

TPA Training Course

Corrosion Management in the Oil & Gas Industry

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Part 1

**Arkhangelsk State Technical University
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Outline (1/2)

- ◆ **Challenges of Corrosion Management in the Oil & Gas industry**
- ◆ **Materials and corrosion prevention methods**
- ◆ **Reminders on "wet" corrosion**
- ◆ **Main families of corrosion cases in the Oil & Gas industry and their prevention**
 - **CO₂ (and H₂S) Corrosion**
 - **H₂S cracking phenomena ("Sour service")**
 - **"Microbiologically Influenced Corrosion" (MIC)**
 - **O₂ Corrosion**

Outline (2/2)

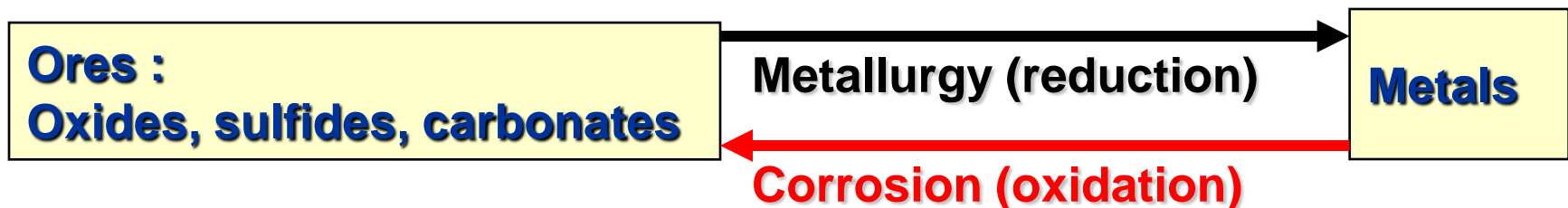
- ◆ **Monitoring of internal corrosion and corrosion-related inspection**
- ◆ **Cathodic Protection**
 - Principles, criteria, limitations
 - Applications: structures in contact with soil, immersed structures, internal of apparatuses, reinforced concrete structures
 - Design, implementation
 - Measurements
- ◆ **Corrosion prevention by paint systems and metallic coatings**
- ◆ **Quality, Standardization, Certification, and R & D**

Corrosion Management in the Oil & Gas Industry

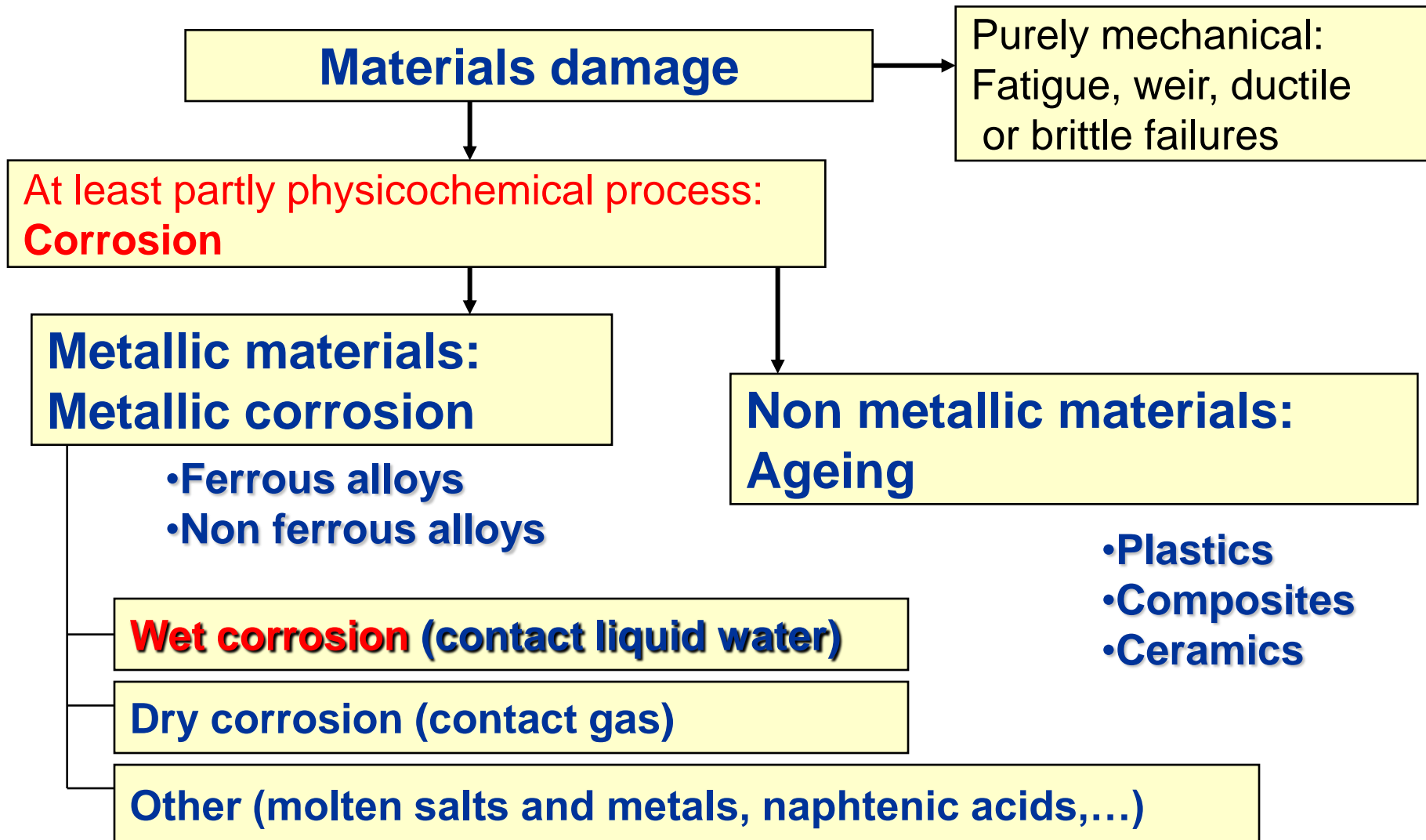
Challenges of Corrosion Management in the Oil & Gas Industry

Definition of Corrosion (ISO 8044)

- ◆ (Metallic) Corrosion is a **physico-chemical interaction** between a metal (or alloy) and its environment, leading to a **degradation of the functional system** represented by the metal (metal loss or crack) or the environment (contamination).
- ◆ It is a **normal return** of metals extracted from ores by metallurgical processes back to oxidised species (oxides, carbonates, sulphides,...)



Materials damage, ageing and main families of corrosions



Necessary conditions for corrosion to occur in Oil & Gas production facilities

**Corrosion takes place if
free liquid water at the contact of the
metal**

and

a corrosive agent is present in water

What is corrosion for an oil and gas operator?

- ◆ **Present or potential damage leading to:**
 - safety/environment hazards/image of company
 - loss of production
 - costs of repair
- ▶ for the operator, before the estimated end of service of a given equipment
- ◆ **Corrosion Management** is a key issue for ensuring **Integrity of Facilities**

Corrosion represents the major part of risks related to materials damage

Overall cost of corrosion: 0.3 to 0.5 \$/boe

The threats



Gas leak



Corrosion under Passive Fire Protection

The threats



**Explosion of a gas pipeline due to
External Stress Corrosion Cracking**

The threats



Internal corrosion of an oil tank

Corrosion Management in the Oil & Gas Industry

Materials and Corrosion Prevention methods

Materials used in Oil & Gas industry

◆ **Base material: Carbon steels**

- Generally the cheapest, easy for manufacturing pipes and plates and for assembling them (welding).
- It is the material with which corrosion assessment studies are carried out. If not selected because corrosion prevention is too difficult or expensive (life cycle cost), then **alternative materials** are selected

◆ **Low alloy steels**

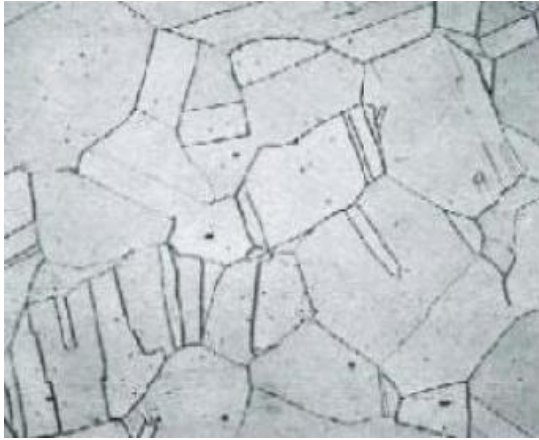
- Not often used. Ex: low Cr alloy steels (a little less corroded in mild CO₂ environments), 9 % Ni for cryogenic applications (LNG)

Materials used in Oil & Gas industry

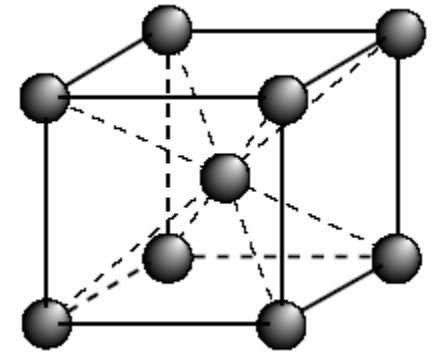
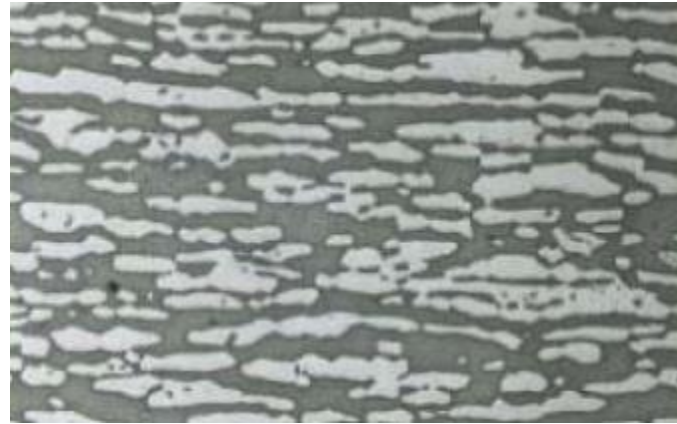
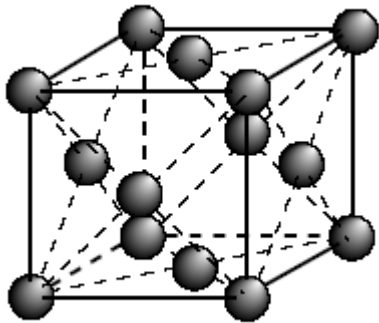
- ◆ **"CRA's" = "Corrosion Resisting alloys"**
 - **Stainless steels** = Steels containing **more than 11 % Cr** which makes them rust-free in moderately corrosive atmospheres. A lot of compositions, with increasing alloying elements (Cr, Mo, Ni, others)
 - **Stainless steels present various structural forms:** ferritic, martensitic, austenitic (non magnetic), "duplex" and "superduplex" = austeno-ferritic
 - **Nickel-based alloys**, generally austenitic. Used when a greater corrosion resistance than stainless steels is necessary or for specific mechanical properties
 - Ex: Alloys 625, 825, 400, K500

Various structures of stainless steels

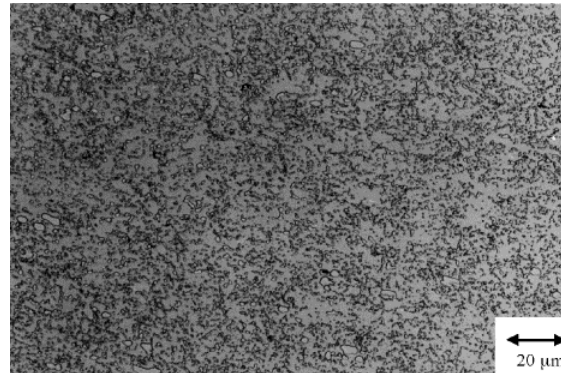
Austeno-ferritic 50/50 ("Duplex")



Austenite (γ)
Centered faces cubic

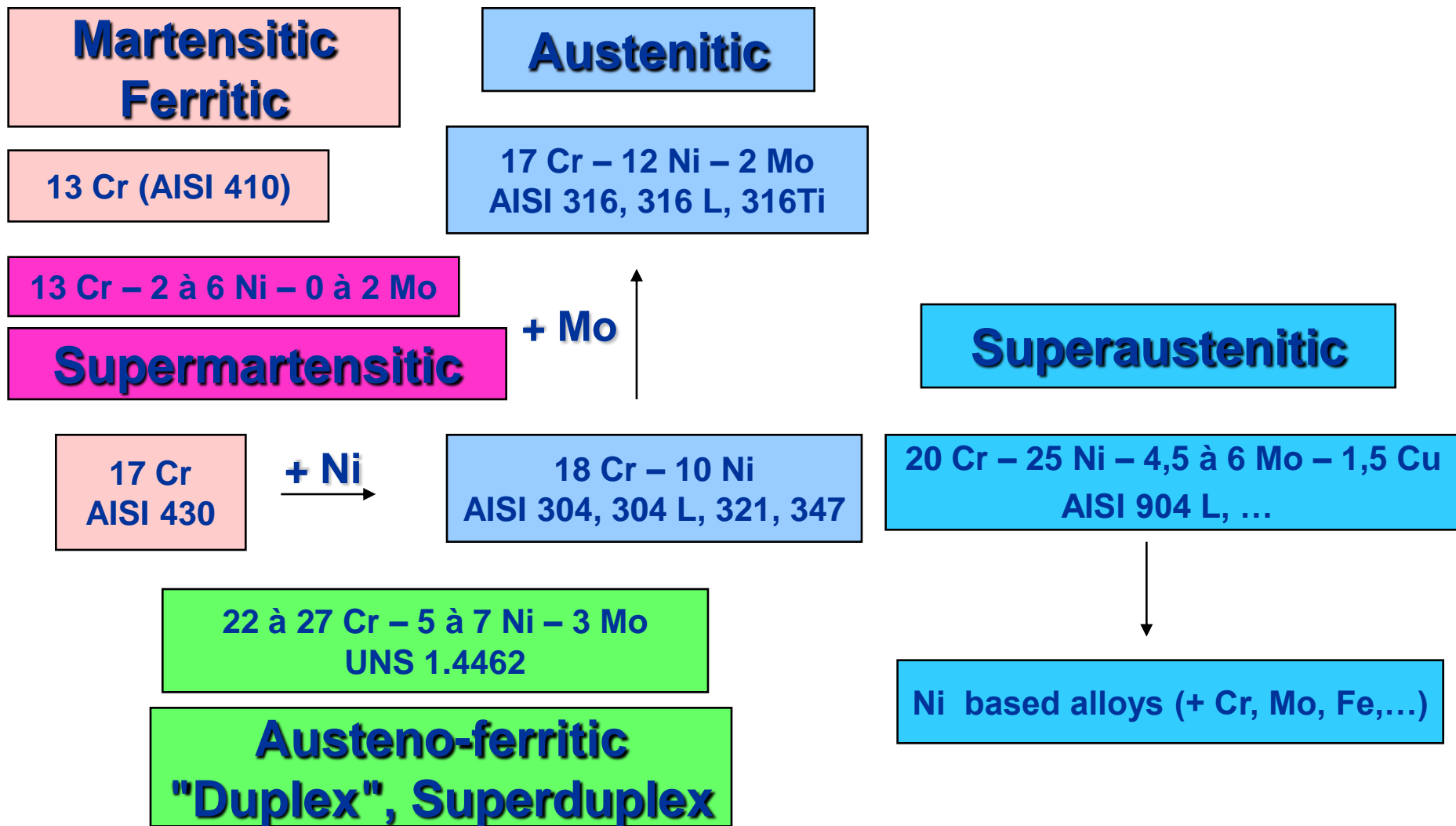


Ferrite (α)
Centered cubic



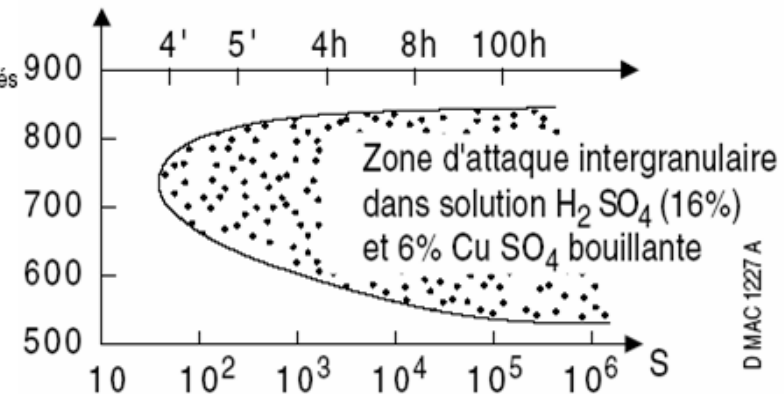
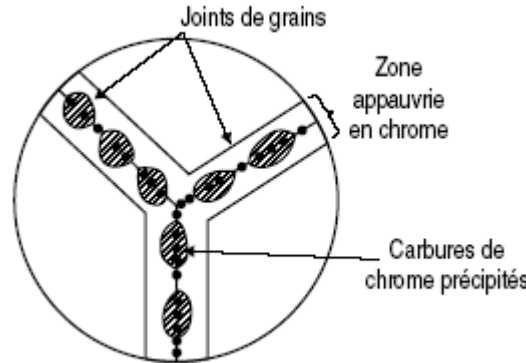
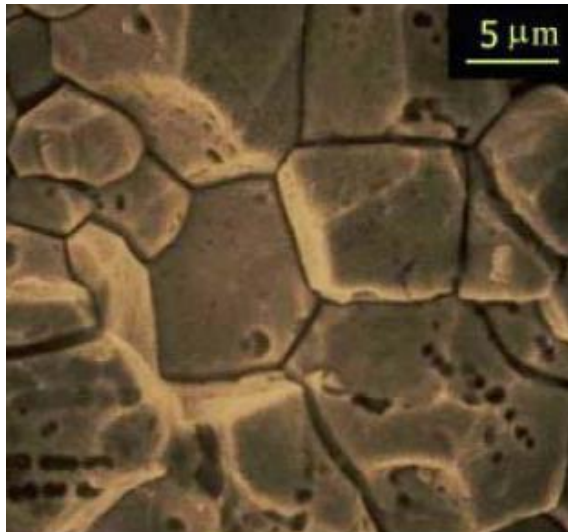
Martensite

