

CORROSION DAMAGE AND DEGRADATION

N. Mary (09.2023 – Tohoku Univ.)





1. PART 1. INTRODUCTION OF DAMAGE AND DEGRADATION



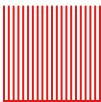
2. CORROSION BASIS

3. CORROSION TESTING, MONITORING,
INSPECTION

4. CORROSION PREVENTION



- **CORROSION BASIS**



INTRODUCTION

Most commonly used metals are unstable in the atmosphere (except gold and platinum)

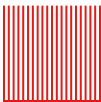
Corrosion is the process of a metal returning to the material's thermodynamic state.

For most materials it means the formation of oxide or sulfides

These changes are electrochemical reactions that follow the laws of thermodynamics.

- added dimension of chemistry and electricity
- reaction time and temperature dependent
- corrosion rate affected by ion and corrodent concentration

→ this explains why some reactions are reversible or controllable while others are not



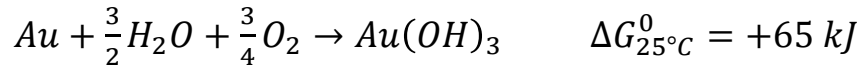
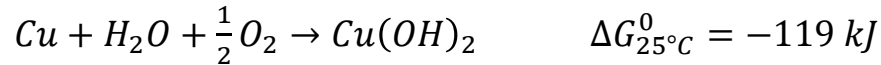
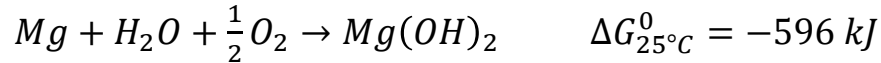
INTRODUCTION



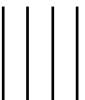
Two parameters of the system (material) change:

- Gibbs free Energy ΔG :
 - Thermodynamical or chemical potential which reduces when a system attains equilibrium.
 - Major factor on the spontaneity of reduction-oxidation reaction in electrochemistry

More negative of ΔG , the greater the tendency for the reaction to go



Note that large negative ΔG may or may not be rapid \rightarrow kinetic !



INTRODUCTION

Two parameters of the system (material) change:

- Gibbs free Energy ΔG :
- Pilling-Bedworth ratio (note it exists exceptions and limitations)
 - Parameter (1923) derived from metal oxidation in High Temperature
 - Metal-oxide PB ratio describe as the ratio of the metal oxide volume produced by the oxygen and the metal reaction of the consumed value of metal

$$R_{PB} = \frac{V_{oxide}}{V_{metal}} = \frac{M_{oxide} \times \rho_{metal}}{n \times M_{metal} \times \rho_{oxide}}$$

- If $R_{PB} < 1$: oxide film too thin \rightarrow break down (Mg case)
- If $1 < R_{PB} < 2$: oxide film passivating \rightarrow passive films (Ti, Cr, Al, ...)
- If $R_{PB} > 2$: oxide film chips off \rightarrow no protection (Fe, Cu)



DIFFERENT ORIGIN OF CORROSION

Metal vs environment: High temperature

- At low temperature : diffusion of O_2 and metal through compact oxide film
- At moderate and high temperature:
 - combination of oxide film formation and oxide volatility
 - Formation of volatile metal and oxide species at M-O interface, transport through oxide lattice and mechanically formed cracks in oxide layer
 - Direct formation of volatile oxide gases
- At high temperature
 - Gaseous diffusion of oxygen through a barrier layer of volatilized oxides
 - Spalling of metal and oxide particles

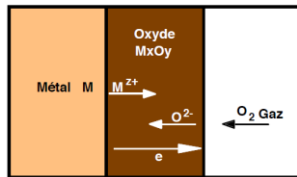


Figure III - 2 : Mécanisme de l'oxydation d'un métal à haute température

Linear law (Ba, Ma) $\xi = kt$
 Parabolic law (Fe, Ni, Cu) $\xi^2 = 2kt$
 Log law (Zn) $\xi = \xi_0 + k \ln(t)$

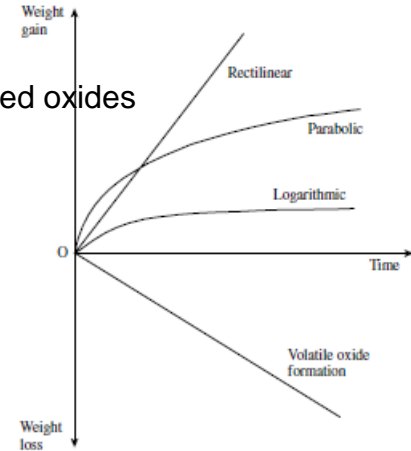


Figure 1.36 Oxidation rate loss showing weight gain and weight loss with different kinetic forms. (Reproduced from *Corrosion for Science and Engineering*, Trethewey and Chamberlain, Copyright Pearson Education Ltd)

DIFFERENT ORIGIN OF CORROSION

Metal vs environment: aqueous environment

- Water adsorption at the metal surface

➔ Atmospheric (H_2O, SO_2, Cl^-)

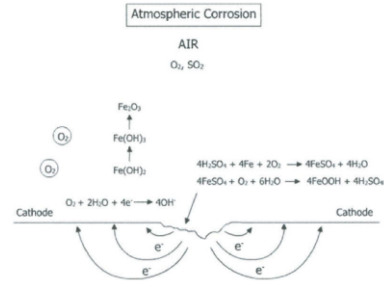
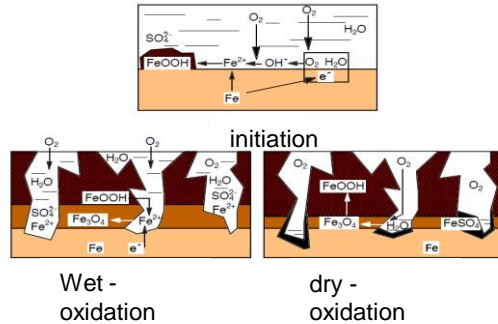
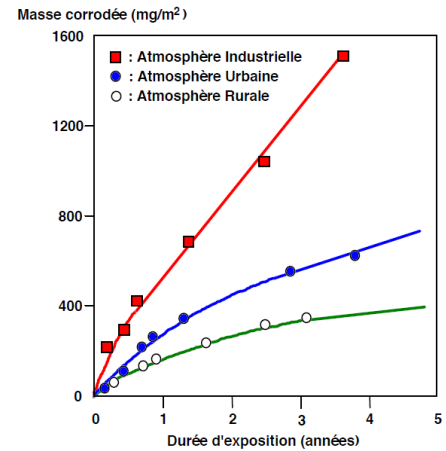


Figure 4.3 Effect of SO₂ and humidity on metallic corrosion. Reaction occur in a very thin (invisible) aqueous layer



3 : Corrosion de l'acier sous différentes atmosphères (d'après K. Barton)

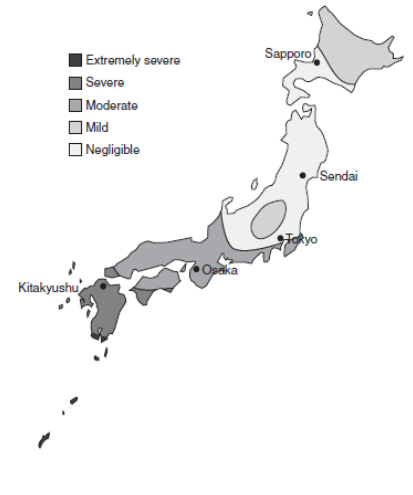
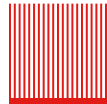


Figure 9.37 Corrosivity map of Japan.

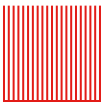
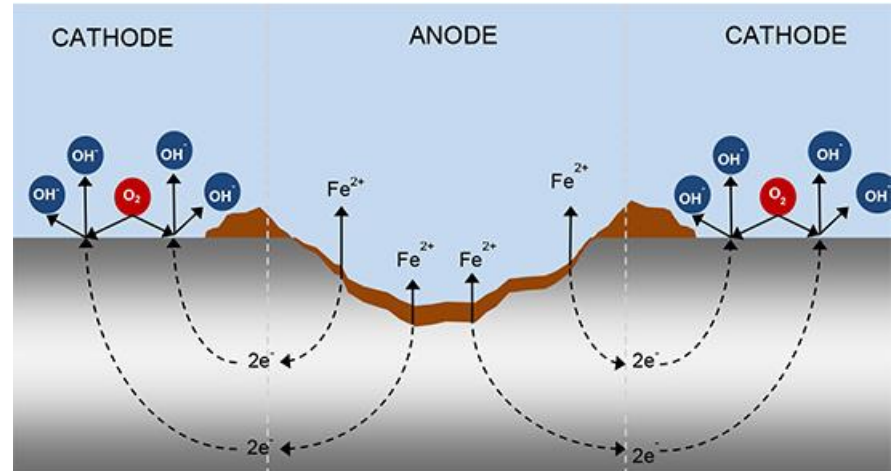
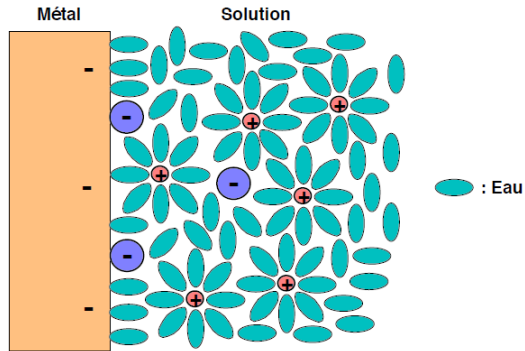


DIFFERENT ORIGIN OF CORROSION

Metal vs environment: aqueous environment

- Water adsorption at the metal surface

➔ Aqueous solution



DIFFERENT ORIGIN OF CORROSION

Metal vs environment: aqueous / atmospheric environment

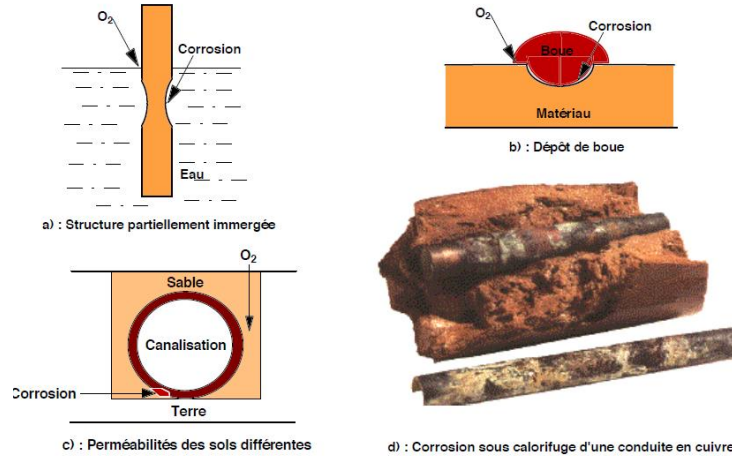
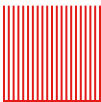


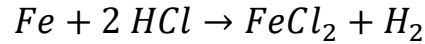
Figure IV - 9 : Exemples de corrosion par aération différentielle



AQUEOUS CORROSION

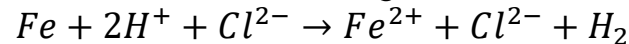
Most basic corrosion reactions involves the oxidation of a pure metal when exposed to a strong acid.

