the polarisation curve.

Linear domains are usually observed for polarisations larger than 100 mV.

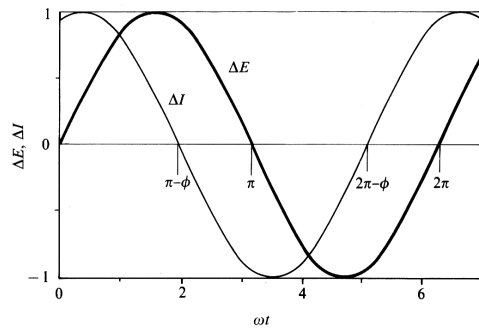
# Polarisation curve of iron measured close to the corrosion potential



$$i_{cor} = \frac{\beta_a \beta_c}{r_{cor} (\beta_a + \beta_c)}$$

# Other electrochemical techniques

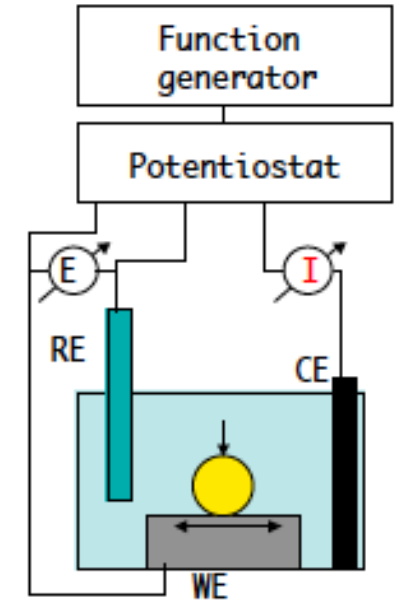
- Electrochemical Impedance Spectroscopy
  - Principle: measurement the response in current  $I$  to a sinusoidal potential  $E$  signal as a function of frequency



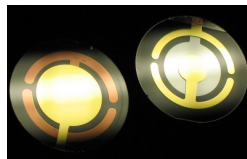
$$E(t) = E_0 \sin(\omega t)$$

$$I(t) = I_0 \sin(\omega t - \phi)$$

$$Z = \frac{E(t)}{I(t)} = Z_0 \exp(j\phi) = Z_0 (\cos \phi + j \sin \phi)$$



- Electrochemical Quartz Crystal Microbalance (EQCM)
  - Principle: measurement of the change in frequency of a quartz crystal resonator



$$\Delta f_m = \frac{-2f_0}{\sqrt{\rho_q \mu_q}} \Delta m = -C_f \Delta m$$

# Take-home messages

- Corrosion is a system property that depends on the combination of material, environment and physical parameters
- Corrosion is of electrochemical nature and it is determined by the type and kinetics of oxidation (i.e.  $\text{Fe} \rightarrow \text{Fe}^{+2} + 2\text{e}^-$ ) and reduction (i.e.  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ ) reactions
- The corrosion reactions are driven by the electrode potential established at the electrode/solution interface and the reaction rate is given by the current

# References

**Corrosion and surface chemistry of metals** (1<sup>st</sup> Edition)

Authors: Dieter Landolt

ISBN: 978-2-940222-11-7