Various structures of stainless steels



Intergranular corrosions of austenitic stainless steels

Dechromisation close to grain boundaries due to diffusion of Cr at high temperature causing precipitation of $\text{Cr}_{23}\text{C}_6 \rightarrow$ corrosion



Stabilisation of SS against selective corrosion through:

- Reduction of % C \rightarrow low C steels (304 L, 316 L,...)
- Addition of alloying element more reactive with C, such as Ti or Nb (316 Ti, 321, 347)

Materials used in Oil & Gas industry

◆ Non ferrous metallic alloys

- Used for specific applications where steels are not adapted.
Ex: seawater applications
- Naturally resisting alloys : Copper based alloys such as Cu-Ni 90/10 or 70/30, aluminium bronzes, brasses, bronzes, etc
- Passivated alloys (may be prone to depassivation in some cases): Al alloys, Ti alloys

◆ Non metallics

- Thermoplastics. Ex: PE, PVC, PVC-C, others
- Composites (with a reinforcement such as glass or carbon fibers). Ex; Glass Reinforced Epoxy (GRE)

Non ferrous materials



Propeller in bronze



Fins in Al

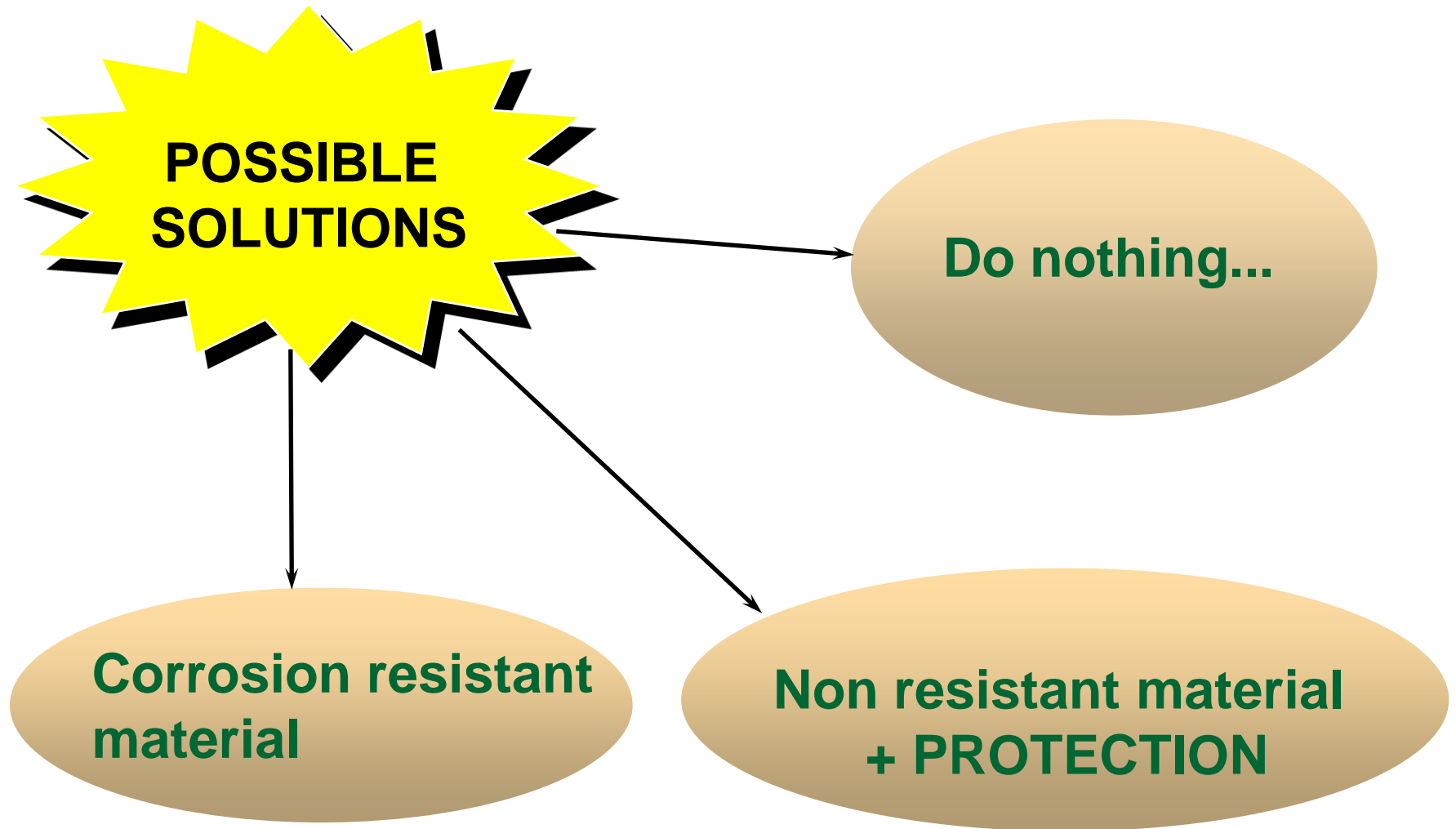


Heat exchanger tubes in Cu-Ni 90-10

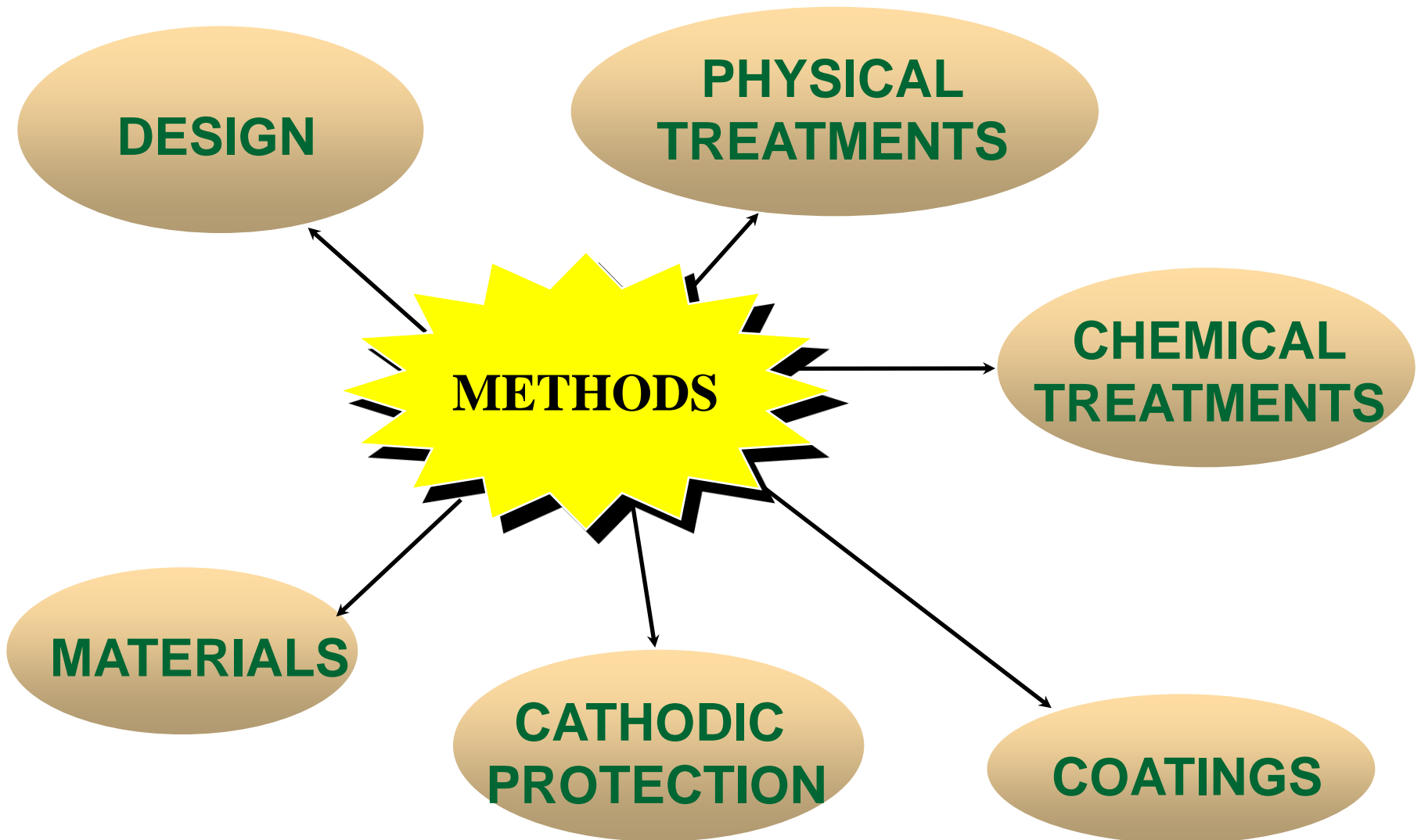
Seawater piping in GRE



Corrosion prevention



Usual corrosion prevention methods



Basis of corrosion assessment in Oil & Gas

- ◆ **Internal corrosion** of facilities has to be treated first because risks vary a lot from an oil & gas field to another, which is not so obvious for external corrosion.
- ◆ Assessment of internal corrosion risks is carried for the **basic material, carbon steel** (compositions and grades have a marginal role)
- ◆ It depends first on **presence of liquid water at the contact of steel**:
 - **At bottom line** for pipes and vessels containing oil and/or gas with separated water (coming from reservoir or condensation)
 - **At top of line** for pipelines transporting wet hot gas (condensation)
 - On the whole surface for water pipelines.

Basis of corrosion assessment in Oil & Gas

- ◆ An **oxidizing species in water** at contact with steel is necessary:
 - **CO₂** is the most frequent oxidizing species for **weight loss corrosion**. It is the first corrosive species to consider for the corrosion management design (material, chemical treatments and corrosion allowance), together with **light organic acids**
 - Presence of **H₂S** **reduces corrosion rate** when **CO₂/ H₂S < 50 to 200** (corrosion products containing iron sulfides more protective than iron carbonates)
 - **Traces of O₂** are very detrimental (injection water and oil). Often introduced with seawater (for jet cleaning)

The more complete the knowledge of chemical composition of gas and water, the better and less conservative the corrosion assessment.

Corrosion Management in the Oil & Gas Industry

Reminders on "wet" corrosion

Reminders of Chemistry

◆ Chemical reactions:

■ total

reactants (atoms, molecules, ions) --> products (idem)

■ partial (equilibrium)

reactants (atoms, molecules, ions) \Leftrightarrow products (idem)

K, equilibrium constant

◆ Electrochemical reactions:

reactants or products contain e^-

◆ Oxidation reaction:

when e^- is a product

◆ Reduction reaction:

when e^- is a reactant

Reminders of Chemistry

- ◆ **ionisation of water:**



- ◆ **notion of pH necessary because of the very low concentration of H⁺ ions in « neutral » water: [H⁺]=10⁻⁷ Mol/l**

$$\text{pH} = \log_{10} (1/[\text{H}^+])$$

Nota: To be compared with [H₂O] = 1000 / 18 = 55,5 Mol/l

- ◆ **neutrality of “aqueous phase” if pH = 7**

- ◆ **acidity** if pH < 7, through dissolution of species increasing [H⁺]

- ◆ **basicity (alcalinity)** if pH > 7, through dissolution of species decreasing [H⁺], hence increasing [OH⁻]

Reminders of Chemistry

- ◆ Water is a very good **solvent**
- ◆ Dissolution in water of gases, liquids and solids up to the **saturation concentration** (function of temperature, pressure and salinity)
- ◆ Dissolution of **neutral solids**:
 - **NaCl** (total ionisation, saturation **increases when temperature increases**):
$$\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$$
- ◆ Dissolution of **neutral gases**:
 - **O₂** (saturation 7 mg/l in standard conditions = 25 °C, 1 atm, **decreases when temperature increases**)

Reminders of Chemistry

◆ Dissolution of acidic gases:

- **HCl** (total ionisation, strong acid):



- **H₂S** (partial ionisation, weak biacid):



- **CO₂** (partial ionisation after hydrolysis, weak biacid):



- **Cl₂** (after hydrolysis giving HClO, weak acid):



Reminders of Chemistry

◆ Dissolution of **basic gases**:

- **NH₃** (partial ionisation after hydrolysis, weak base):



◆ Dissolution of **acidic solids**:

- **FeCl₃** (total ionisation followed by acid hydrolysis):



◆ Dissolution of **basic solids**:

- **NaOH** (total ionisation, strong base):



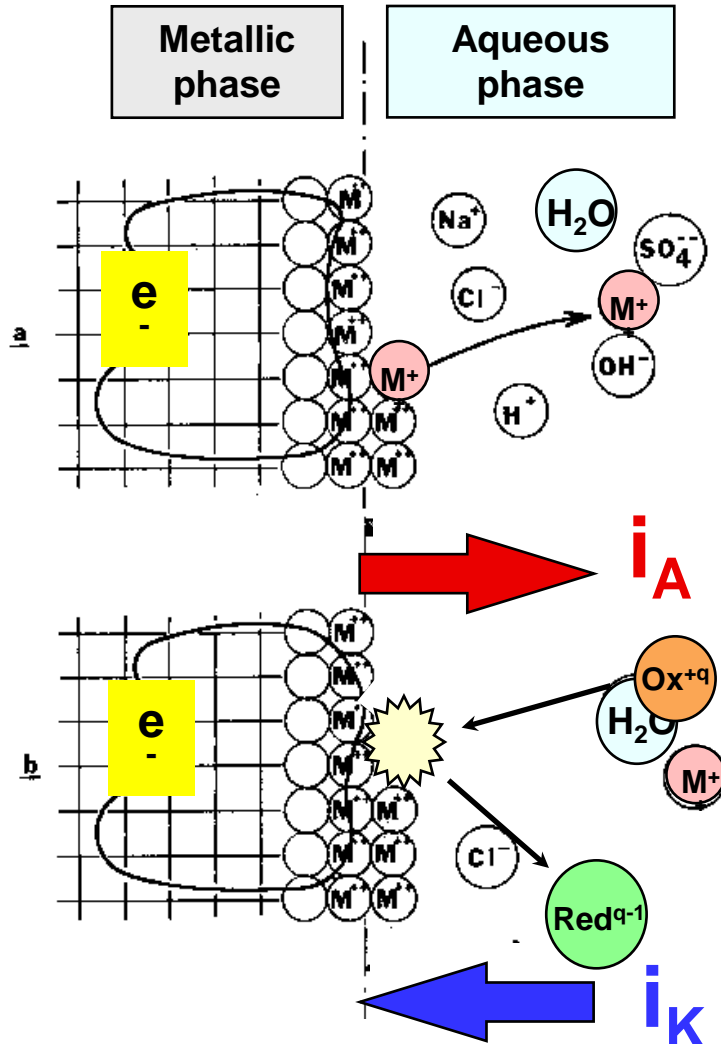
Basic reasons of corrosion by liquid water

- ◆ **Metallic and aqueous phase are both electrical conductors:**
 - **electronic conduction for metallic phase:** delocalised electrons can move in the network constituted by metallic cations ► High conductivity, low resistivity
 - **ionic conduction in aqueous phase due to :**
 - ionisation of water : $\text{H}_2\text{O} \Leftrightarrow \text{H}^+ + \text{OH}^-$
 - presence of other anions (Cl^- , HCO_3^- , CO_3^{2-} , HS^- , S^{2-} , SO_4^{2-} ,...) and cations (Na^+ , NH_4^+ , Ca^{++} , Fe^{++} ,...) coming from dissolution of gases and solids in contact with liquid water
 - Low conductivity, high resistivity
- ◆ **Metallic cations (Fe^{++} , ...) are the only species that can be present in both phases**

Resistivities and conductivities

Type of conducting medium	Material or environment	Resistivity ρ ($\Omega.m$) ($\rho = 1/\sigma$)	Conductivity σ (S/m) ($\sigma = 1/\rho$)
Metal	Cu	$1,7 \cdot 10^{-8}$	$0,6 \cdot 10^8$
	Al	$2,7 \cdot 10^{-8}$	$0,4 \cdot 10^8$
	Fe	10^{-7}	10^7
Non metal	C graphite	$5 \cdot 10^{-5}$	$2 \cdot 10^4$
Electrolyte	Seawater	0,2 (25°C) - 0,4 (5°C)	2,5 (5°C) - 5 (25°C)
	Sea mud	1	1
	Potable waters	10 to 20	0,05 to 0,1
	Clays	20 to 100	1 to 0,05
	Sands	70 to more than 1000	Less than 10^{-3} to 0,015
	Concrete	50 to more than 1000	Less than 10^{-3} to 0,02
	Pure water	10^9	10^{-9}