For exemple Iron exposed to hydrochloric acid :

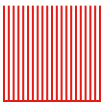


The result of this reaction is the gradual disappears of the iron and the dihydrogen bubbles rising rapidly.

On an electrochemical level, there is also an exchange of electron



- Iron is converted to an iron ion: $Fe \rightarrow Fe^{2+} + 2e$
- Hydrogen gain electrons: $2H^+ + 2e \rightarrow H_2$



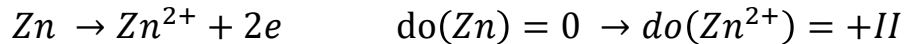
ANODE AND CATHODE



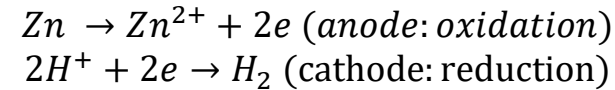
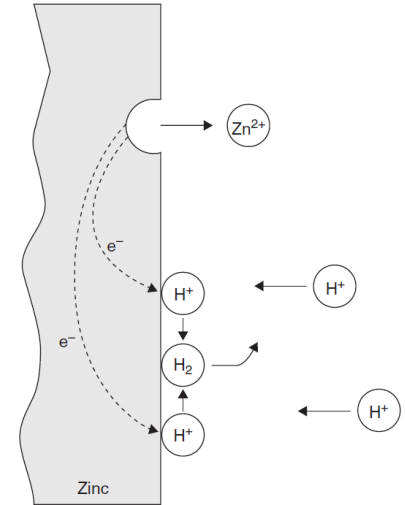
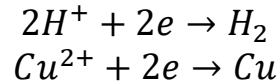
Within electrode, current is carried by both negative and positive carriers

- Negative carriers are electrons and move in a metal
- Positive carriers are ions in solution and current carried by ions depends on its mobility and electric charge of the ions

The reservoir of negative is the metal and release electron by an oxidation reaction



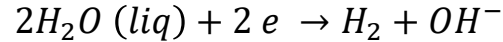
The positive carrier are ions, molecules or metal able to attract electrons of the oxidation



CATHODIC PROCESSES

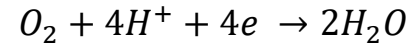
Reduction of hydrogen ions at the cathodic surface disturb the balance between the acidic ions and hydroxyl ions and make the solution less acidic or more alkaline at the corrosion surface

In neutral solution, [Al, Zn, Mg] develops enough energy to split water directly as

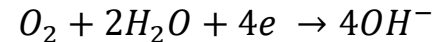


Several other cathodic reactions occurs

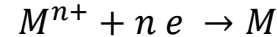
Dissolved dioxygen reduction (acid)



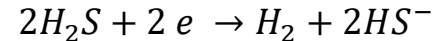
Dissolved dioxygen reduction (neutral)



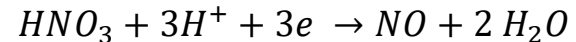
Metal reduction



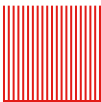
Hydrogen sulfate reductions



Nitric acid reduction



etc.

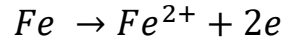


CELL POTENTIAL

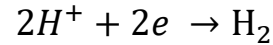
A reaction will occur only if there is a negative free energy change (ΔG)

$$\Delta G = -nFE$$

Where n is the number of electrons, F is the Faraday constant and E is the cell potential



Oxidation (loss of electron)



reduction (gain of electrons)

Each reaction has its own cell potential

$$E = E(H^+/H_2) - E(Fe^{2+}/Fe) = 0 - (-0.44) = +0.44$$

Because the cell potential is positive, the reaction takes place



CELL POTENTIAL

TABLE 2.1

Standard Oxidation-Reduction Potentials
25°C, Volts vs. Hydrogen Electrode

Redox Reaction	Oxidation-Reduction Potential
$\text{Au} = \text{Au}^{3+} + 3\text{e}^-$	+1.498
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$	+1.229
$\text{Pt} = \text{Pt}^{2+} + 2\text{e}^-$	+1.2
$\text{Pd} = \text{Pd}^{2+} + 2\text{e}^-$	+0.987
$\text{Ag} = \text{Ag}^+ + \text{e}^-$	+0.799
$2\text{Hg} = \text{Hg}_2^{2+} + 2\text{e}^-$	+0.788
$\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$	+0.771
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- = 4\text{OH}^-$	+0.401
$\text{Cu} = \text{Cu}^{2+} + 2\text{e}^-$	+0.337
$\text{Sn}^{4+} + 2\text{e}^- = \text{Sn}^{2+}$	+0.15
$2\text{H}^+ + 2\text{e}^- = \text{H}_2$	0.0000
$\text{Pb} = \text{Pb}^{2+} + 2\text{e}^-$	-0.126
$\text{Sn} = \text{Sn}^{2+} + 2\text{e}^-$	-0.136
$\text{Ni} = \text{Ni}^{2+} + 2\text{e}^-$	-0.250
$\text{Co} = \text{Co}^{2+} + 2\text{e}^-$	-0.277
$\text{Cd} = \text{Cd}^{2+} + 2\text{e}^-$	-0.403
$\text{Fe} = \text{Fe}^{2+} + 2\text{e}^-$	-0.440
$\text{Cr} = \text{Cr}^{3+} + 3\text{e}^-$	-0.744
$\text{Zn} = \text{Zn}^{2+} + 2\text{e}^-$	-0.763
$\text{Al} = \text{Al}^{3+} + 3\text{e}^-$	-1.662
$\text{Mg} = \text{Mg}^{2+} + 2\text{e}^-$	-2.363
$\text{Na} = \text{Na}^+ + \text{e}^-$	-2.714
$\text{K} = \text{K}^+ + \text{e}^-$	-2.925

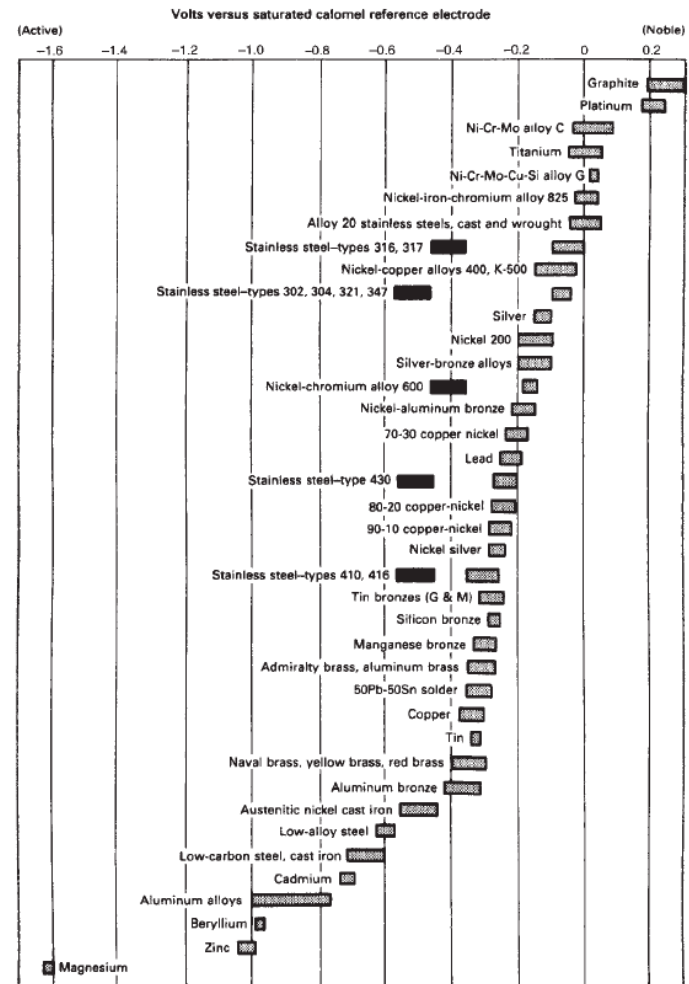


Figure 3.3. Galvanic series in seawater [5]. (Reprinted with permission of ASM International®. All rights reserved. www.asminternational.org.)

CELL POTENTIAL (EXAMPLE)

How behave a brass in either H_2SO_4 or HNO_3 solution?



CELL POTENTIAL (EXAMPLE)

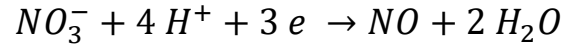


How behave a brass in either H_2SO_4 or HNO_3 solution?

1- Environment

both solutions are acid. H^+ has to be considered rather than O_2

SO_4^{2-} is rather stable in solution whereas NO_3^- is in equilibrium with NO according



→ different behavior are expected because of nature of chemical



CELL POTENTIAL (EXAMPLE)

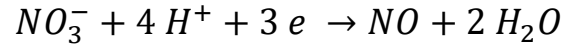


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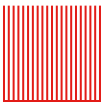
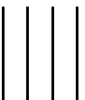
SO_4^{2-} is rather stable in solution whereas NO_3^- is in equilibrium with NO according



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2- Material

2 elements can oxidize $Cu \rightarrow Cu^{2+} + 2e$ and $Zn \rightarrow Zn^{2+} + 2e$



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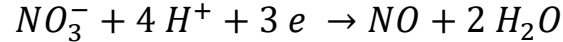


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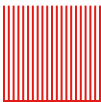
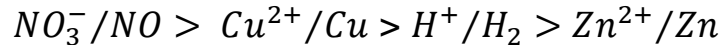


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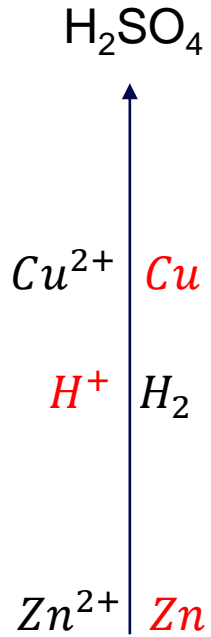
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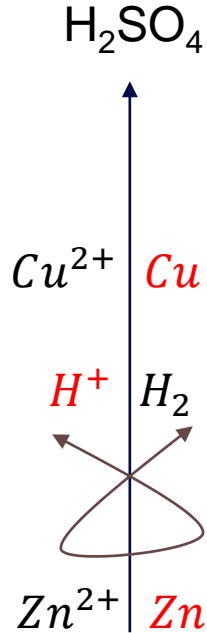
3- Potential scale



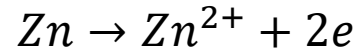
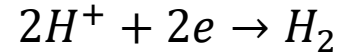
CELL POTENTIAL (EXAMPLE)



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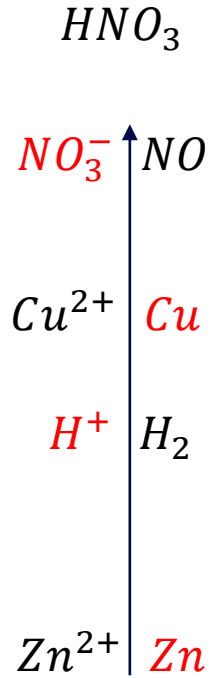


Only 2 reactions take place

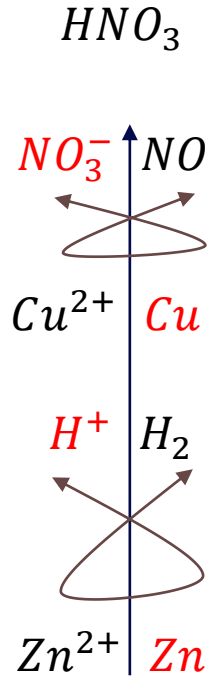


 Zinc electro-dissolution

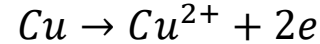
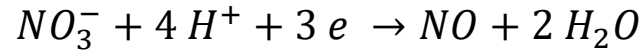
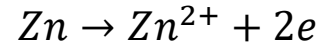
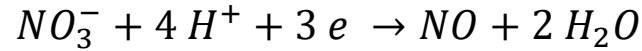
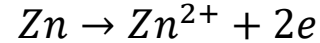
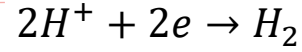
CELL POTENTIAL (EXAMPLE)



CELL POTENTIAL (EXAMPLE)



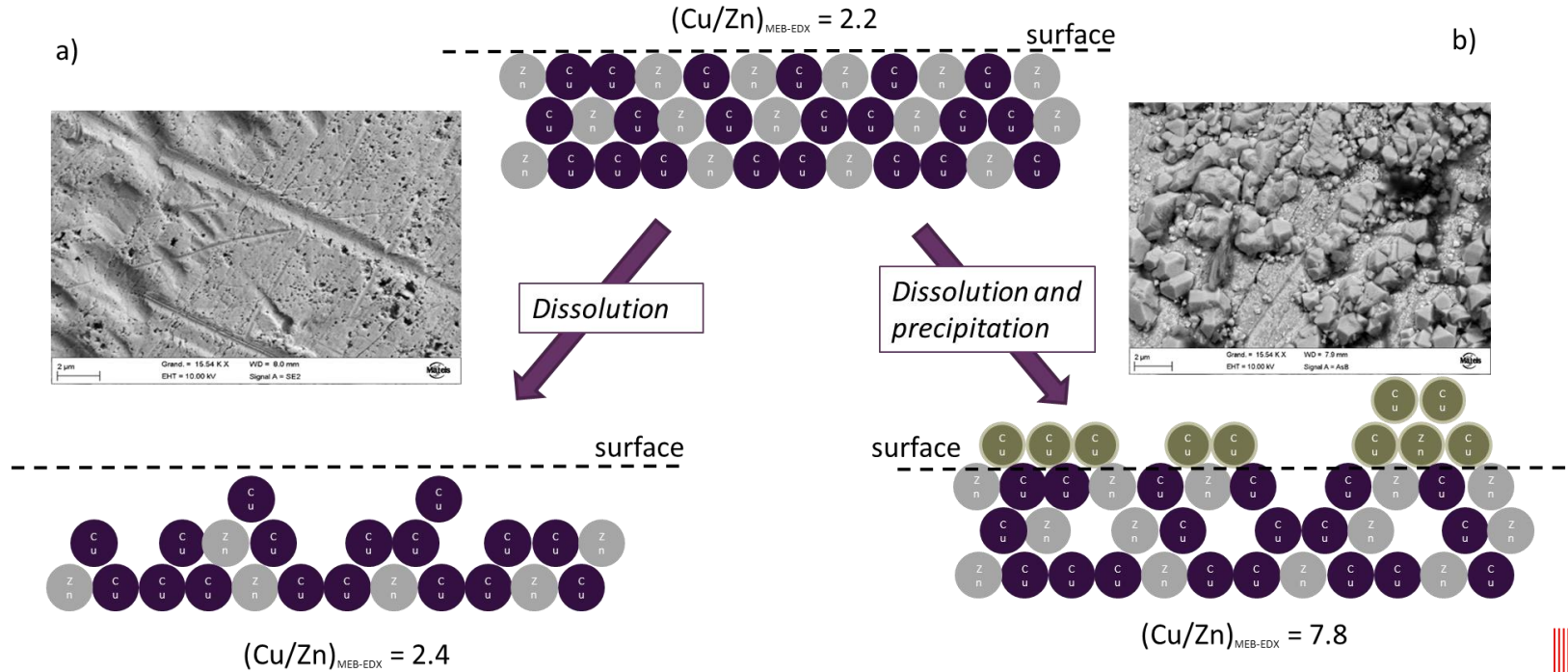
Several equations takes places



Zinc + copper electro-dissolution

CELL POTENTIAL (EXAMPLE)

Consequences on the material surface



TYPE OF LOCAL CELL FORMATION

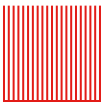
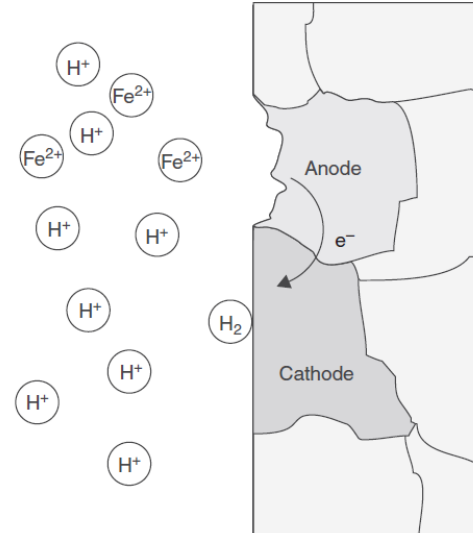


Three main types of cells in corrosion reactions

- Dissimilar Electrodes Cells

Including different materials, similar materials but different mechanical states (cold work metal vs. same annealed metal, grain boundary vs. grains, different crystal orientation).

FIGURE 3.7
Formation of ions at an anodic area and release of hydrogen at a cathodic area in a local cell on an iron surface.



TYPE OF LOCAL CELL FORMATION

Three main types of cells in corrosion reactions

- Concentration cells

Two identical electrodes in contact with different solution.

Salt concentration cell: same solution but different concentration
metal ion concentration

differential aeration cell : dissolve oxygen concentration vs deaerated

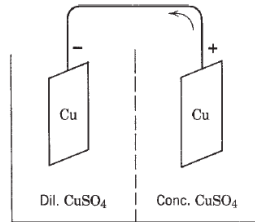


Figure 2.3. Salt concentration cell.

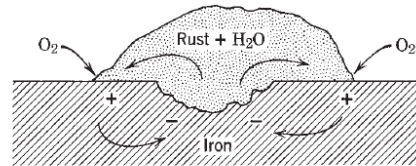


Figure 2.5. Differential aeration cell formed by rust on iron.

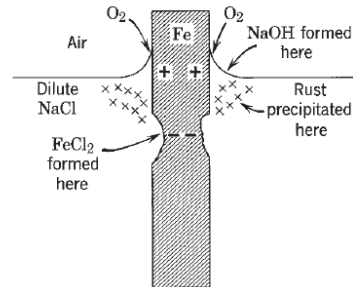


Figure 2.6. Water-line corrosion, showing differential aeration cell.

TYPE OF LOCAL CELL FORMATION



Three main types of cells in corrosion reactions

- Differential temperature cells

Found in heat exchangers, boilers, immersion heaters...