Basics of wet corrosion : its electrochemical nature

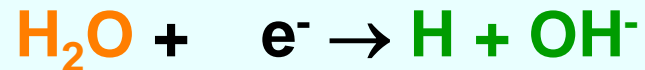
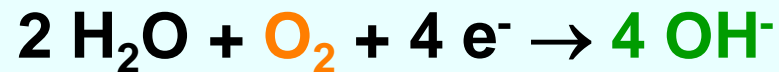


i_A = « Anodic » current :
oxidation of metal

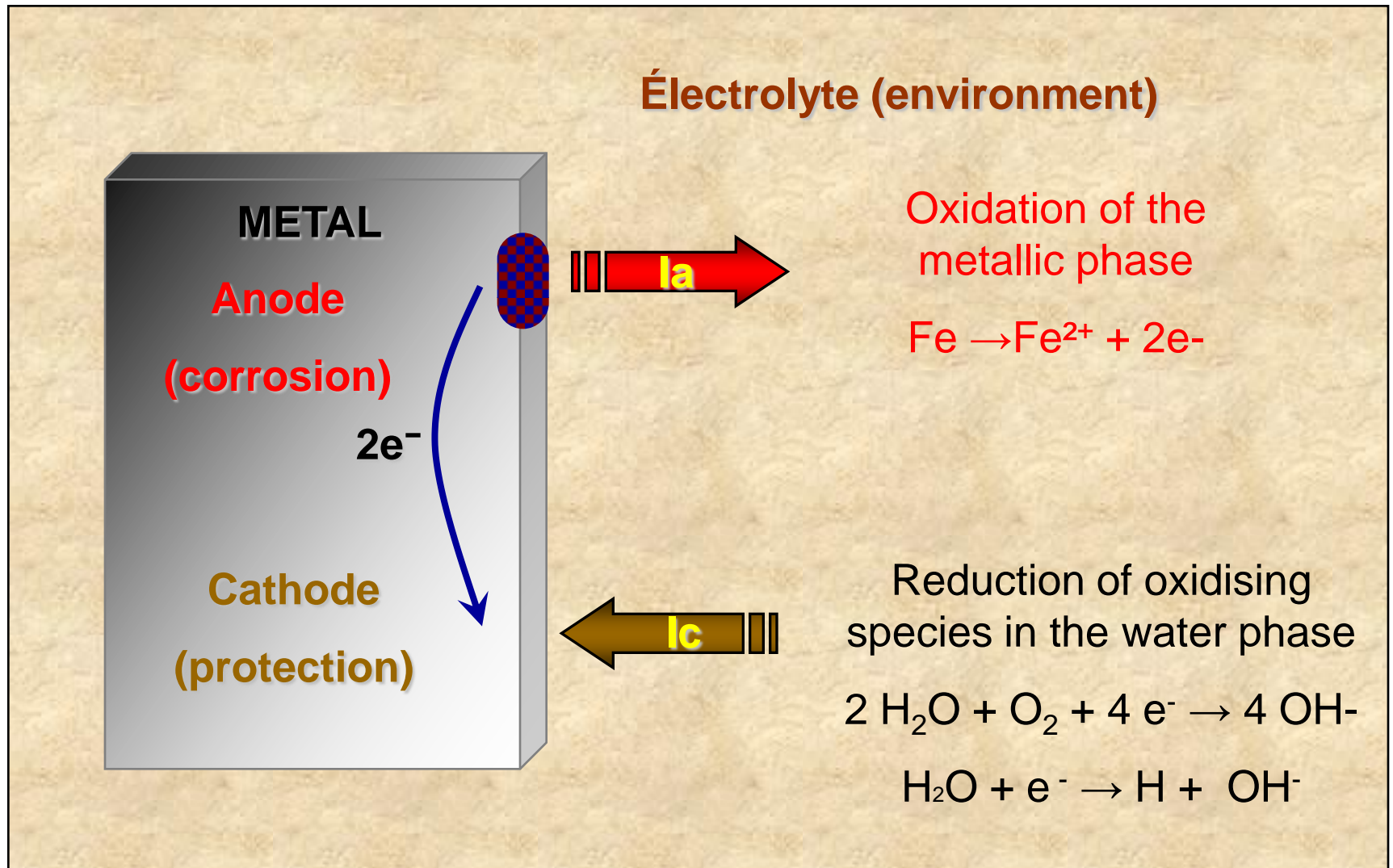
Without the contribution of
an external current,

$$i_A = - i_K$$

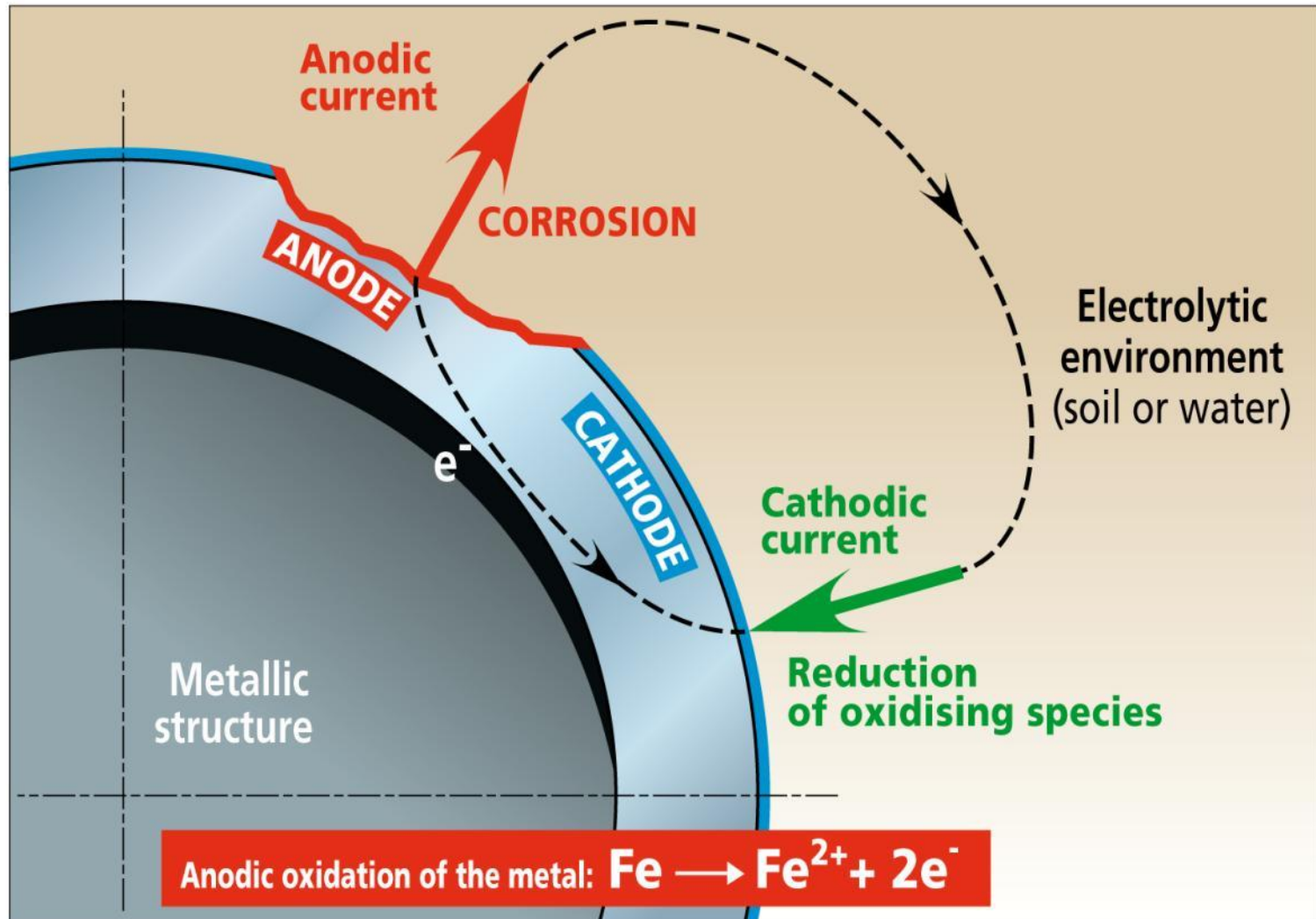
i_K = « Cathodic » current:
reduction of oxidising species



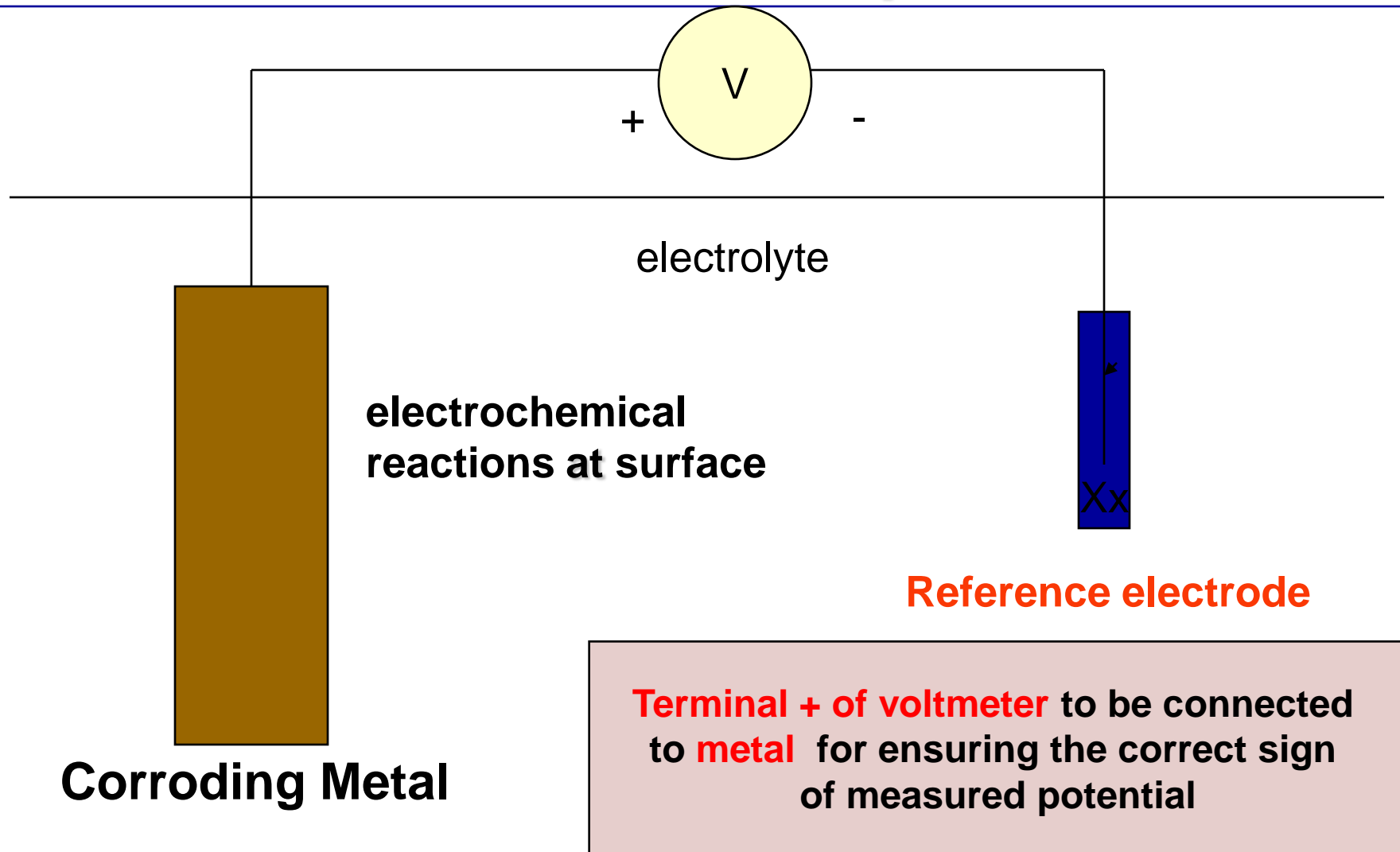
The corrosion cell



The corrosion cell



Laws of electrochemistry applied to corrosion: electrochemical potential



Reference electrodes

- ◆ A reference electrode is an "Half-cell" or metallic electrode on which electrochemical reactions are well known, controlled and reproducible
- ◆ This requires a pure metal in equilibrium with a perfectly defined concentration of its cation in an **electrolyte not contaminated** by other ions perturbing this concentration



$$[M^{n+}] = \text{constant}$$

- ◆ Often, the most practical way to ensure a constant concentration of cation is to prepare a **saturated solution in $[M^{n+}]$**
-

Nernst Law and Series

◆ Nernst Law: $E = E_0 + (RT/nF) \cdot \ln C$

◆ Series of **standard (normal) potentials** E_0 (V/ NHE)
at 25°C for $C = 1$

$Au \Leftrightarrow Au^{3+} + 3e^-$	+1,50	Noble metals
$Pt \Leftrightarrow Pt^{2+} + 2e^-$	+1,20	
$Ag \Leftrightarrow Ag^+ + e^-$	+0,80	
$Hg \Leftrightarrow Hg^{2+} + 2e^-$	+0,85	
$O_2 + 2H_2O + 4e^- \Leftrightarrow 4OH^-$	+0,40	
$Cu \Leftrightarrow Cu^{2+} + 2e^-$	+0,34	
$2H^+ \Leftrightarrow H_2 + 2e^-$	<u>0</u>	Origin of potentials
$Pb \Leftrightarrow Pb^{2+} + 2e^-$	-0,13	
$Ni \Leftrightarrow Ni^{2+} + 2e^-$	-0,26	
$Cd \Leftrightarrow Cd^{2+} + 2e^-$	-0,40	
$Fe \Leftrightarrow Fe^{2+} + 2e^-$	-0,447	Passivation
$Cr \Leftrightarrow Cr^{3+} + 3e^-$	-0,74	
$Zn \Leftrightarrow Zn^{2+} + 2e^-$	-0,76	
$Ti \Leftrightarrow Ti^{2+} + 2e^-$	-1,63	
$Al \Leftrightarrow Al^{3+} + 3e^-$	-1,66	
$Mg \Leftrightarrow Mg^{2+} + 2e^-$	-2,37	<u>Anodes for CP</u>

Reference Electrodes

- ◆ Official Reference Electrode:

- Normal Hydrogen Electrode (NHE)

- ◆ Reference Electrode currently used in the lab:

- Saturated Calomel Electrode (SCE)



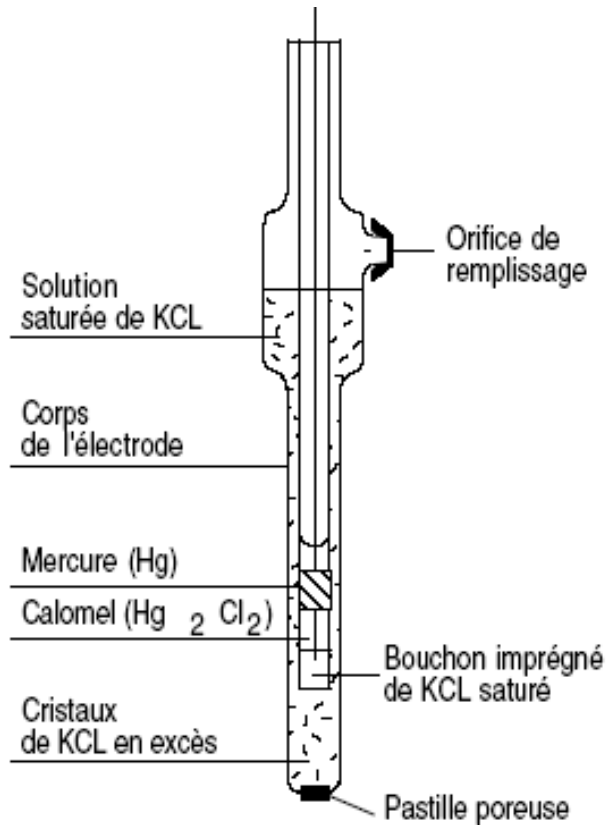
$$K_s = [\text{Hg}^{2+}] \cdot [\text{Cl}^{-}]^2 \text{ (Solubility Product)}$$

- ◆ Reference Electrode currently used in the field:(soils, concrete):

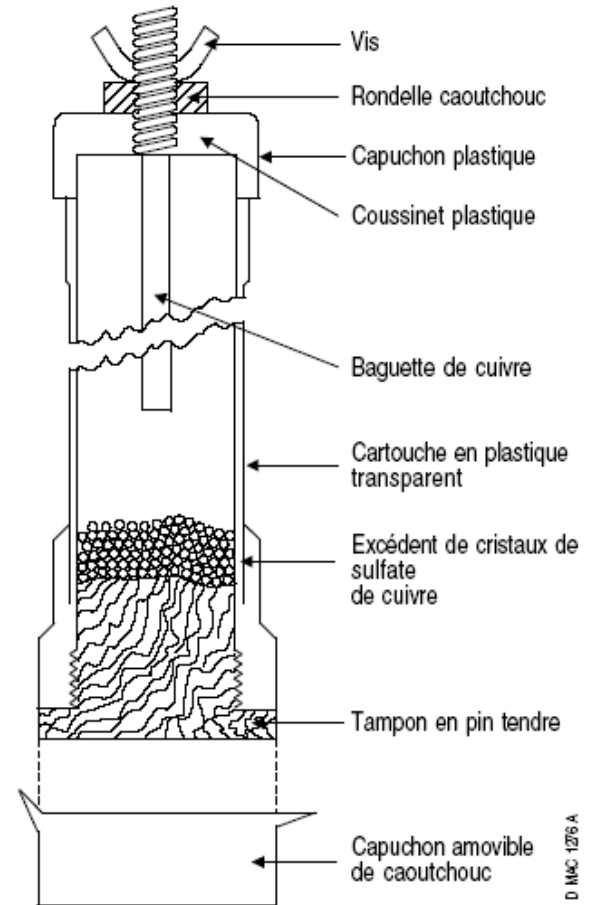
- Saturated Cu-CuSO₄ Electrode (CSE)



Reference Electrodes



Saturated Calomel Electrode



Saturated Cu-CuSO₄ Electrode

Saturated Cu-CuSO4 Reference Electrodes

**Buried
electrodes**



**Electrodes
for ground
surface**

Pseudo-Reference Electrodes

- ◆ Pseudo-reference electrodes (or «measurement electrodes») currently used in the field in **presence of chlorides** (seawater or brackish waters)
- ◆ No electrolyte in the electrode
- ◆ **Silver - Silver chloride - Seawater Electrode** (short to medium duration)