Same material but different temperature

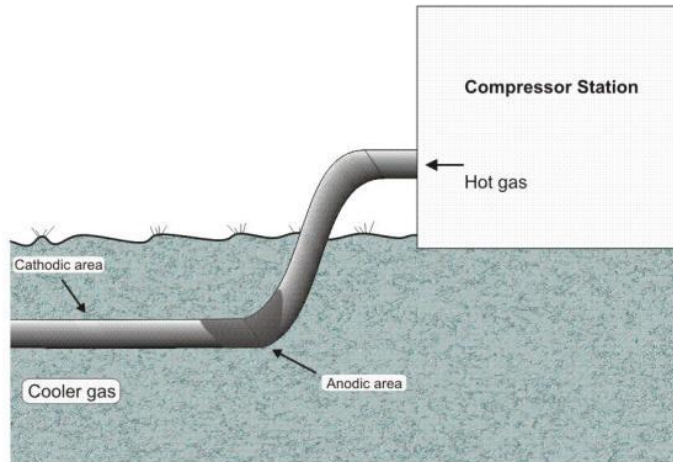


Figure 7.14 Thermogalvanic corrosion.

POTENTIAL PH DIAGRAMS

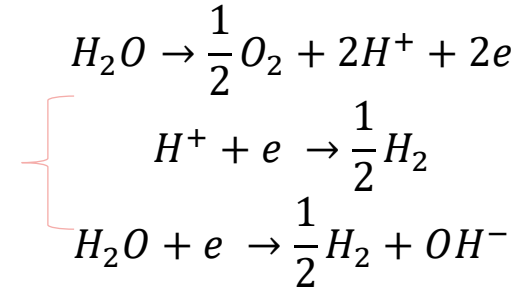


Potential-pH diagrams or Pourbaix diagrams

Graphical representations of the thermodynamical stability of a chemical specie

Application to water stability

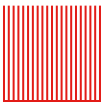
Two couples H_2O/H_2 and O_2/H_2O which can be written as:



And potential are written according to the Nernst equation

$$\Phi = \Phi^\circ - 2.303 \frac{RT}{1F} \log \frac{[H^+]}{P_{H_2}^{1/2}} = 0.06 \log(H^+) = -0.06 \text{ pH}$$

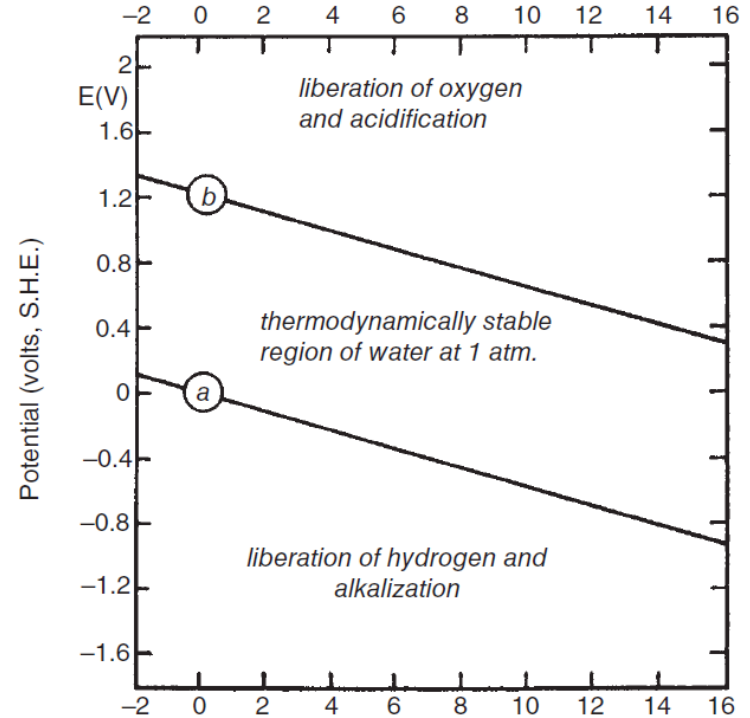
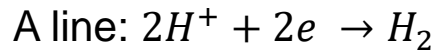
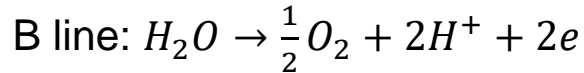
$$\Phi = \Phi^\circ - 2.303 \frac{RT}{1F} \log \frac{[H^+]^2 \cdot (P_{O_2})^{1/2}}{1} = 1.23 - 0.06 \text{ pH}$$



POTENTIAL PH DIAGRAMS

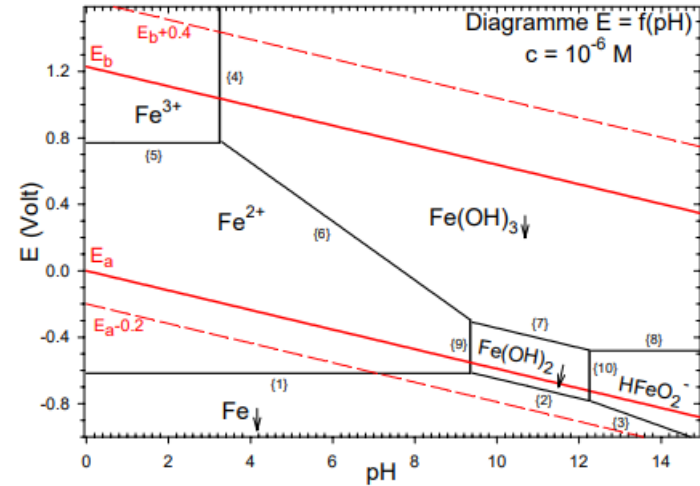
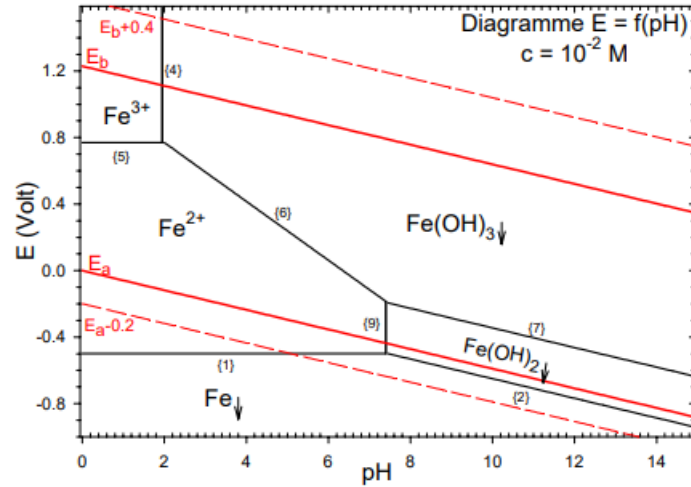
Potential-pH diagrams or Pourbaix diagrams

Graphical representations of the thermodynamical stability of a chemical specie



POTENTIAL PH DIAGRAMS

Iron Pourbaix diagram



Horizontal line does not involve pH : $Fe^{3+} + 3e \rightleftharpoons Fe$

Vertical line involves H^+ or OH^- but not electron: $Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$

oblique lines are driven by the Nernst equation: $\Phi = \Phi^\circ - 2.303 \frac{RT}{nF} \log \left(\frac{[Fe^{3+}]}{[Fe]} \right)$

POTENTIAL PH DIAGRAMS

Iron Pourbaix diagram as a function of temperature

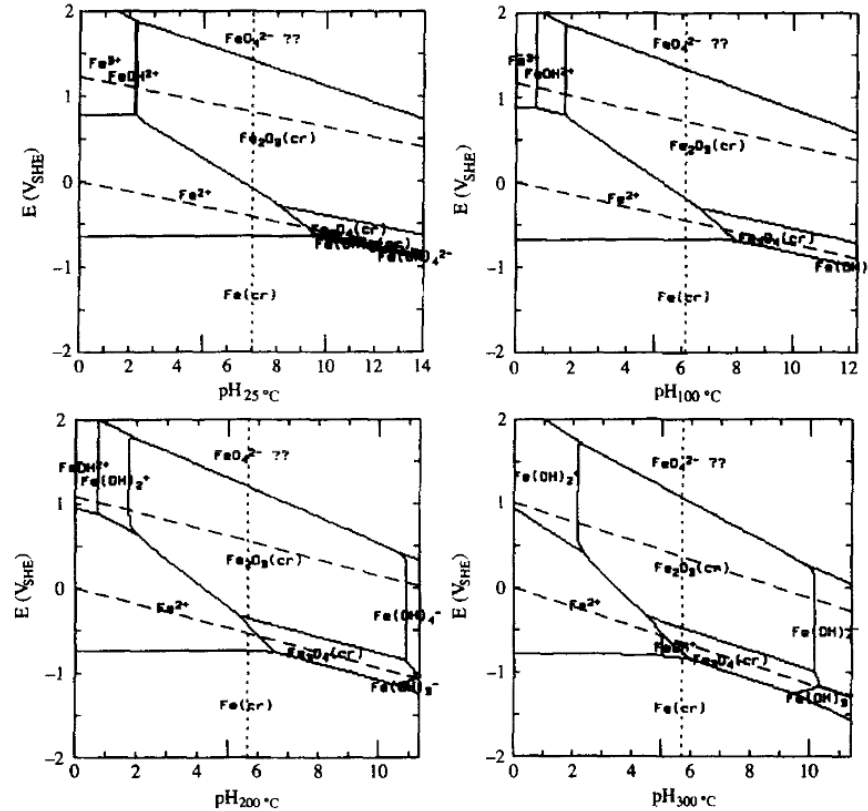
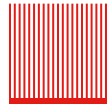
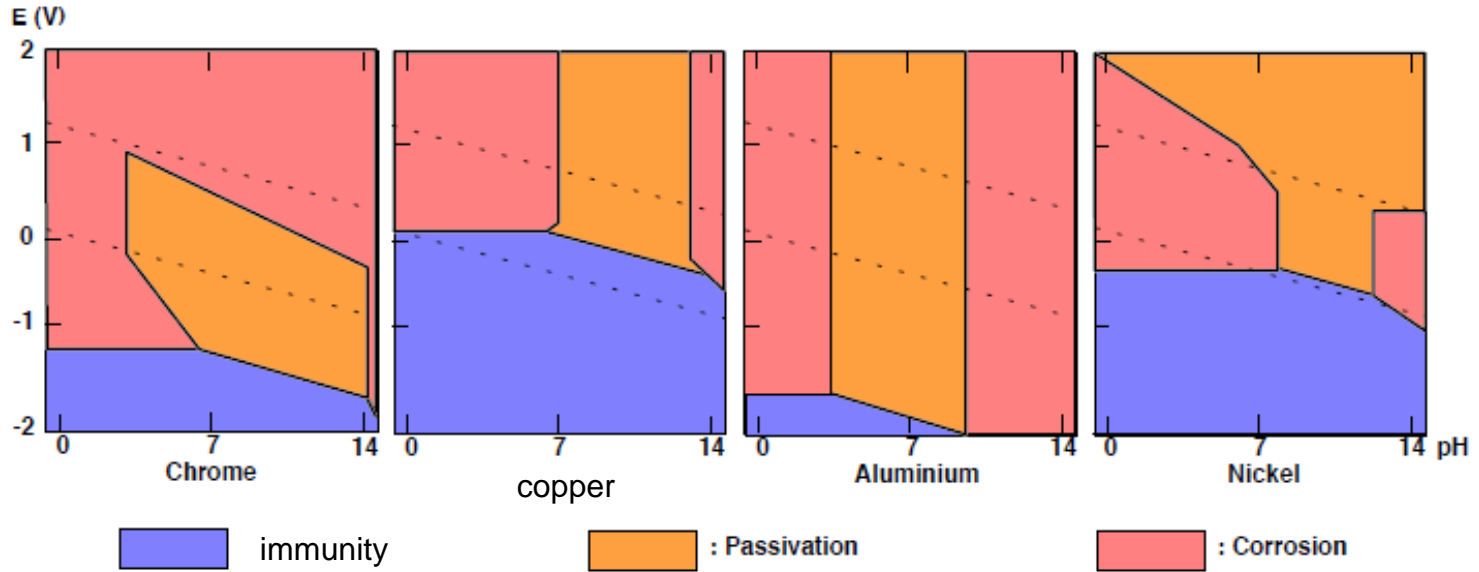