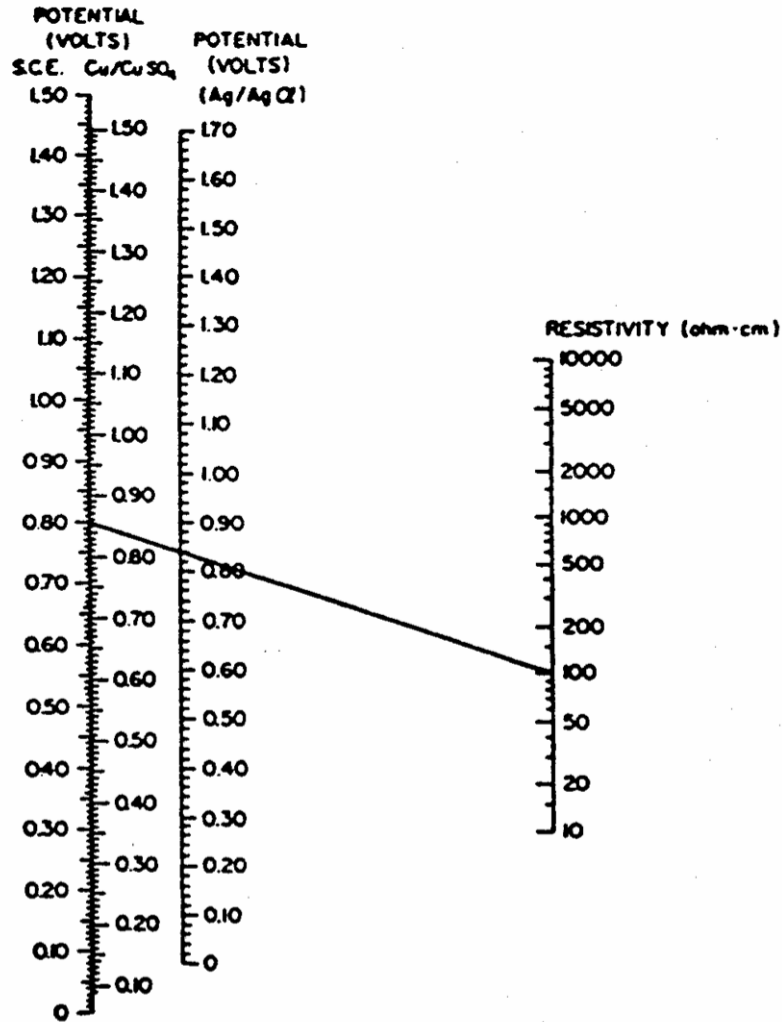
Potential **function of [Cl⁻]**, i.e. of actual environment

- ◆ **Zinc - seawater Electrode** (long duration)

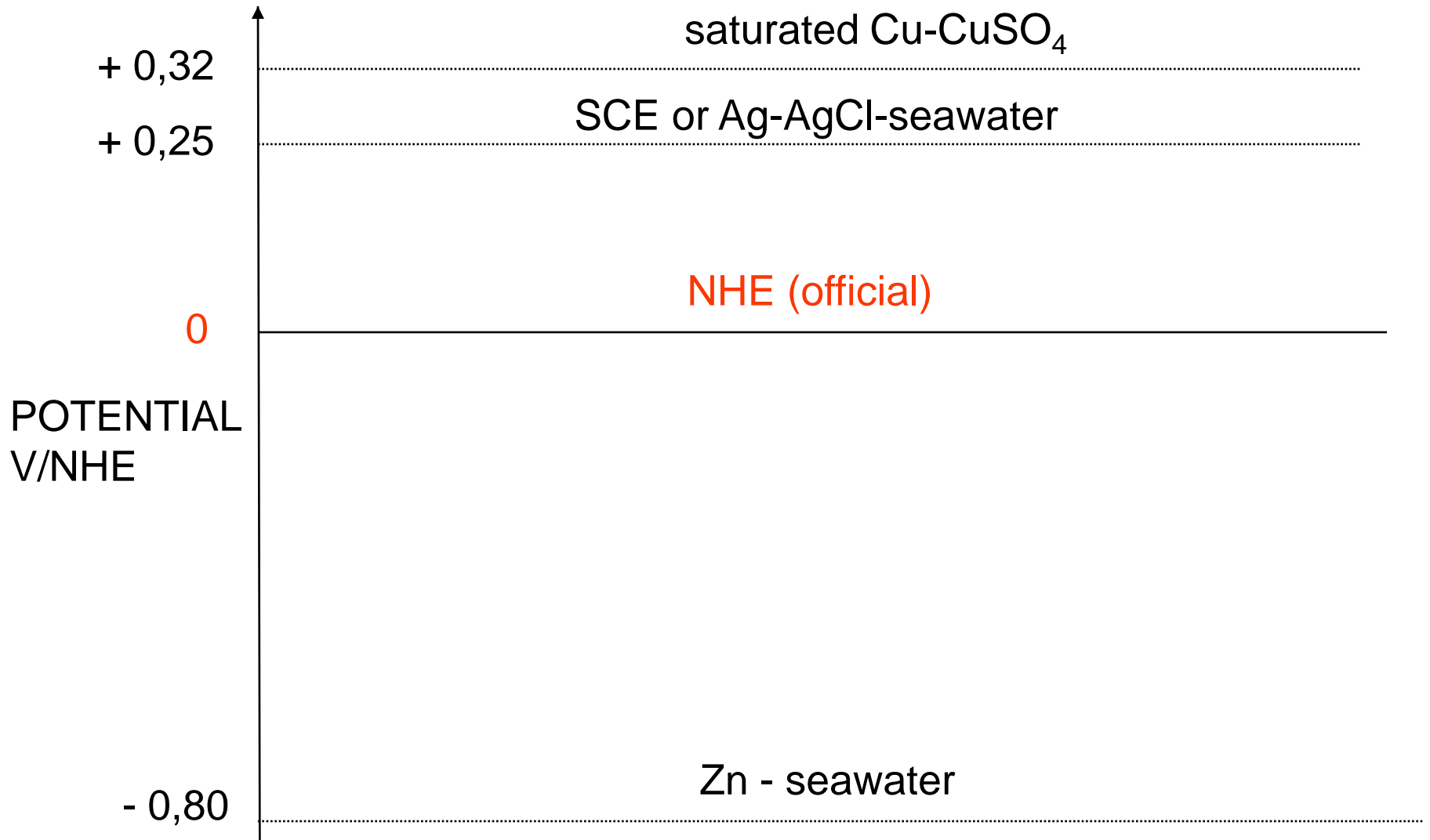


Potential **function of [Zn⁺⁺]**, not defined

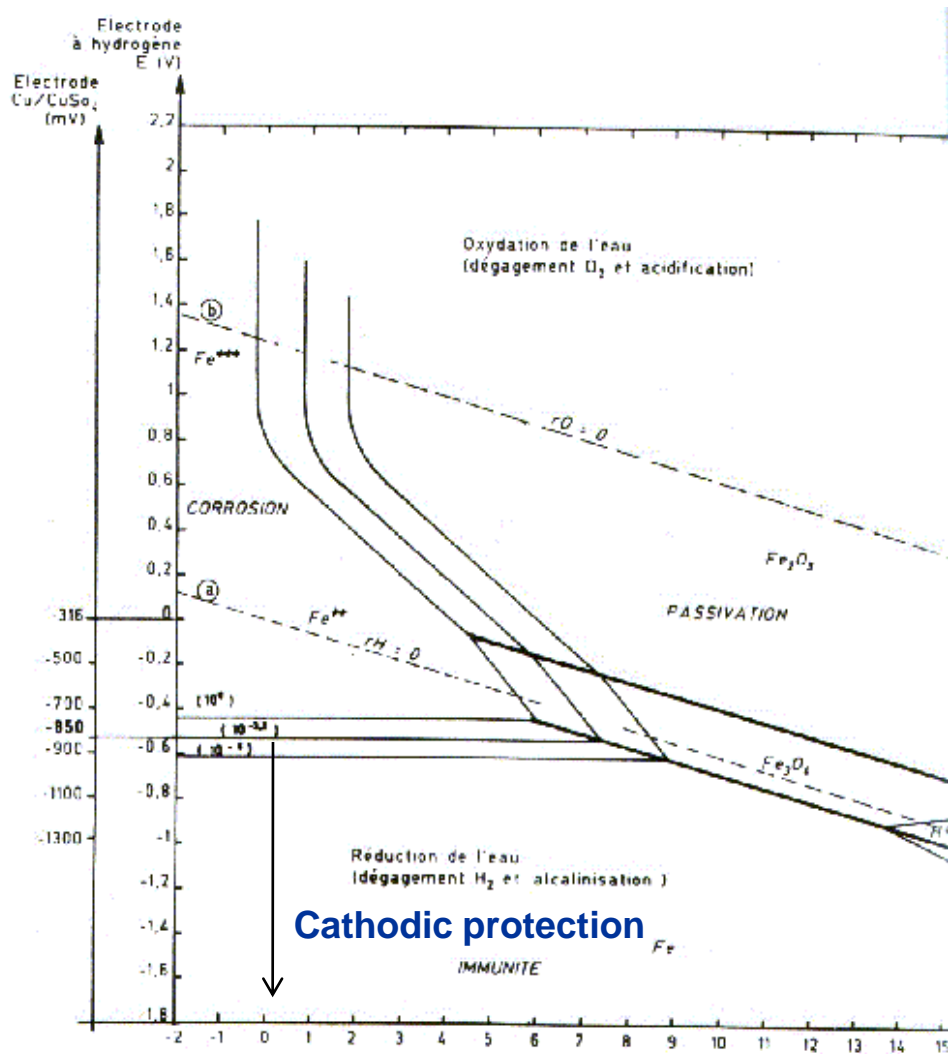
Correcting measured potential with Ag-AgCl- Seawater electrode vs. water resistivity



Correlations between Reference Electrodes



Potential – pH (Pourbaix) diagram for Fe – H₂O at 25°C



Current intensity / current density, Faraday's law

- ◆ **Current Density j = intensity I divided by interface area S ($j = I/S$)**
- ◆ **Faraday's Law:**
 - **equivalence intensity \Leftrightarrow material weight**

$$1 \text{ Faraday (1F)} = 96500 \text{ cb/mol} \Leftrightarrow A/n$$

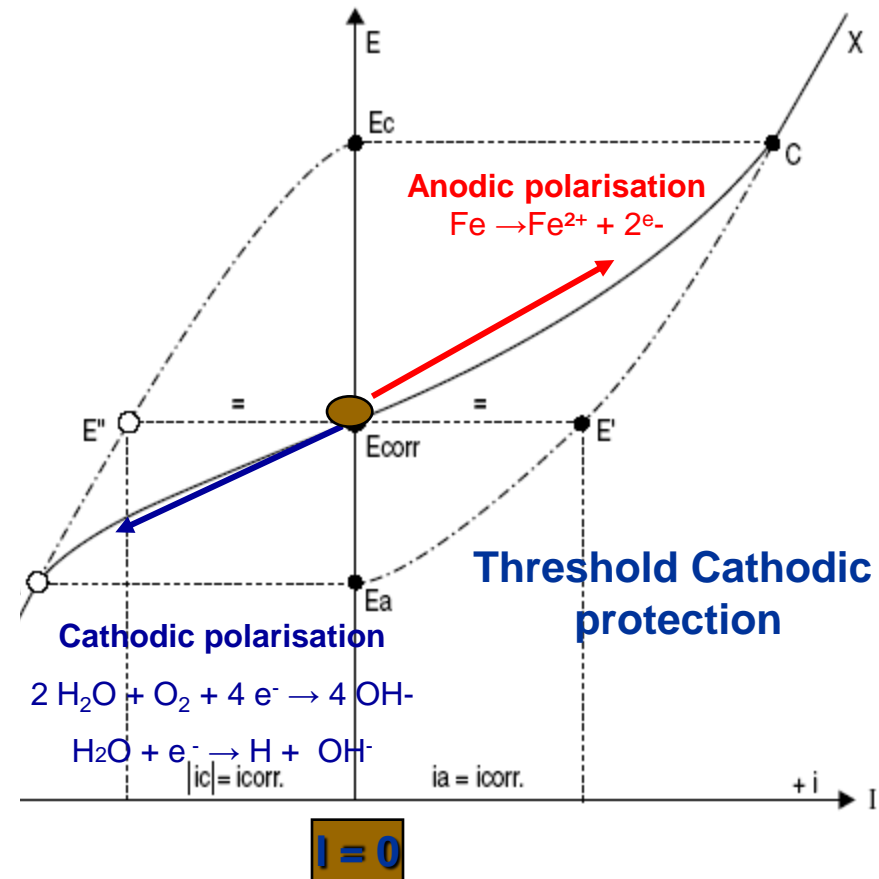
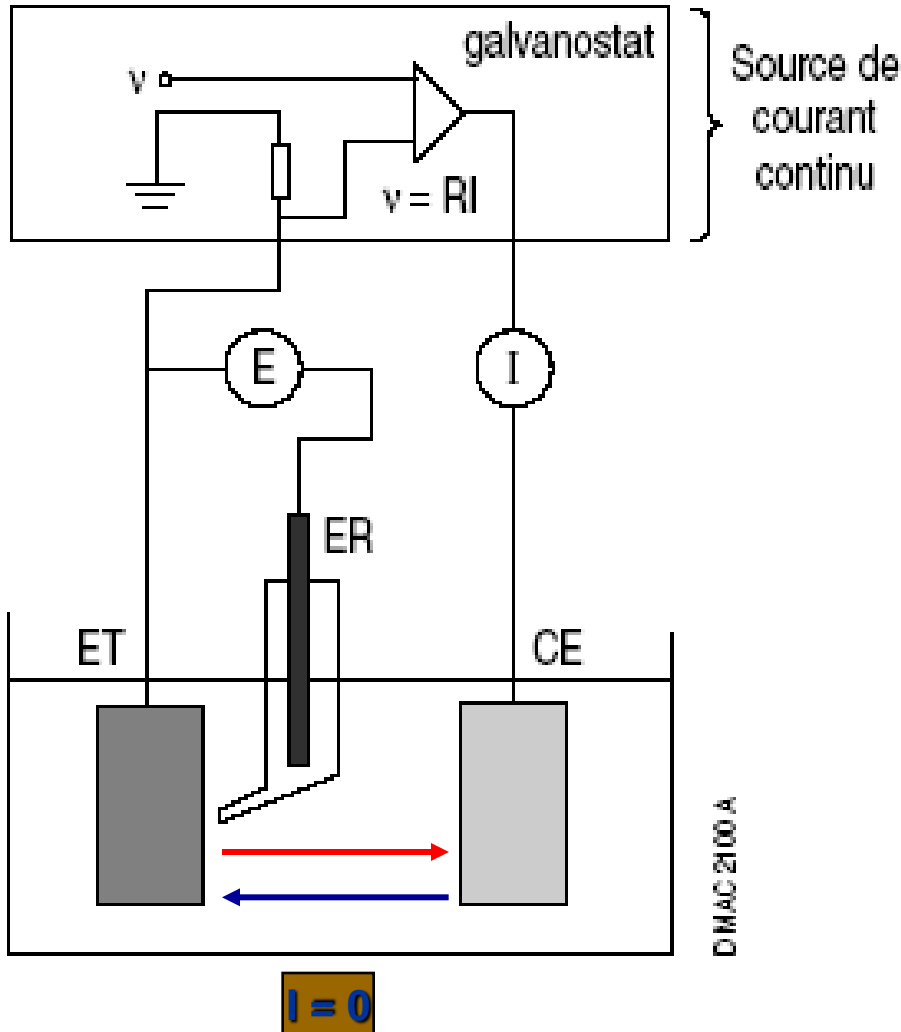
(A , atomic mass, n valence)

e.g. for Fe: $1F \Leftrightarrow 56/2 = 28 \text{ g}$
(or consumption rate 9 kg/A.yr)