Fig. 2. Pourbaix diagrams for iron at 10^{-6} m at 25, 100, 200 and 300°C.

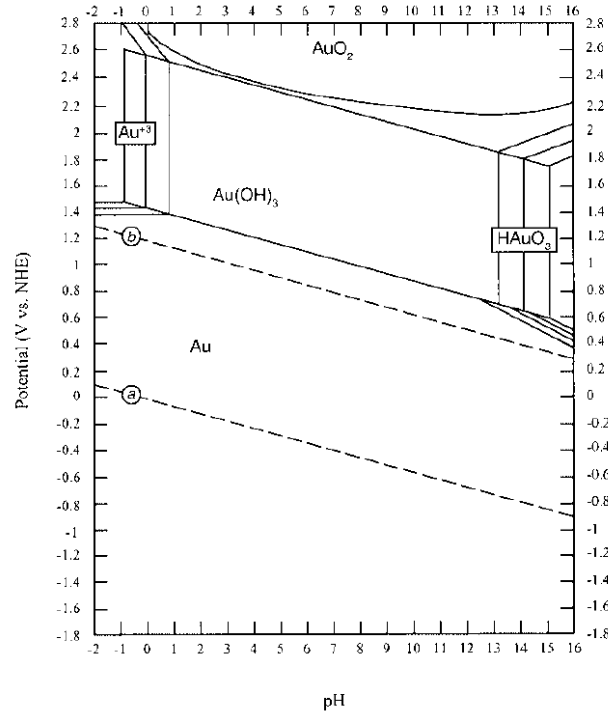


POTENTIAL PH DIAGRAMS

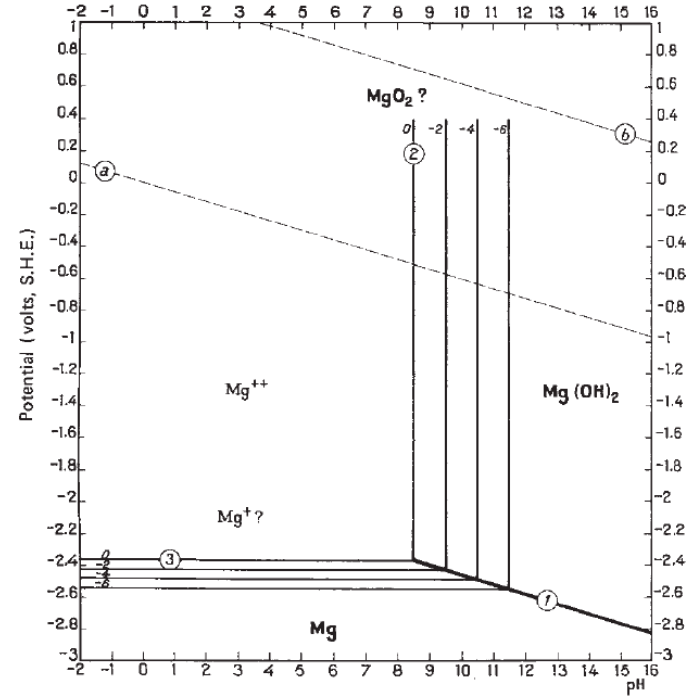


POTENTIAL PH DIAGRAMS

Gold Pourbaix diagram



Mg Pourbaix diagram



POTENTIAL PH DIAGRAMS

Data indicate the conditions for which oxide-hydroxyde are form but do not inform about their barrier effectiveness

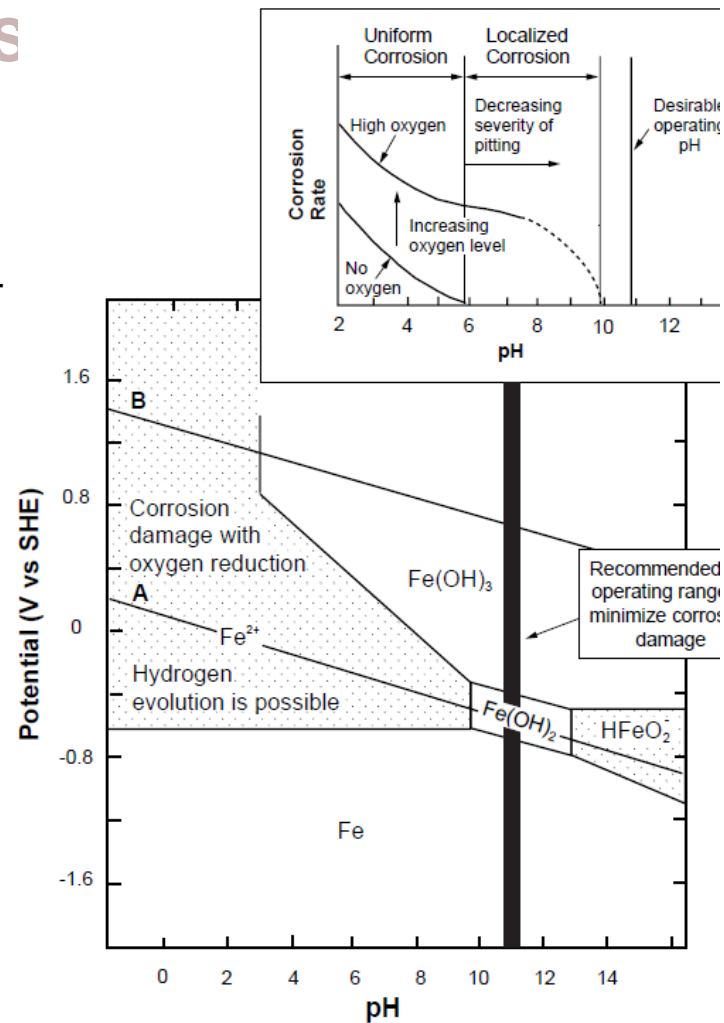


Figure 1.5 E-pH diagram of iron in water at 25°C and its observed corrosion behavior.

CORROSION MONITORING – CORROSION RATE



In practice, we are concerned with rates of corrosion (i.e. kinetic).

- Aluminium has a pronounced tendency to react however its rate is very slow so it meet the requirement of a structural metal.

Direct corrosion measurements techniques

Intrusive techniques

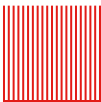
Physical techniques (mass loss, electrical resistance, visual,...)

Electrochemical techniques

Nonintrusive techniques

Physical techniques for metal loss (U.S., Eddy Current,...)