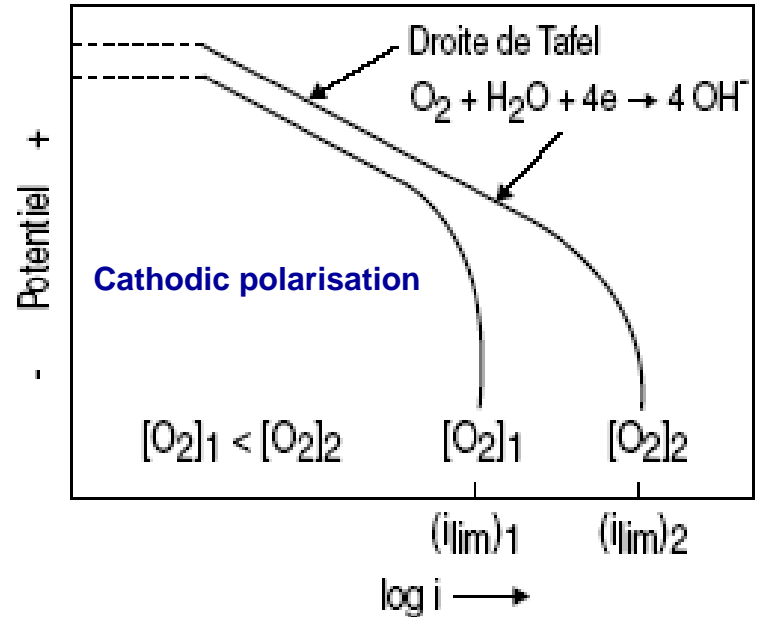
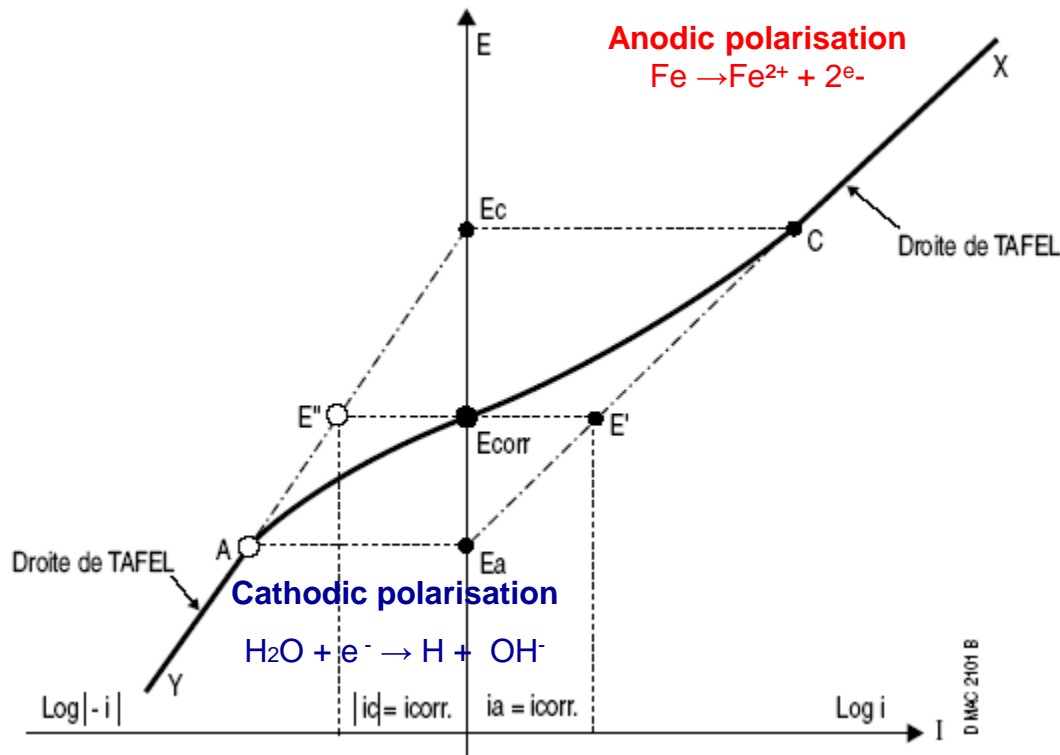
■ **Corrosion rate: $dm/dt = A_j/nF$**

e.g. for Fe: $1\text{mm/yr} \Leftrightarrow 7.8 \text{ kg/m}^2.\text{yr} \Leftrightarrow 863 \text{ mA/m}^2$

Polarisation curves



Shape of polarisation curves, types of polarisation



Activation Polarisation
 (Tafel Law: $E = a + b \log i$)

Concentration Polarisation
 (effect of O_2 diffusion)

Polarisation curves of iron in aerated water

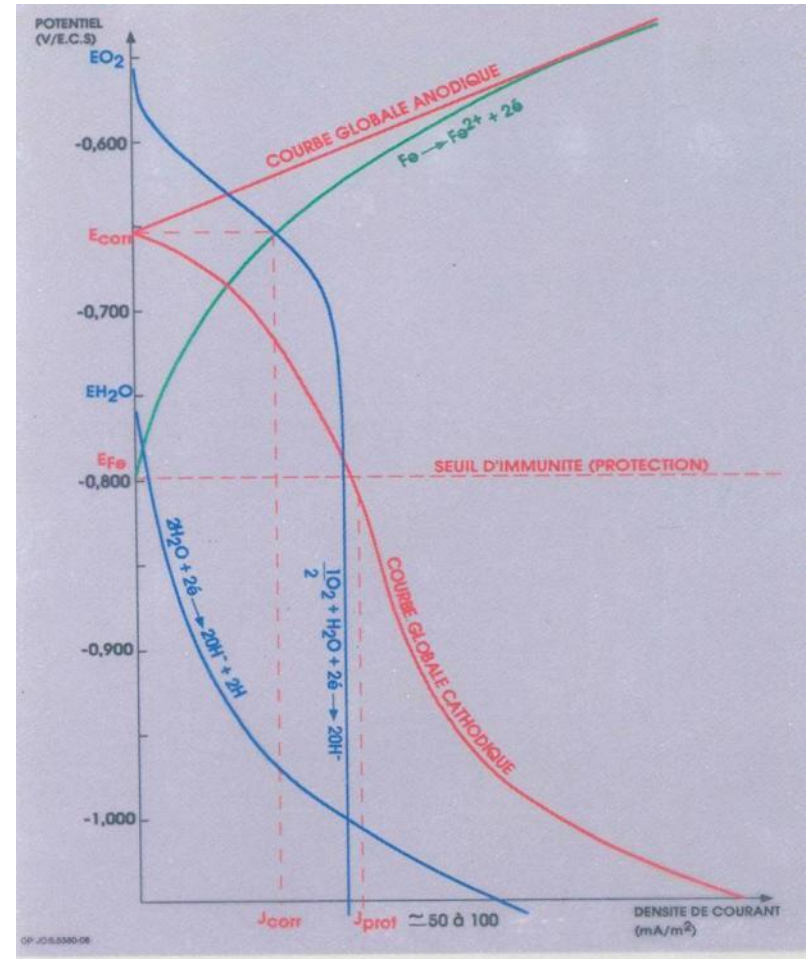
Increase of corrosion

Natural corrosion potential

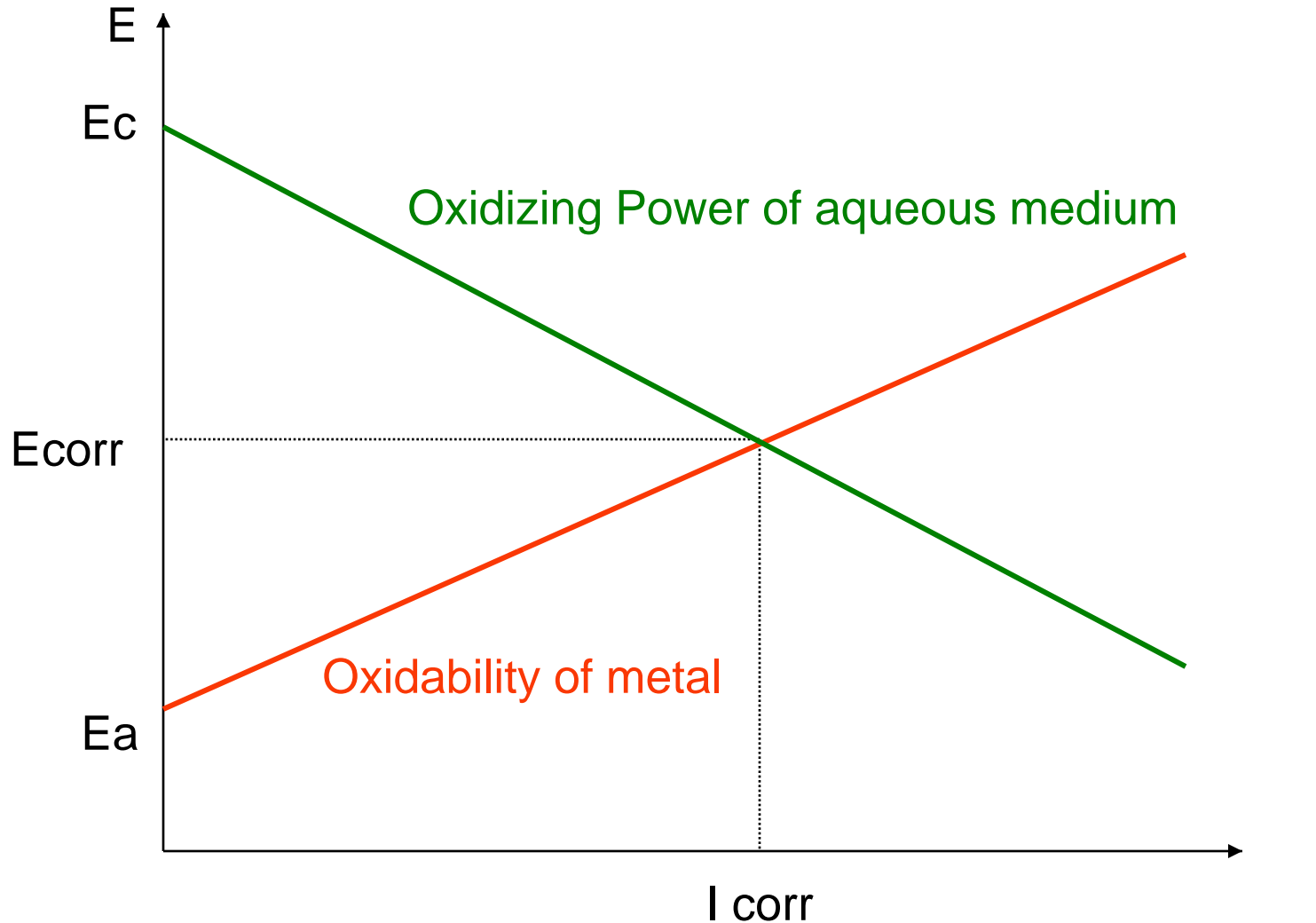
Cathodic protection potential

Significant evolution of hydrogen

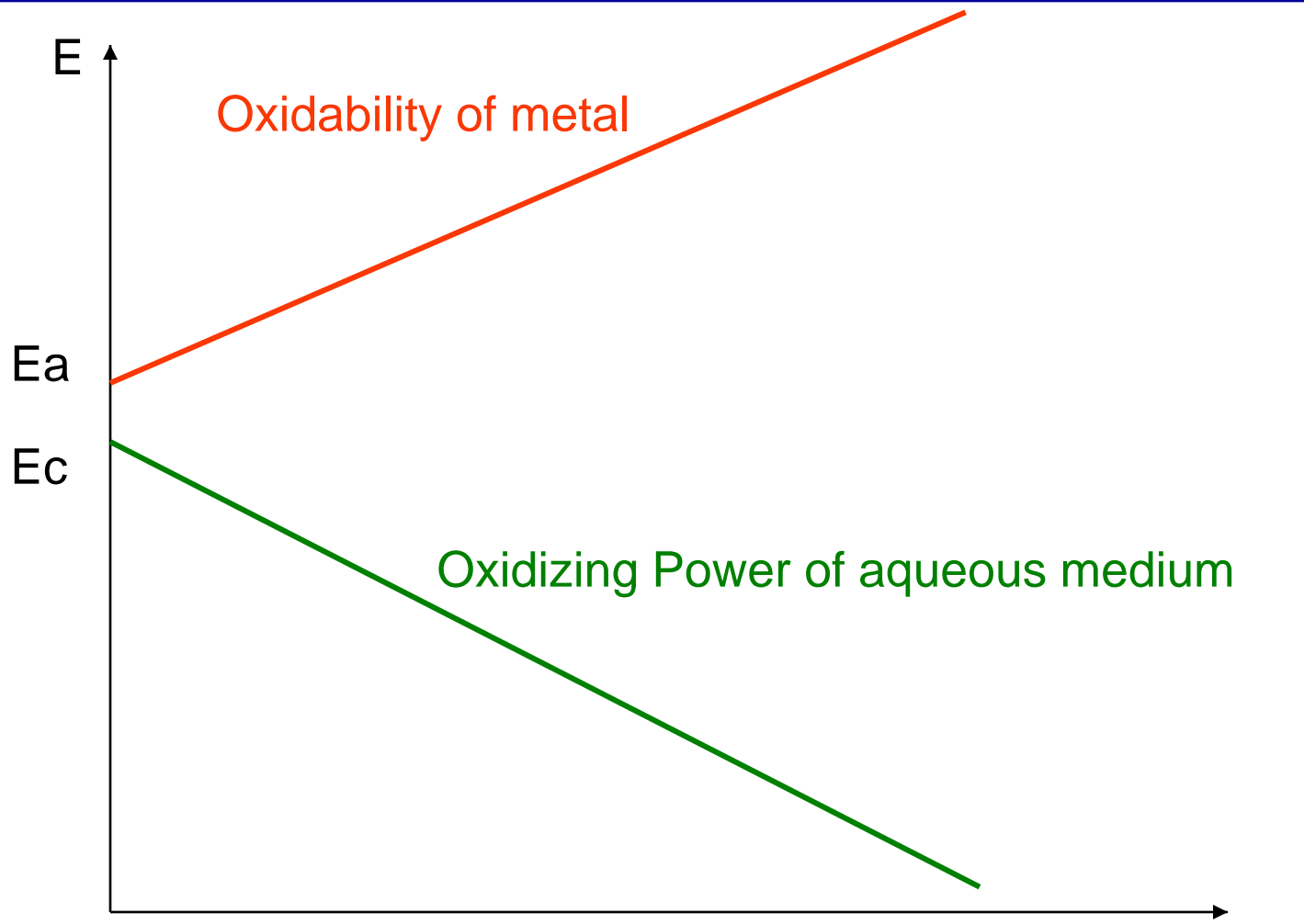
Over cathodic protection



Evans Diagram: case of corrosion



Evans Diagram: case of non corrosion



Secondary reactions

- ◆ Species produced by anodic and cathodic electrochemical reactions of the primary corrosion process react together to form **corrosion products** :

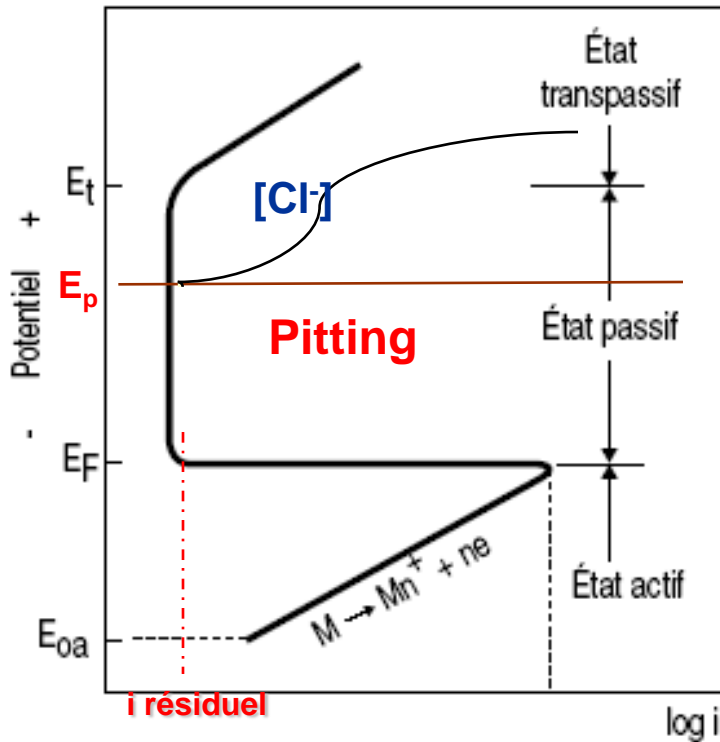


- ◆ Atomic H formed at cathode react to form more stable molecular H₂:



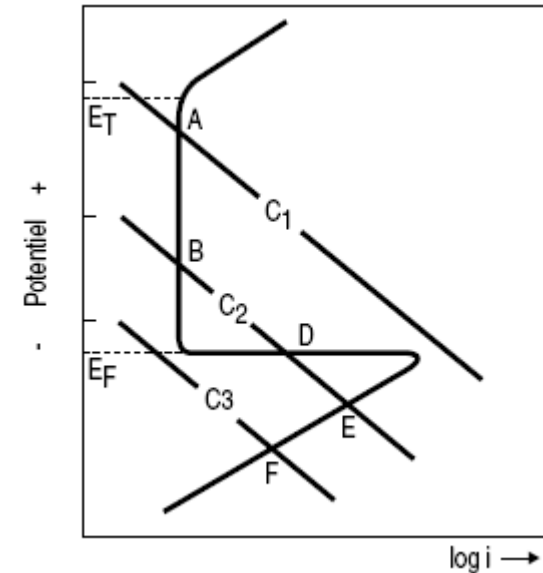
- ◆ However a part of H is introduced into the metallic structure and can lead to **H embrittlement** (increased by the presence of some species in the water: **H₂S**, **CN⁻**, **HF**, **As**, ...)

Passivation



D MAC 2104 A

Courbe de polarisation anodique d'un alliage passivable.