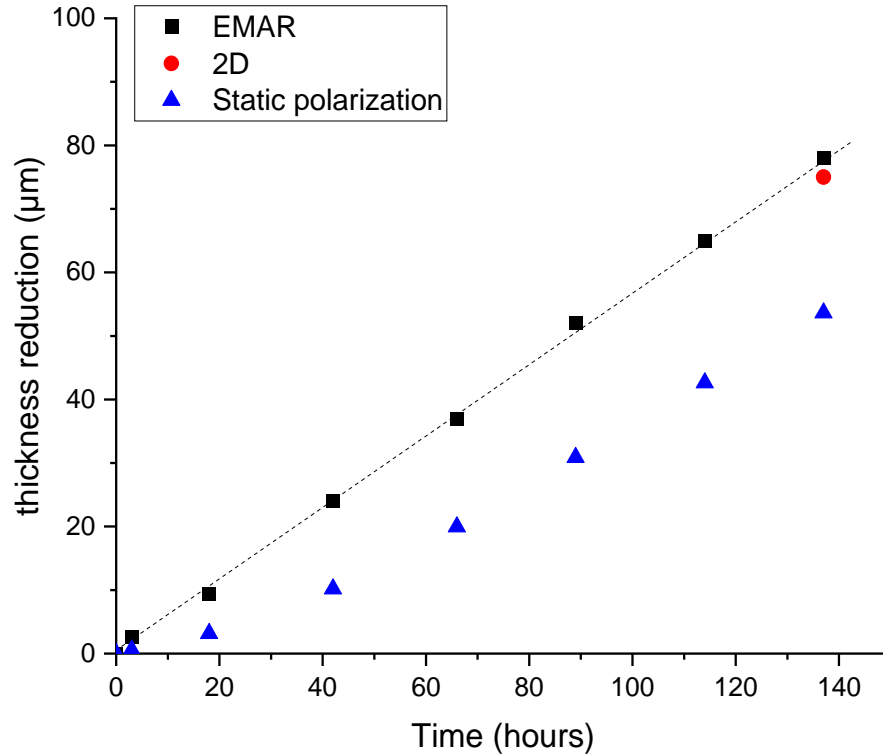
Physical tech. for crack detection and propagation (A.E., Ultrasonic)



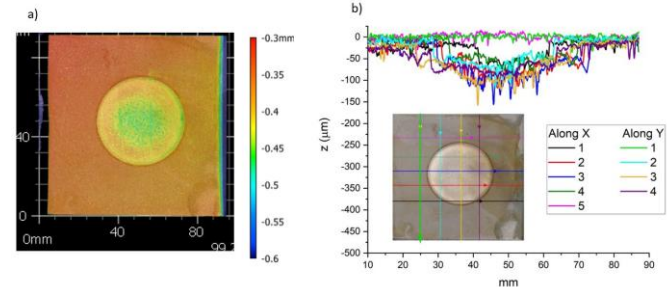
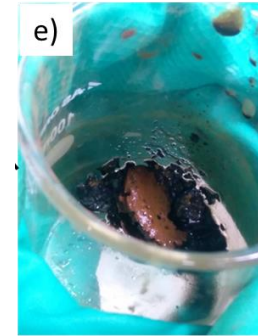
CORROSION MONITORING – CORROSION RATE



Example of application of direct techniques



Electrochemical technique
under estimate the mass loss



CORROSION MONITORING – CORROSION RATE

indirect corrosion measurements techniques

On line techniques

hydrogen monitoring, corrosion potential

water chemistry (pH, conductivity, etc.)

fluids, Pressure, temperature

Off line techniques

water chemistry

residual inhibitor

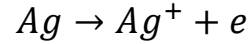
chemical analysis of samples



ELECTROCHEMICAL TESTS



The current released by one anodic reaction can be converted into an equivalent mass loss or corrosion penetration rate with the Faraday's law



1 mol of silver oxidation leads to one mol of Ag^+ and one mol of electron (i.e. 6.022×10^{23} electrons)

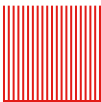
1 mol of electron is equal to 1 faraday (F) or 96,485 C/mol (of electron)

Combining Faraday's principles with specific electrochemical reaction of known stoichiometry leads to $Q = F \times \Delta N \times n$ where ΔN is the change in number of moles, n is the number of electrons per molecule of the species being reacted.

The charge Q can be defined in terms of electric current:

$$Q = \int_0^t I. dt$$

Where I is the total current in amperes (A), t the process duration in second



CORROSION RATE

The corrosion current itself can be either estimated by using electrochemical methods or by using weight loss data and a conversion chart based on Faraday principle.

	mA cm⁻²	mm y⁻¹	mpy	g m⁻² day⁻¹
mA cm⁻²	1	3.28 <i>M/nd</i>	129 <i>M/nd</i>	8.95 <i>M/n</i>
mm y⁻¹	0.306 <i>nd/M</i>	1	39.4	2.74 <i>d</i>
mpy	0.00777 <i>nd/M</i>	0.0254	1	0.0694 <i>d</i>
g m⁻² day⁻¹	0.112 <i>n/M</i>	0.365 <i>/d</i>	14.4 <i>/d</i>	1

where mpy = milli-inch per year

n = number of electrons freed by the corrosion reaction

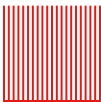
M = atomic mass

d = density

*Note: the table should be read from left to right, i.e.,

$$1 \text{ mA cm}^{-2} = (3.28 \text{ M/nd}) \text{ mm y}^{-1} = (129 \text{ M/nd}) \text{ mpy} = (8.95 \text{ M/n}) \text{ g m}^{-2} \text{ day}^{-1}$$

TABLE 3.1 Conversion between Current, Mass Loss, and Penetration Rates for all Metals*



CORROSION RATE

Quelques grandeurs accessible

For uniform attack metals are classified into three groups according to their corrosion rates and intended application.

1. < 0.15 mm/y — Metals in this category have good corrosion resistance to the extent that they are suitable for critical parts valve seats, pump shafts and impellers, springs...

2. 0.15 to 1.5 mm/y— Metals in this group are satisfactory if a higher rate of corrosion can be tolerated, for example, for tanks, piping, valve bodies, and bolt heads.

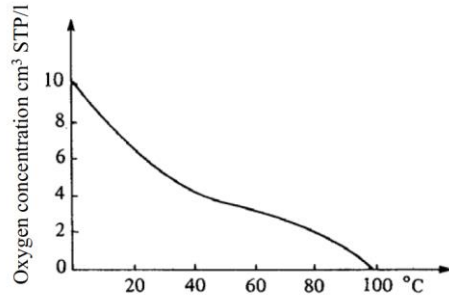
3. > 1.5 mm/y (> 0.05 ipy) — Usually not satisfactory.



CORROSION UNDER OXYGEN REDUCTION

Extensive and intensive parameters playing a rôle (as exemple)

T



Concentrations of oxygen in air-saturated water as a function of temperature [6.6]. (Reproduced from Tomashov ND. Theory of Corrosion and Protection of Metals. New York: Macmillan, 1966.)

[O₂]

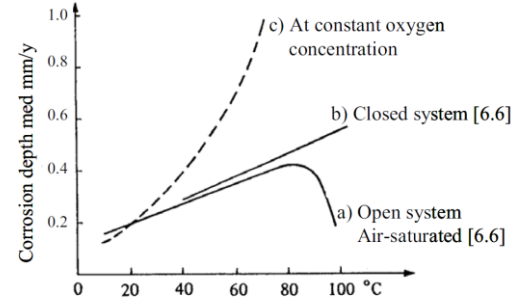


Figure 6.4 Corrosion rate of steel in water as a function of temperature for an open system (a), a closed system (b), and a system where the oxygen concentration is kept constant (c).

Flow

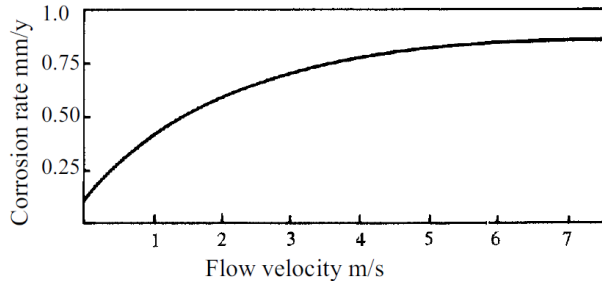


Figure 6.8 Corrosion rate as a function of flow velocity. Steel in seawater at 23°C

[ξ_{water}]

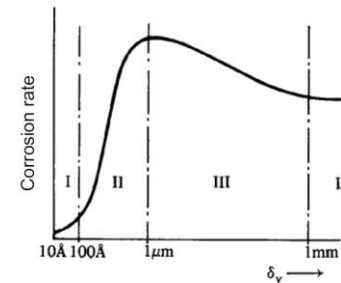
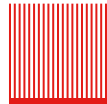
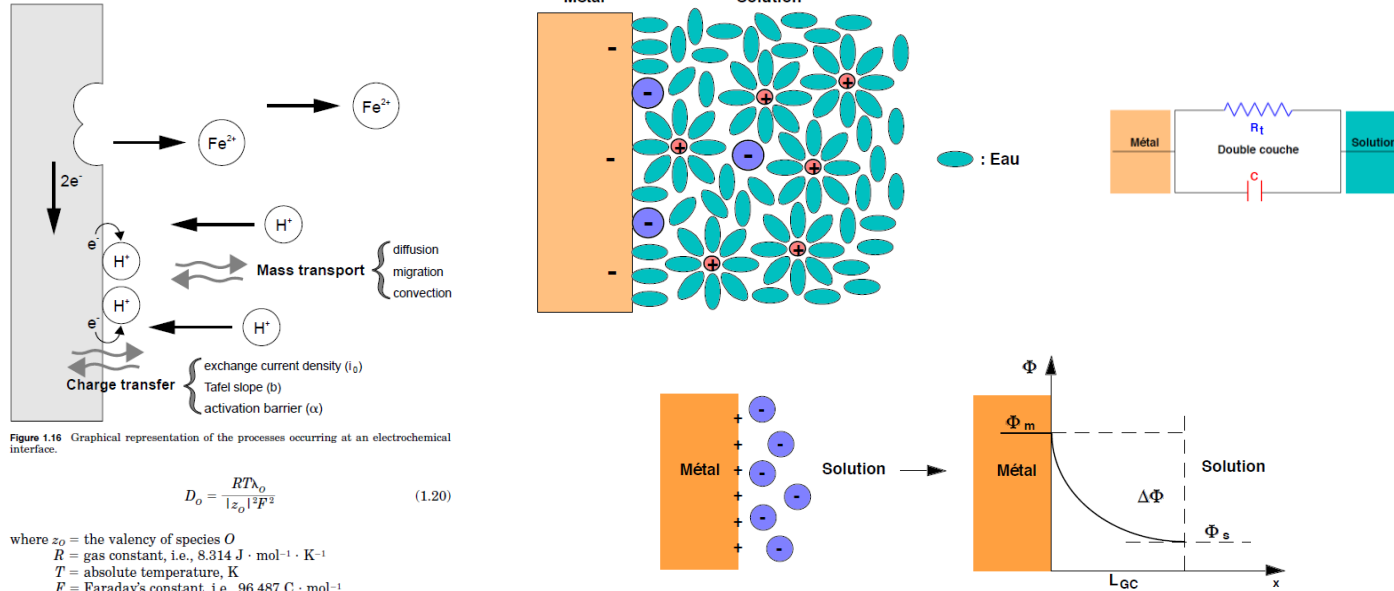


Figure 6.11 Rate of atmospheric corrosion as a function of water film thickness (after Tomashov [6.6]).

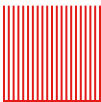


ELECTROCHEMICAL TESTS



Electrochemical techniques:

- Based on electron quantities, current, potential
- Direct information about corrosion rate or mechanism



ELECTROCHEMICAL TEST

Electrochemical setup at the lab scale

3 electrodes cell :

- Anode electrode : metal in contact with the electrolyte on which anodic reaction takes places
- Cathode electrode : metal in contact with the electrolyte on which cathodic reaction takes places
- Potentiostat : providing the potential to the electrochemical system while counting the number of electron exchanged
- Electrolyte : electrically conductive fluid or moist soil

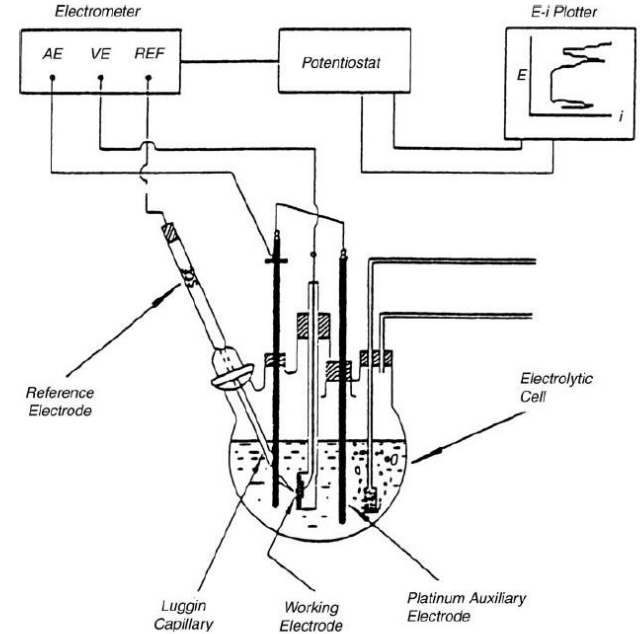


Figure 1.26 Electrochemical cell used for potentiodynamic polarization studies

ELECTROCHEMICAL TEST

Secondary reference electrodes

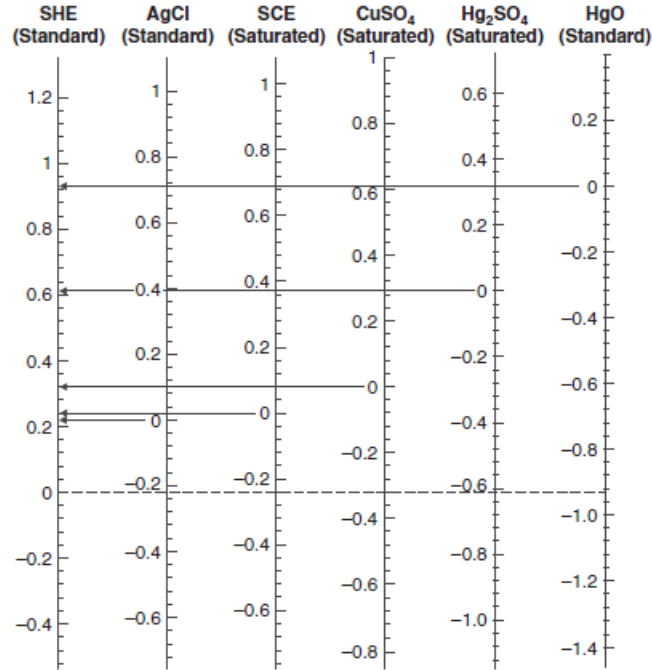
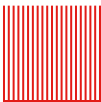
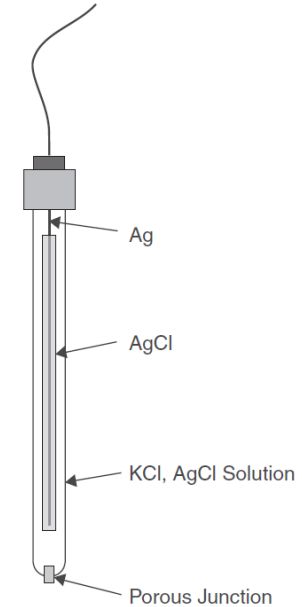


FIGURE 4.3 Graphical scheme to compare potentials of the most commonly used reference electrodes.

FIGURE 4.4
Schematic of a silver/silver chloride reference electrode.



ELECTROCHEMICAL TEST

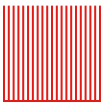
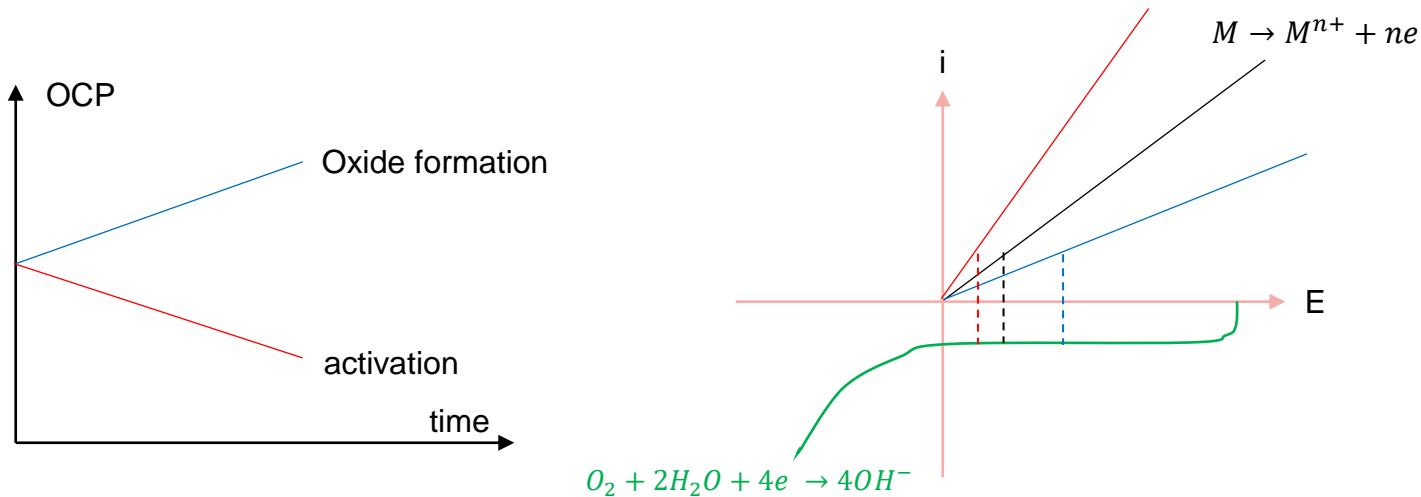
Potential measurements

(Rest potential, Open circuit potential, free potential)

Simplest measurement without electrical perturbation of the system

At this potential anodic and cathodic current are equal but different to zero

OCP evolution informs about the material evolution



ELECTROCHEMICAL TEST

Potential measurements

(Rest potential, Open circuit potential, free potential)

Simplest measurement without electrical perturbation of the system

At this potential anodic and cathodic current are equals but different to zero

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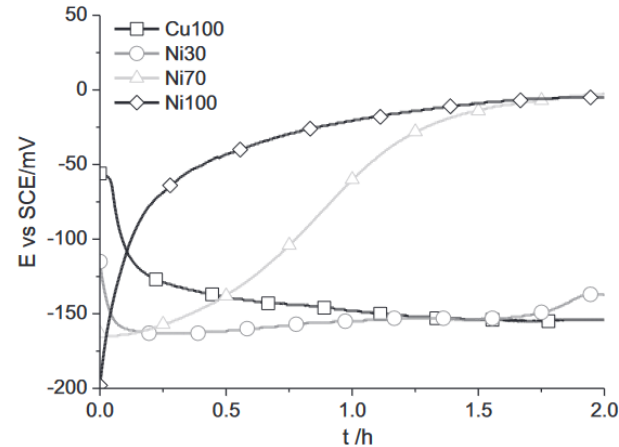
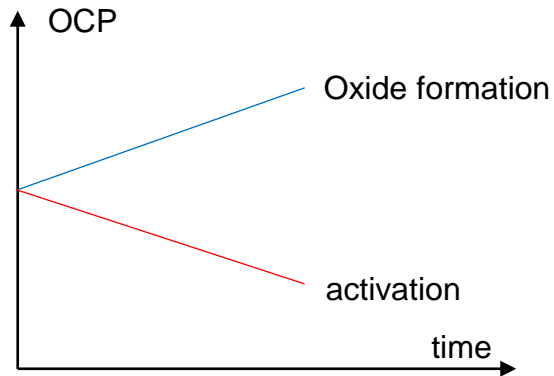
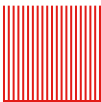


Fig. 2. OCP measurements on Ni100, Ni70, Cu100 and Ni30 in aerated synthetic groundwater. Temperature: 25 °C; pH: 8.8.