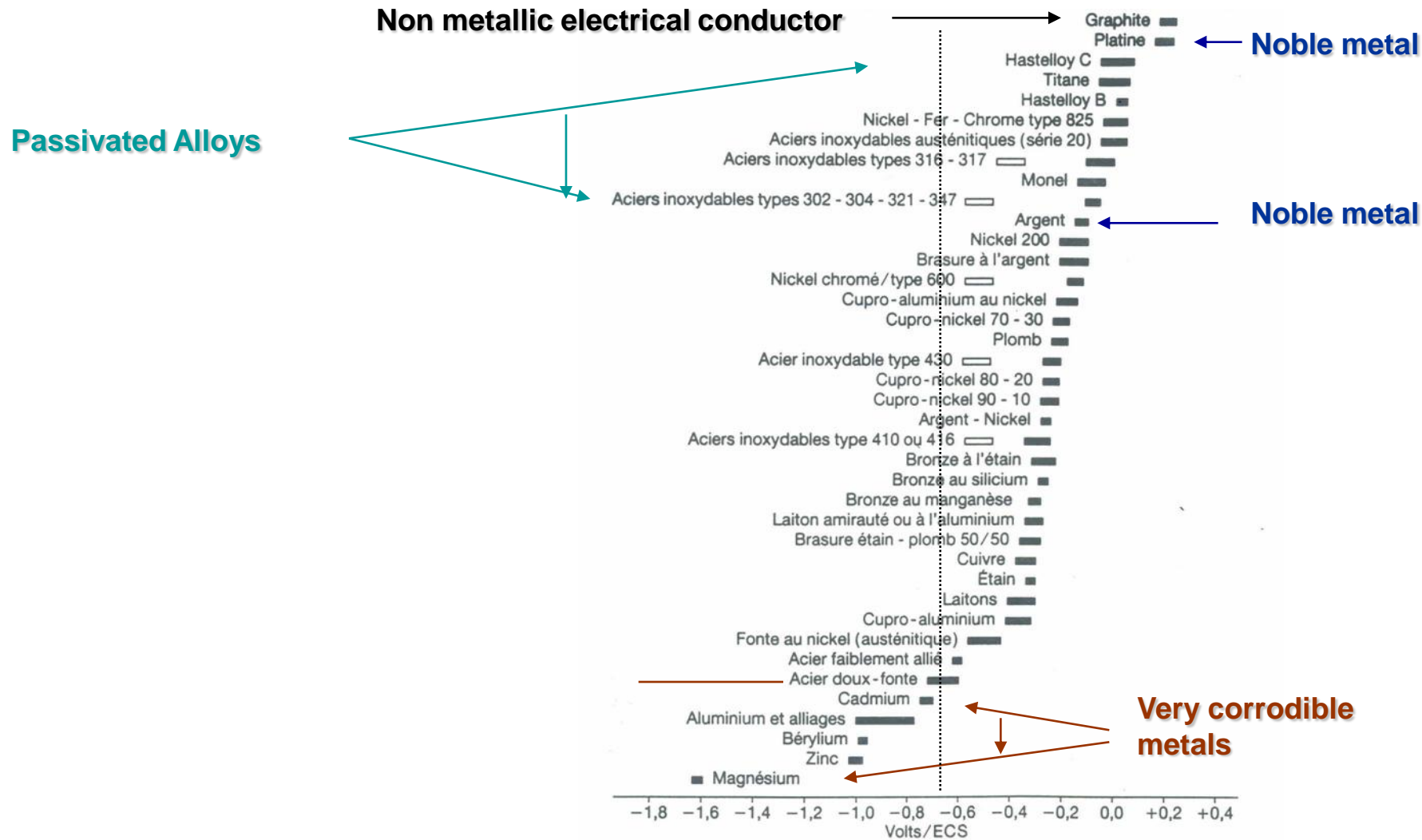


- C1: stable passivity
- C2: unstable passivity
- C3: corrosion

Passivation due to:

- adsorption species (thickness 2 à 3 nm): stainless steels, Ni-Cr alloys,...
- films of oxides: Al, Ti, Ta, Nb

Series of natural corrosion potentials in seawater



Main forms of corrosion

◆ GENERAL CORROSION

- anodes and cathodes not localised at the interface

◆ LOCALIZED CORROSIONS

- anodes and cathodes localised at the interface due to **heterogeneities**

- $I = S_a \times j_a = S_c \times j_c$

⇒ **Concentration of corrosion if $S_a \ll S_c$**

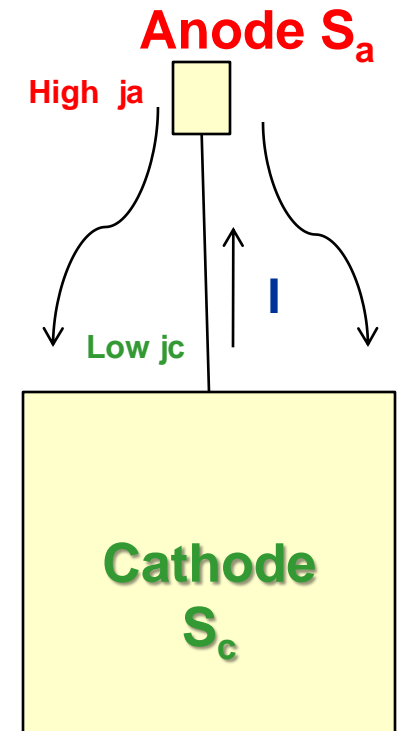
- **Heterogeneities:**

- **in the metallic phase or at the surface :**

- ✓ *galvanic (polymetallic) corrosion, pitting, selective corrosions (graphitisation of cast iron, dezincification of brass,...), intergranular corrosions (sensibilised stainless steels,...)*

- **in the corrosive environment :**

- ✓ *differential aeration corrosion, crevice corrosion of stainless steels, geological cells, ...*



Galvanic corrosion

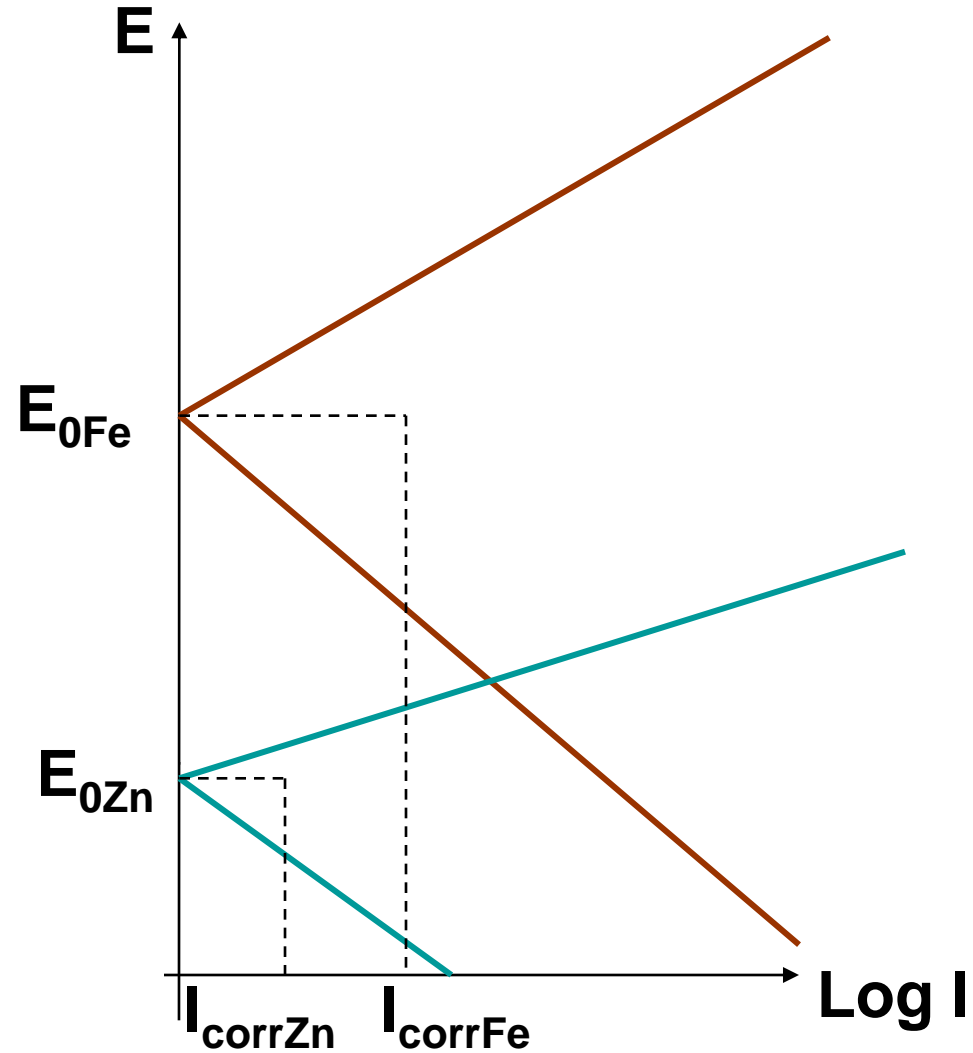
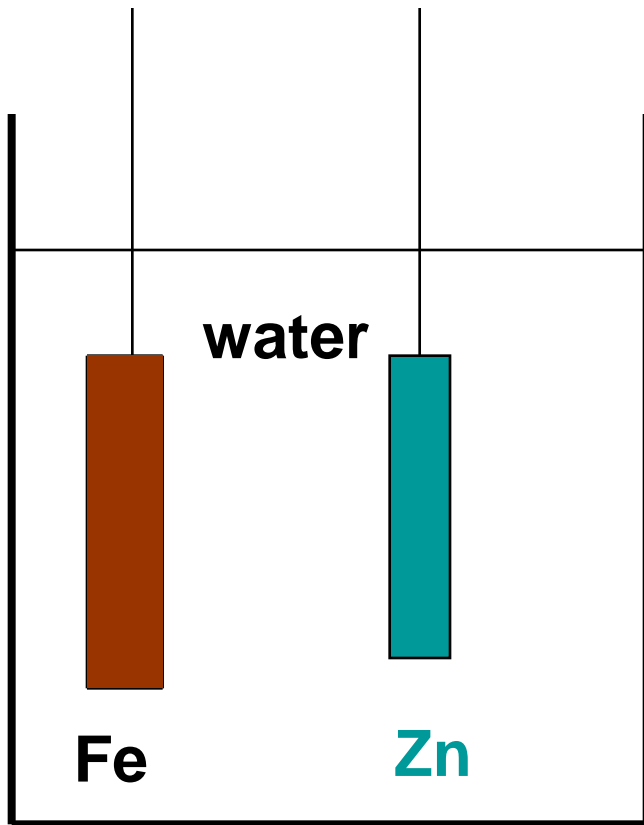


Corrosion of Al coupled with brass in seawater

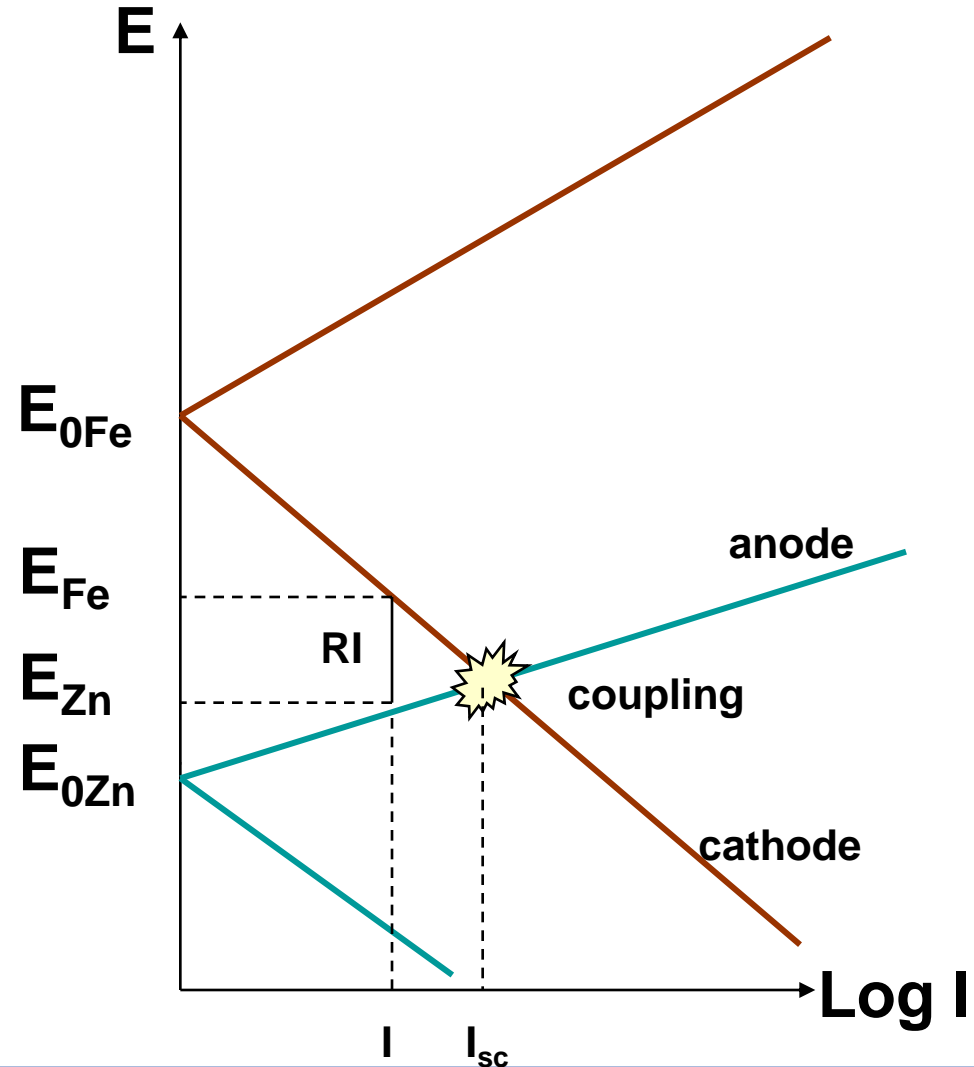
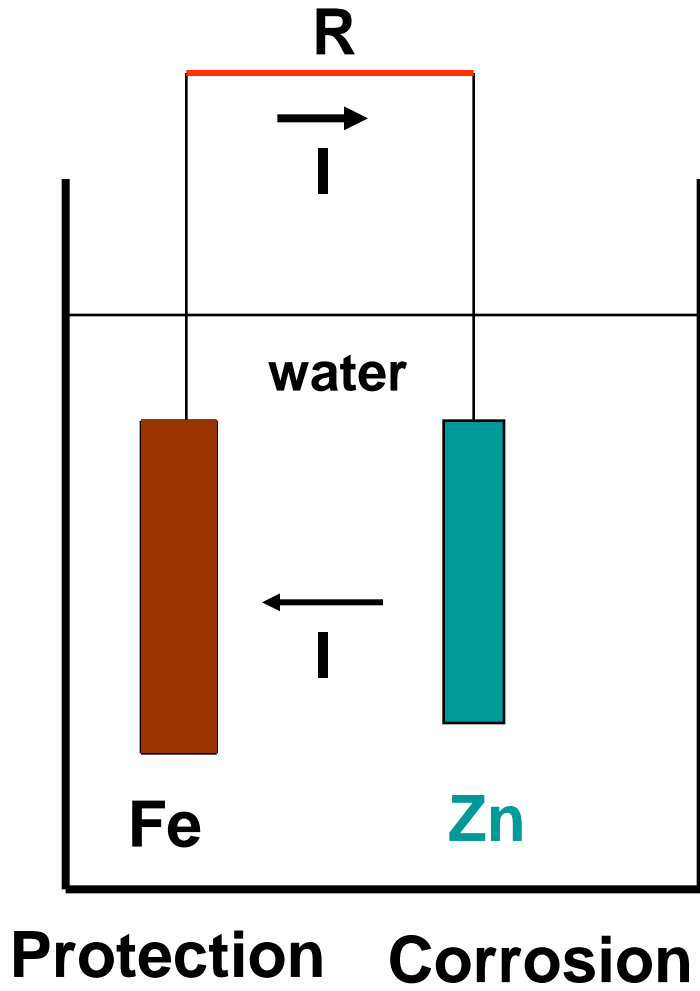


Corrosion of Al in contact with a gasket in graphite containing rubber

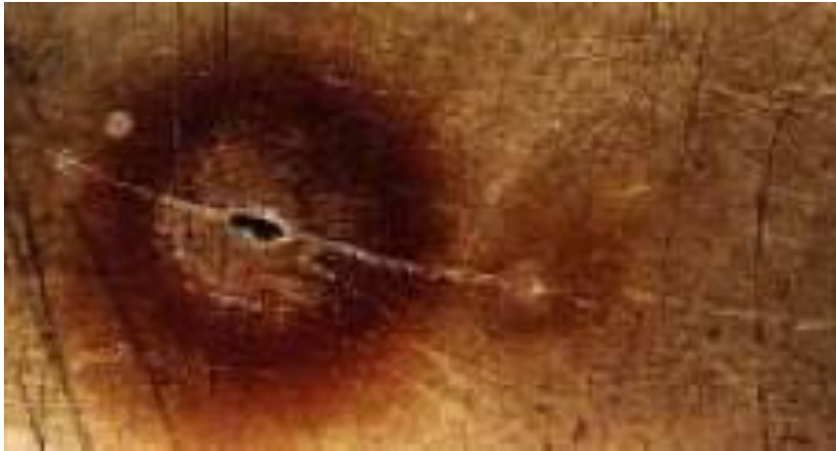
2 metals in one electrolyte



After coupling: Galvanic (bimetallic) corrosion



Pitting corrosion



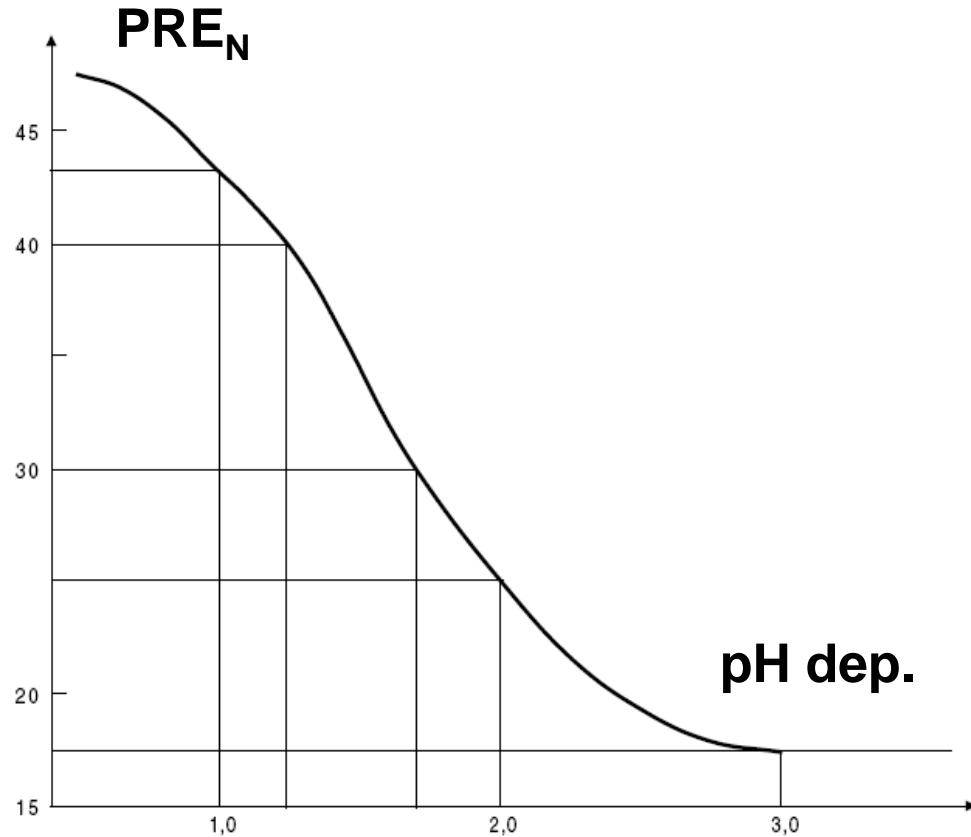
316 SS in seawater

- Initiation at an heterogeneity (ex. Inclusion, scratch, ...)
- Propagation by acidification inside the pit

When $E > E_p$

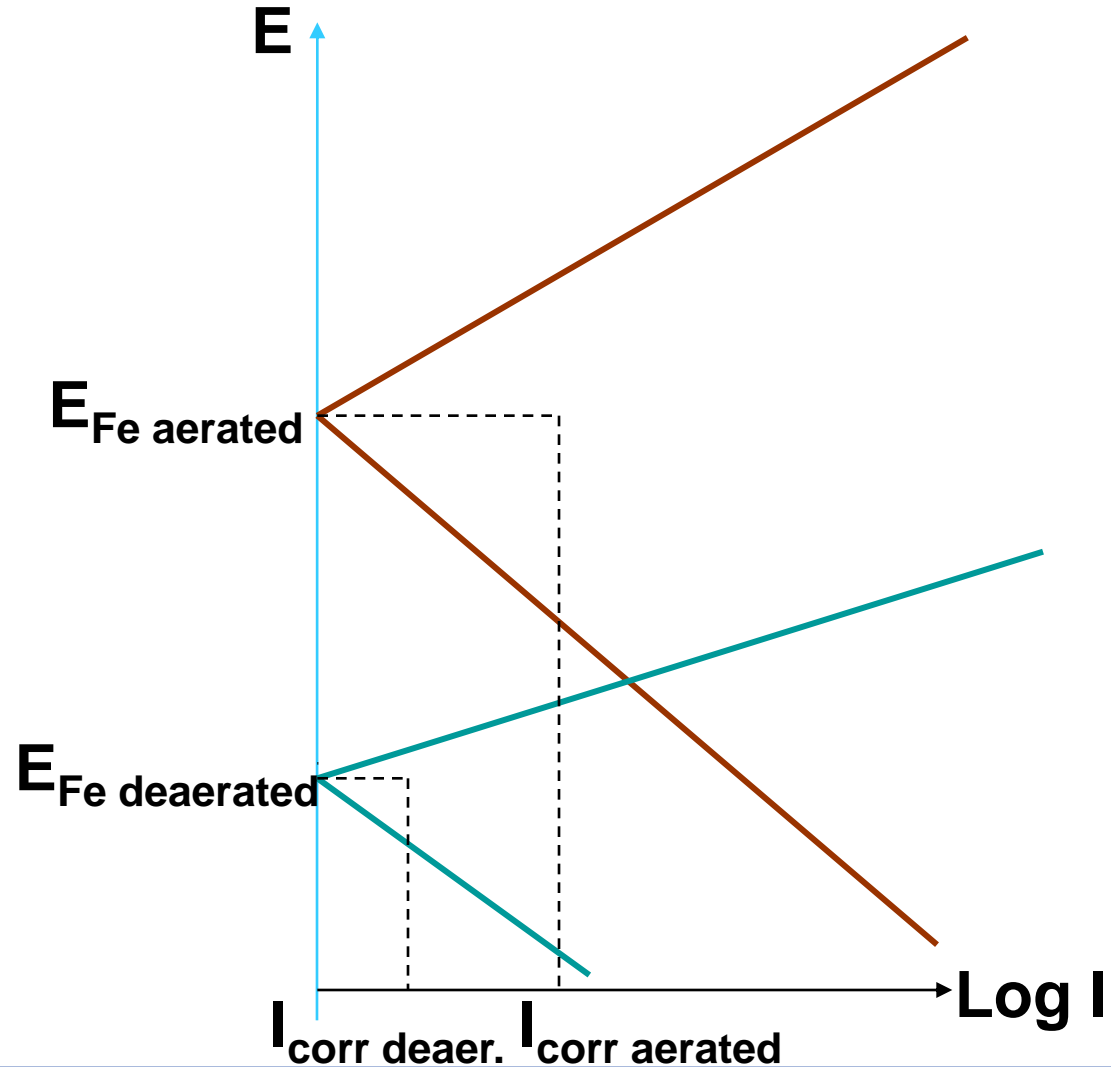
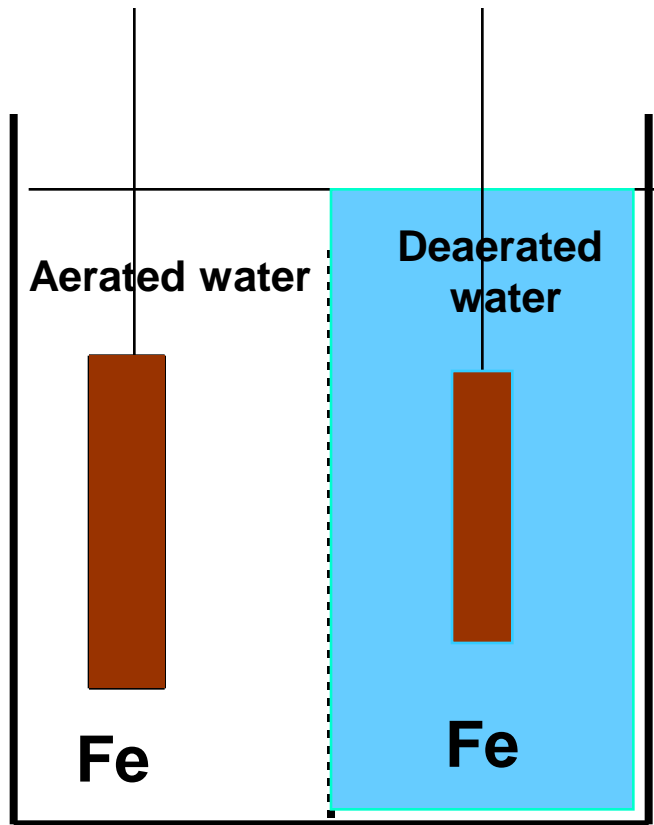
Pitting Resistance Equivalent and Depassivation pH of stainless steels

- Breakdown of passivity function of "depassivation pH"
- "Pitting Resistance Equivalent" (PRE) for classification of stainless steels in relationship with their resistance to localized corrosions in chloride containing waters (or in hydrochloric acid)

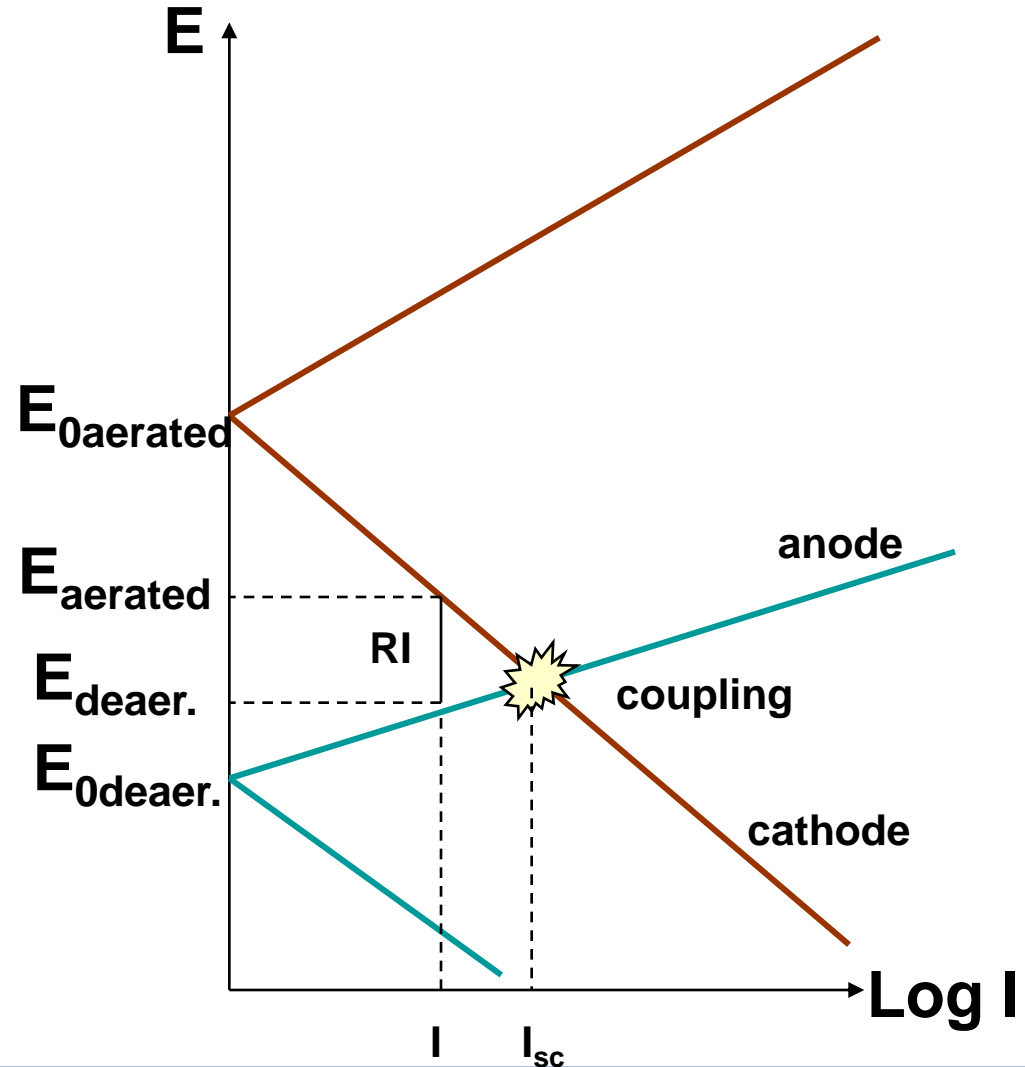
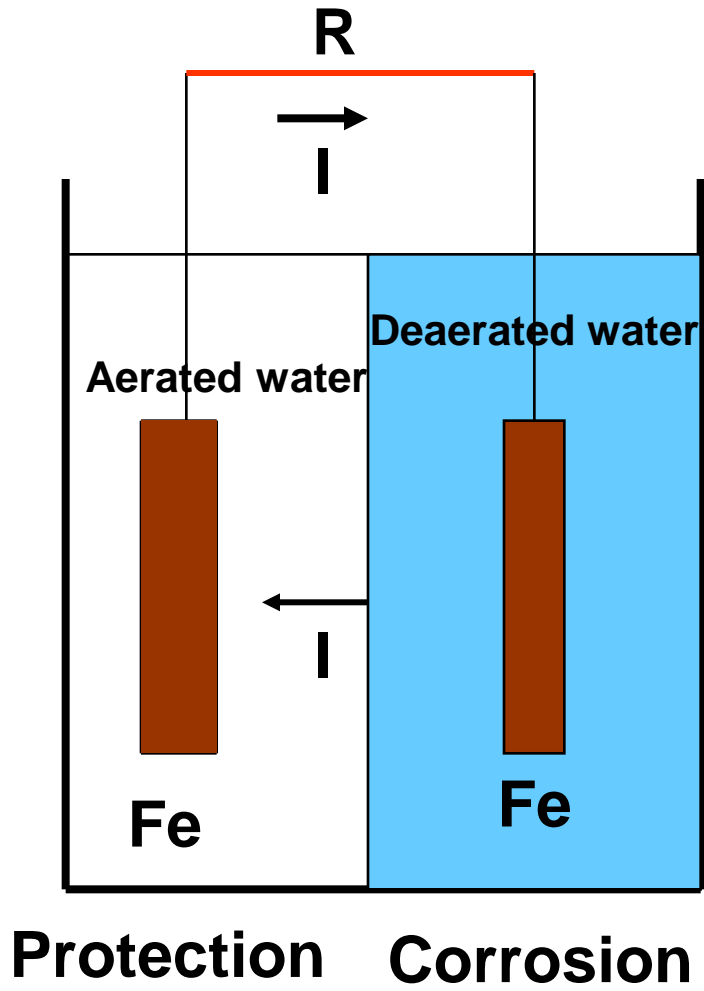


$$\text{PRE} = \% \text{Cr} + 3.3 \% \text{Mo} + 16 \% \text{N} + 0.5 \% \text{Ni} + 1.7 \% \text{W}$$

One metal in 2 electrolytes

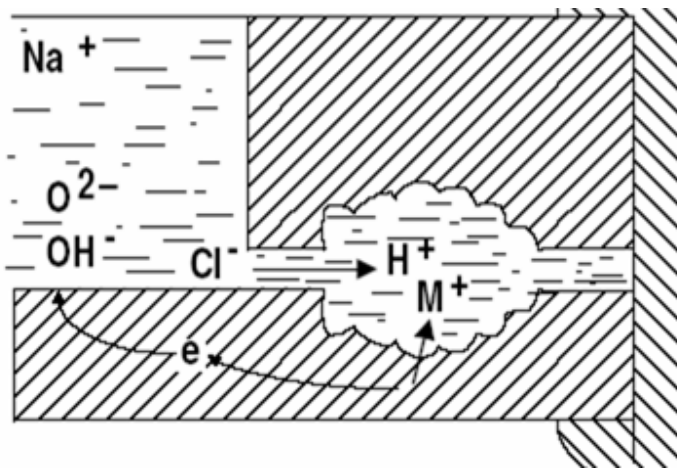


After coupling: Differential aeration corrosion



Crevice corrosion

- ◆ **Depassivation** of stainless steels exposed to **zones of low renewal** of water containing **Cl⁻** (gaskets, deposits, crevices,...)
- ◆ Caused by **lowering of pH** due to hydrolysis of cations **Cr³⁺**



Complex corrosions

◆ Mechanical effects:

- In the metallic phase or at the interface: Stress corrosion cracking, Hydrogen embrittlement, fatigue corrosion,...
- In the water phase: erosion-corrosion, abrasion-corrosion, cavitation-corrosion

◆ Biological effects:

- Biofilms (seawater)
- Bacterial Corrosion or "Microbiologically Induced Corrosion" (MIC)

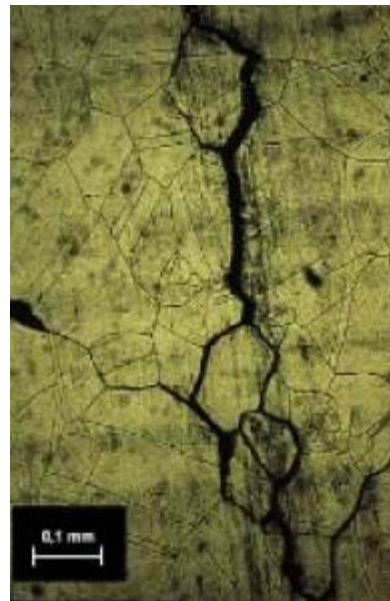
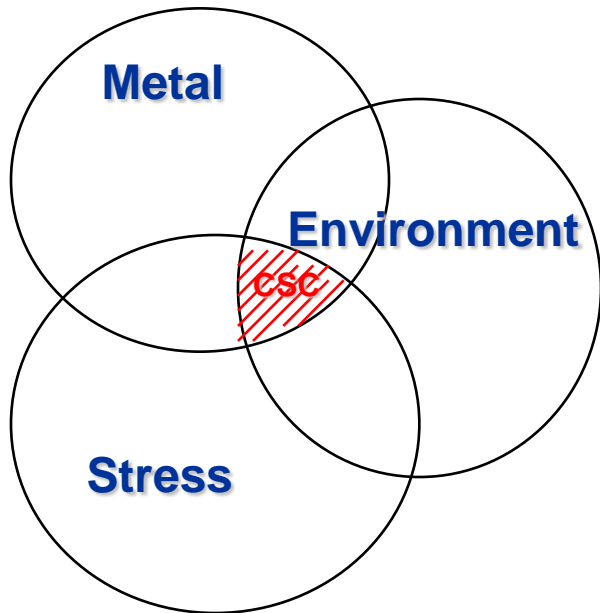
◆ Electrical effects:

- D.C. stray currents, Telluric currents, A.C. stray currents

Stress Corrosion Cracking (SCC)

Couples metal – environment leading to SCC

Acier au carbone	H ₂ S humide, soude, solutions de cyanure (HCN), nitrates en solution
Aciers inox	Chlorures, bromures, soude, potasse, eau de mer
Laiton	Ions ammonium (NH ₄ ⁺), Hg
Alliages d'aluminium	Hg
Titane	Méthanol



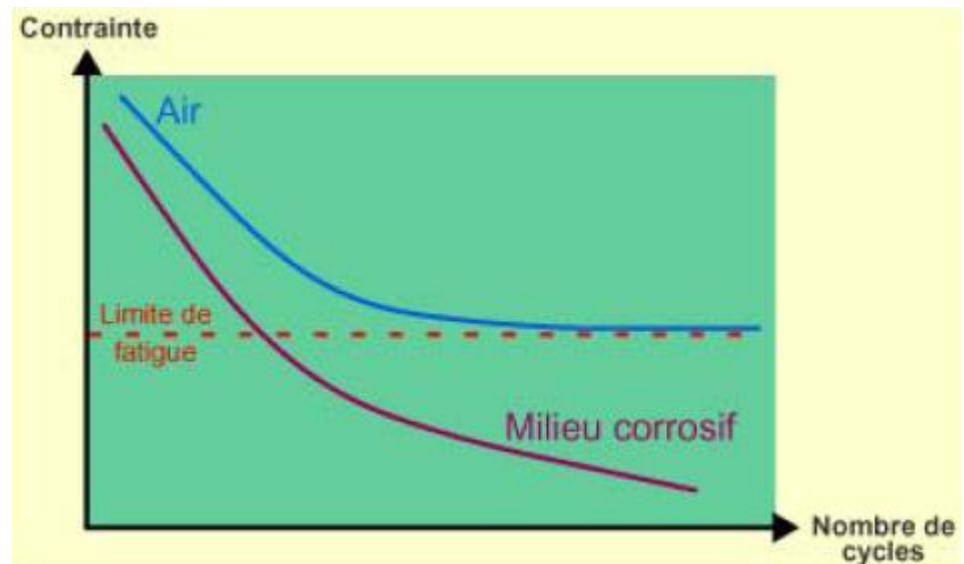
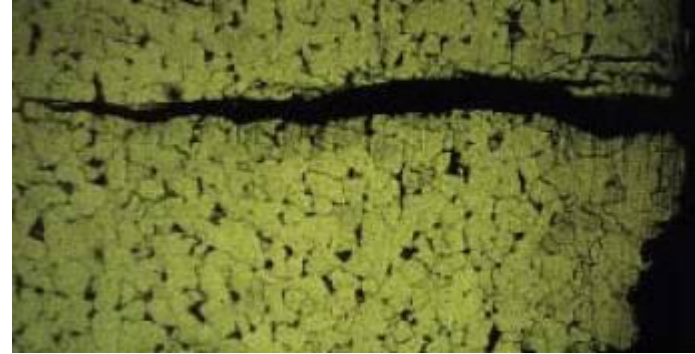
Intergranular



Transgranular

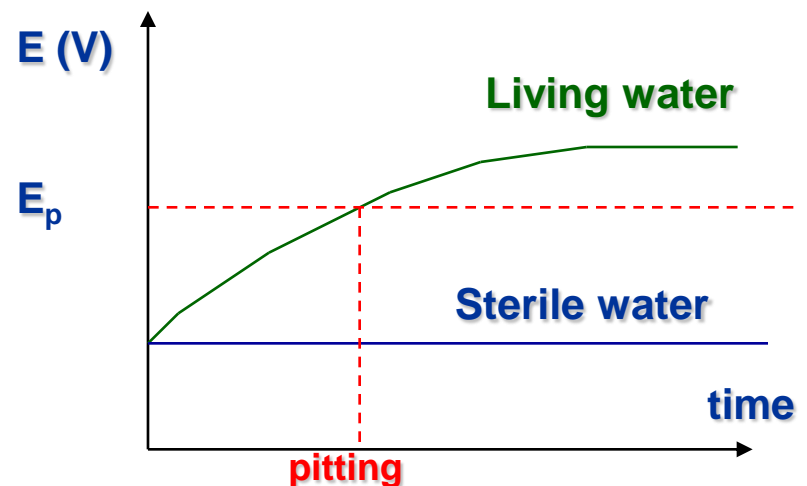
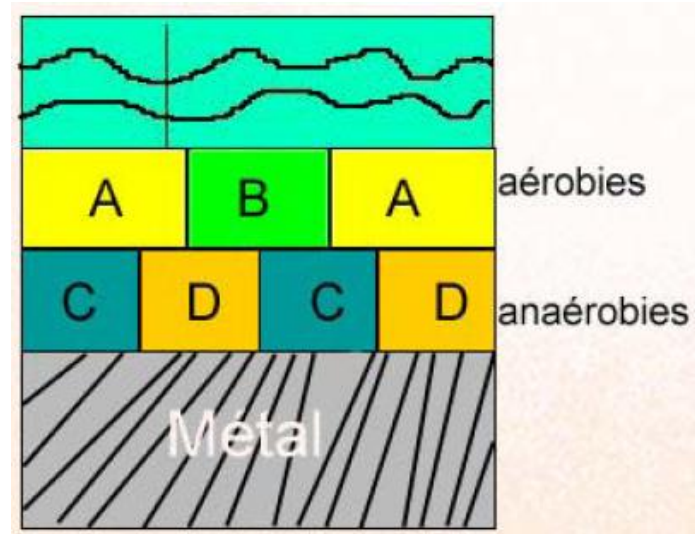
Fatigue-corrosion

- Fatigue cracks generally containing corrosion products
- Very dangerous because **no fatigue limit** (\neq pure fatigue)
- Major issue for marine and offshore structures
→ corrosion to be prevented.



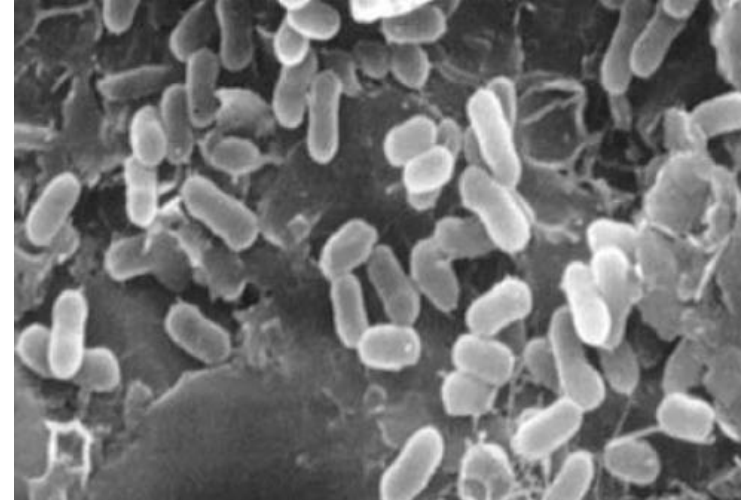
Biofilm

- ◆ Exposure of a solid substrate in a non sterile water leads to a rapid settlement by micro-organisms: formation of a biofilm: polyméric network, highly hydrated (85 to 90% water), including micro-organisms and debris.
- ◆ This provokes a significant change of surface conditions.
- ◆ **Potential of stainless steels becomes more positive (noble) with time**, hence a lower resistance to pitting.



"Microbiologically Induced Corrosion" (MIC)

- ◆ Bacteria are monocellular microorganisms (a few μm)
- ◆ Metabolisms may lead to a local increase of corrosivity
- ◆ Sulfidogenic bacteria (producing H_2S) are the most dangerous and frequent
- ◆ **Exponential growth when local conditions are favorable:** average salinity, presence of nutrients and breathing species, average temperature, pH near neutrality, local absence of oxygen,...



Limits

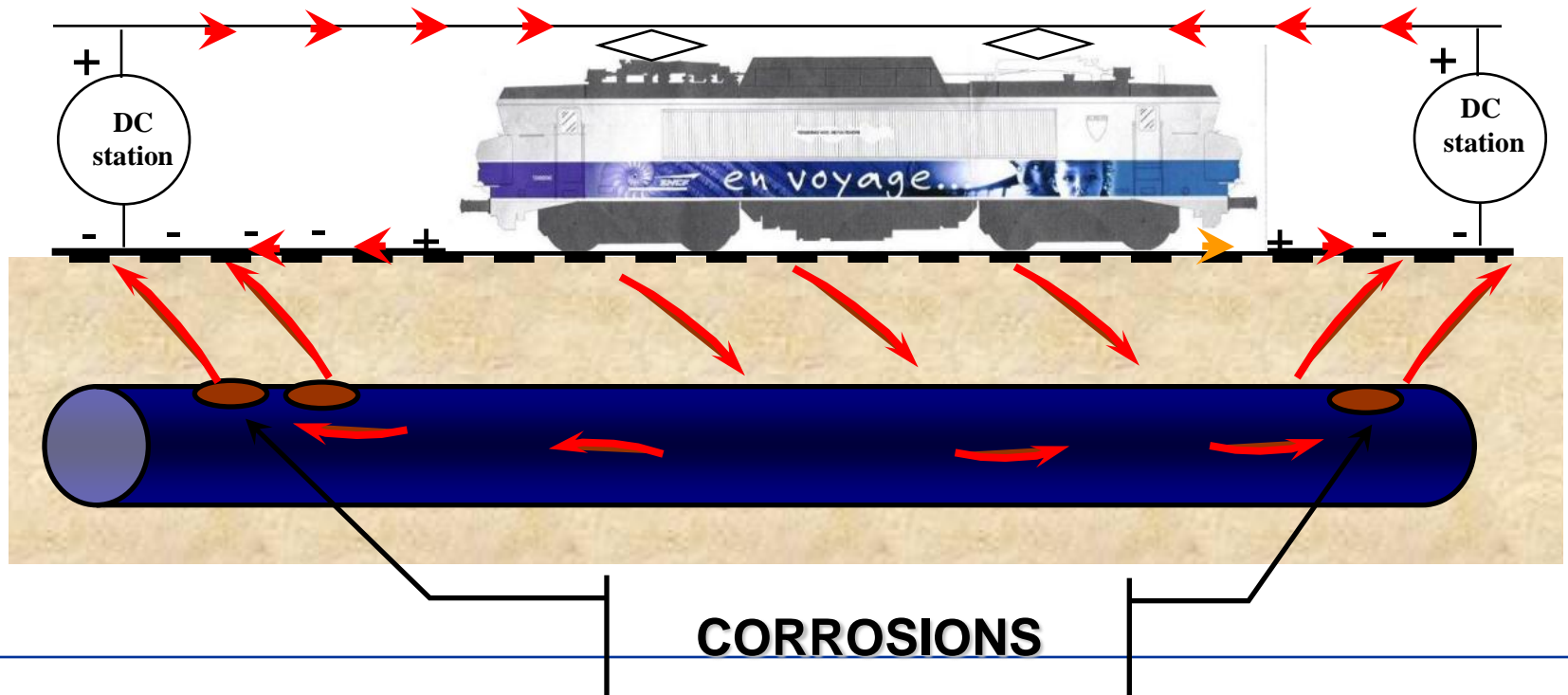
pH	0 - 12
Salinité (NaCl)	0 - 300 g/L
Température	5 - 110 °C
Pression	1 - 500 bars

Stray currents, telluric currents

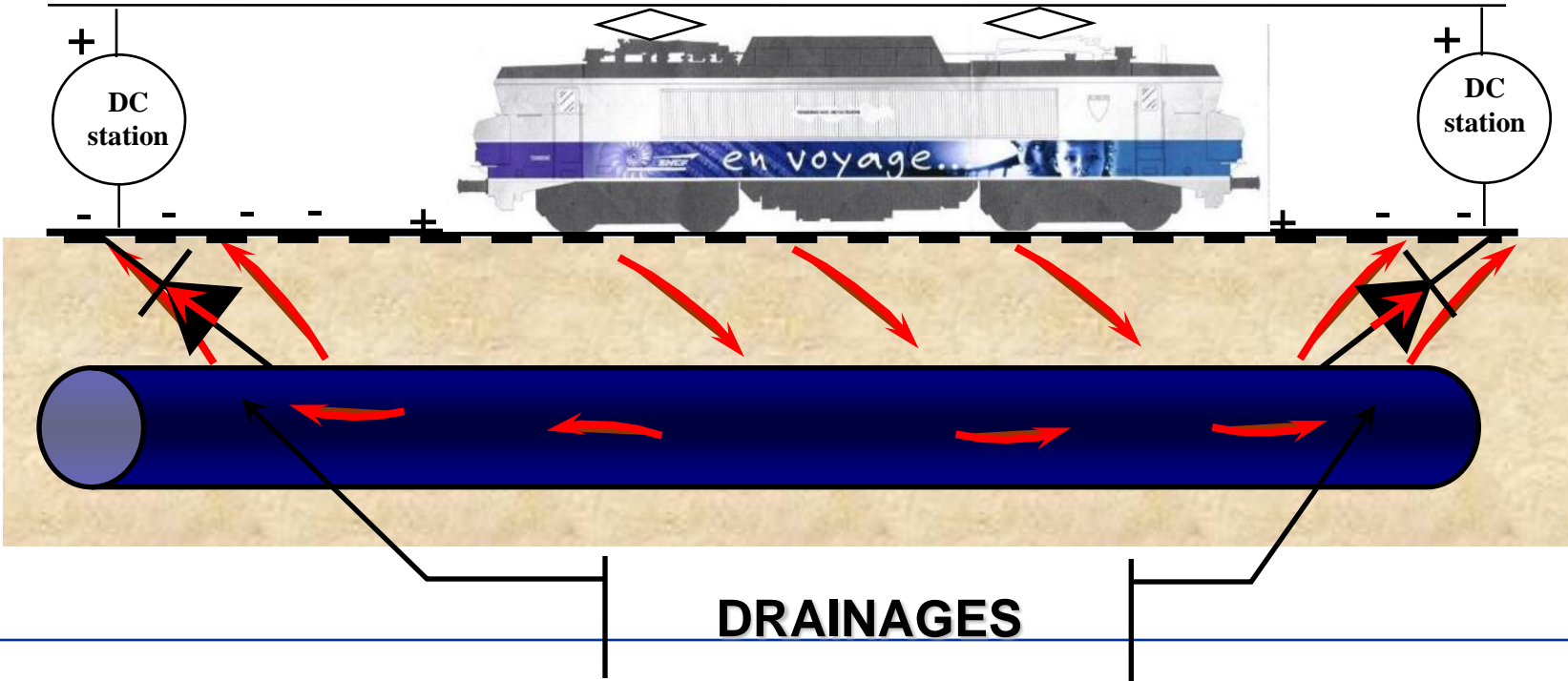
- ◆ **"Stray currents"** are electrical currents, varying in their intensity, and direction, circulating in the ground and issued most often from electrical traction networks (trains, tramways)
- ◆ **"Telluric currents"** are varying electrical currents due to geomagnetism, present in some regions of the world and leading to fluctuations of potential on buried pipelines. They may be reduced using isolating joints and mitigated through installation of galvanic anodes at the right locations.

Corrosion due to DC stray currents

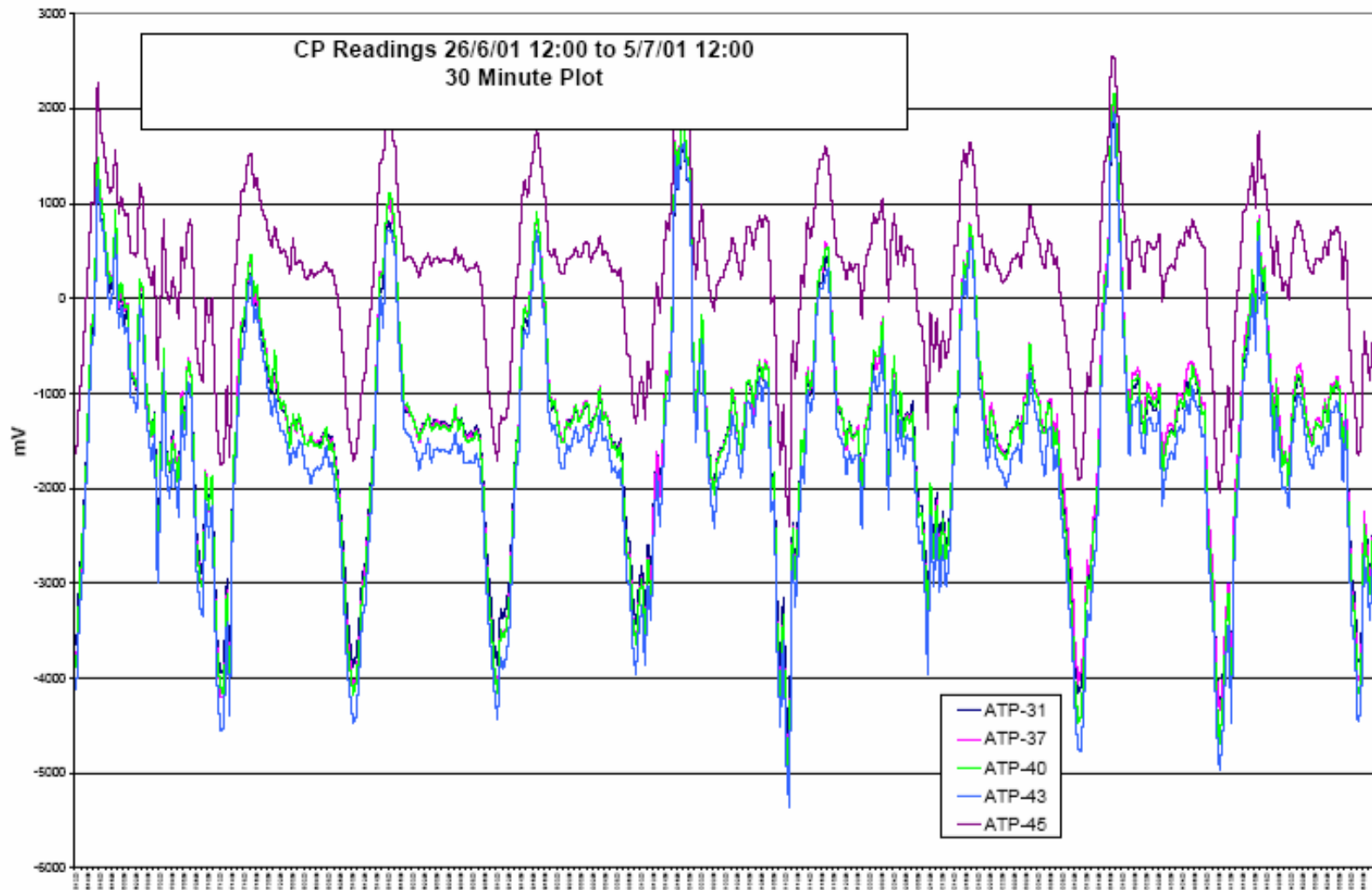
Stray currents from dc traction



Drainage of DC stray currents



Telluric currents on pipeline



TPA Training Course

Corrosion Management in the Oil & Gas Industry

End of Part 1