ELECTROCHEMICAL TEST

Current measurements : cathodic and anodic contributions

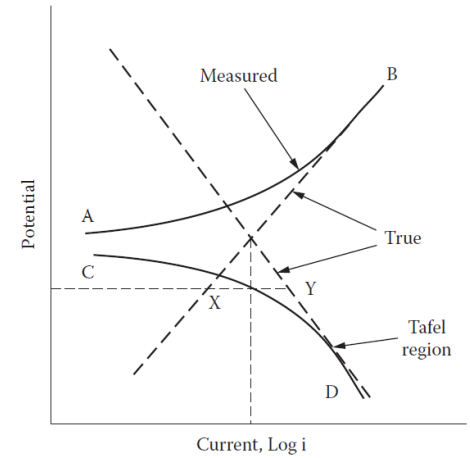
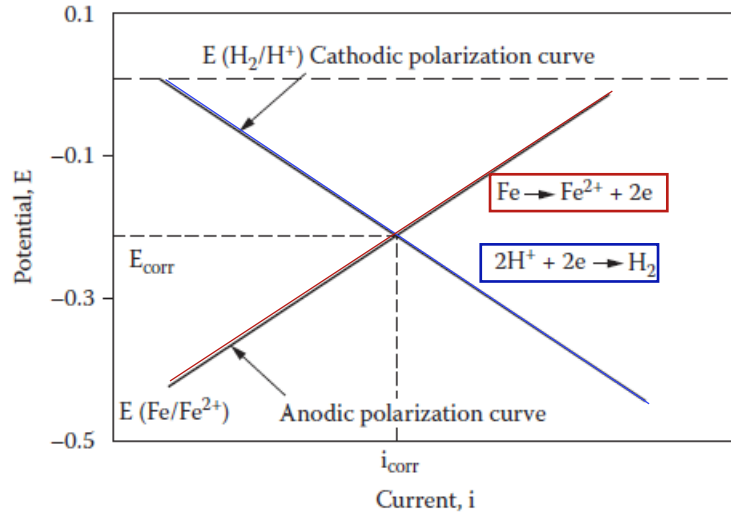


FIGURE 2.10
Anodic and cathodic polarization curve.

TABLE 7.10 Examples of Maximum Scan Rates for Performing Valid Polarization Plots

Solution resistance, $\Omega\text{-cm}^2$	Polarization resistance, $\text{k}\Omega\text{-cm}^2$	Capacitance, $\mu\text{F}\text{-cm}^{-2}$	Maximum scan rate, $\text{mV}\cdot\text{s}^{-1}$
10	1	100	5.1
10	10	100	0.51
10	100	100	0.05
10	1000	100	0.005
100	1	100	6.3
100	10	100	0.51
100	100	100	0.05
100	1000	100	0.005
10	1	20	25
10	10	20	2.5
10	100	20	0.25
10	1000	20	0.025
100	1	20	50
100	10	20	2.6
100	100	20	0.25
100	1000	20	0.025

ELECTROCHEMICAL TEST

Linear Polarization resistance (LPR)

The LPR is defined as $\Delta E / \Delta i$ slope at the corrosion potential

With the Stern-Geary approximation

$$R_p = \frac{B}{i_{corr}} = \left(\frac{\Delta E}{\Delta i} \right)_{\Delta E \rightarrow 0}$$

$$\text{With } B = \frac{b_a \cdot b_c}{2.3(b_a + b_c)}$$

b_a and b_c are calculated from tafel slope or literature

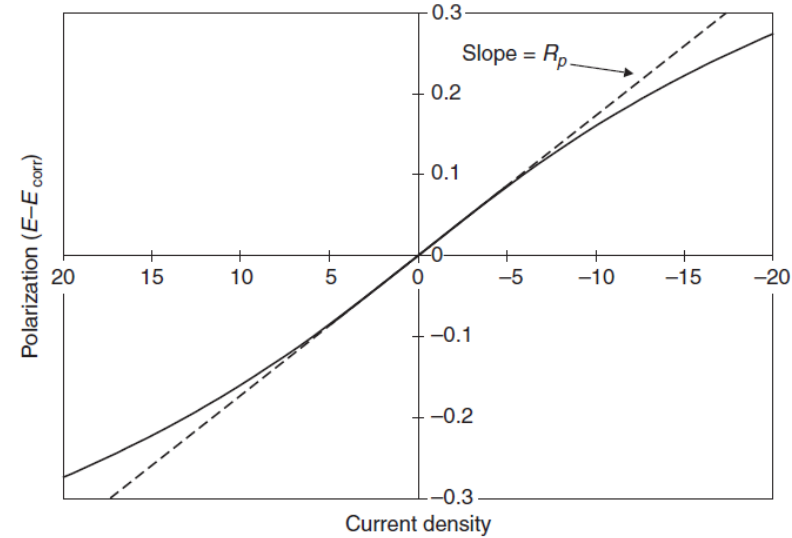


FIGURE 5.21 Hypothetical linear polarization plot.



ELECTROCHEMICAL TEST

Current measurements : cathodic reaction (contraction controlled processes)

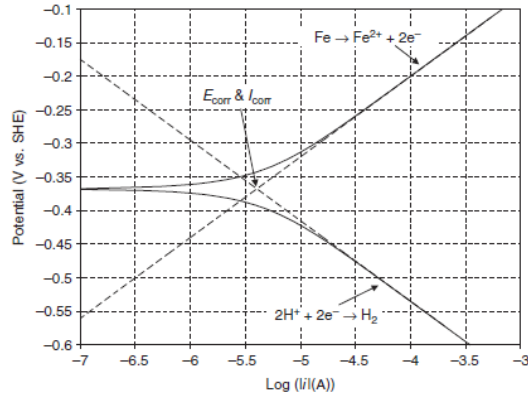


FIGURE 5.15 Polarization behavior of carbon steel in a deaerated solution maintained at 25°C and a pH of five.

$$E_{corr} = -0.368 \text{ V}$$

$$I_{corr} = 4 \mu\text{A} \cdot \text{cm}^{-2}$$

$$CR = 0,05 \text{ mm/y}$$

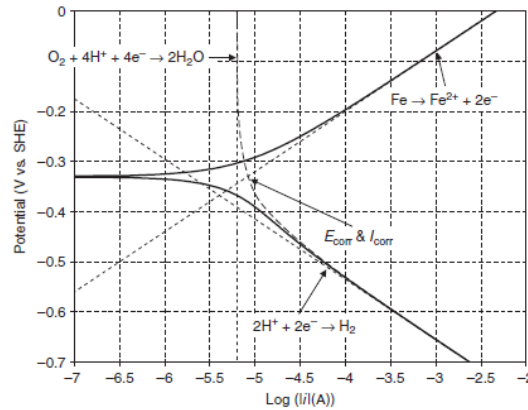


FIGURE 5.16 Polarization behavior of carbon steel in a stagnant aerated solution maintained at 25°C and a pH of five.

$$E_{corr} = -0.33 \text{ V}$$

$$I_{corr} = 8 \mu\text{A} \cdot \text{cm}^{-2}$$

$$CR = 0.1 \text{ mm/y}$$

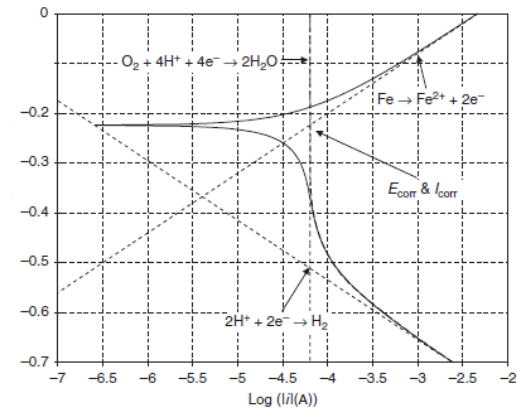


FIGURE 5.17 Polarization behavior of carbon steel in an agitated aerated solution maintained at 25°C and a pH of five.

$$E_{corr} = -0.22 \text{ V}$$

$$I_{corr} = 63 \mu\text{A} \cdot \text{cm}^{-2}$$

$$CR = 0.8 \text{ mm/y}$$

Effet of mass transoport of O_2 in weak acid solutions

ELECTROCHEMICAL TEST

Current measurements : anodic reaction modified by the environment

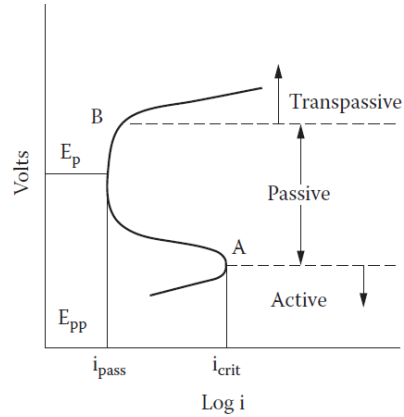


FIGURE 2.11
Anodic polarization curve for material exhibiting active-passive behavior.

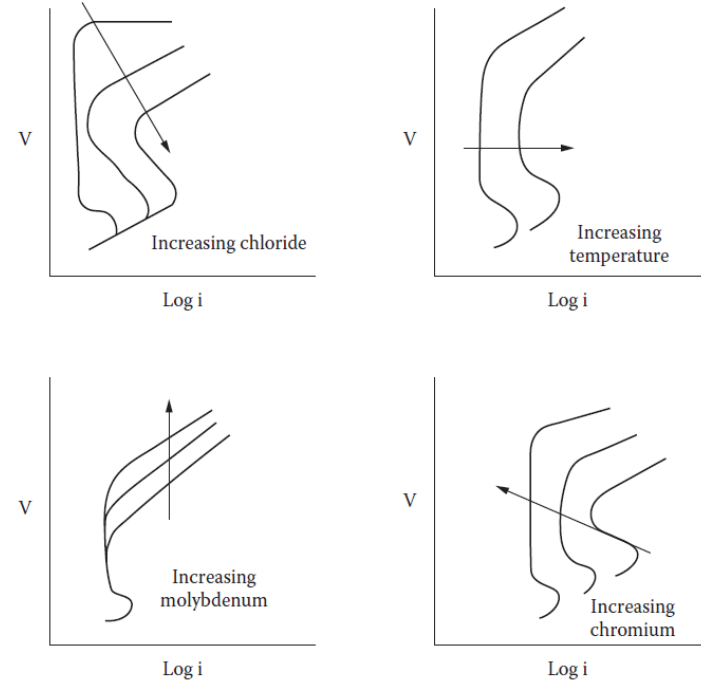


FIGURE 2.13
Effects of environment and alloy content on anodic polarization behavior.

ELECTROCHEMICAL TEST

Current measurements : anodic reaction modified by the environment

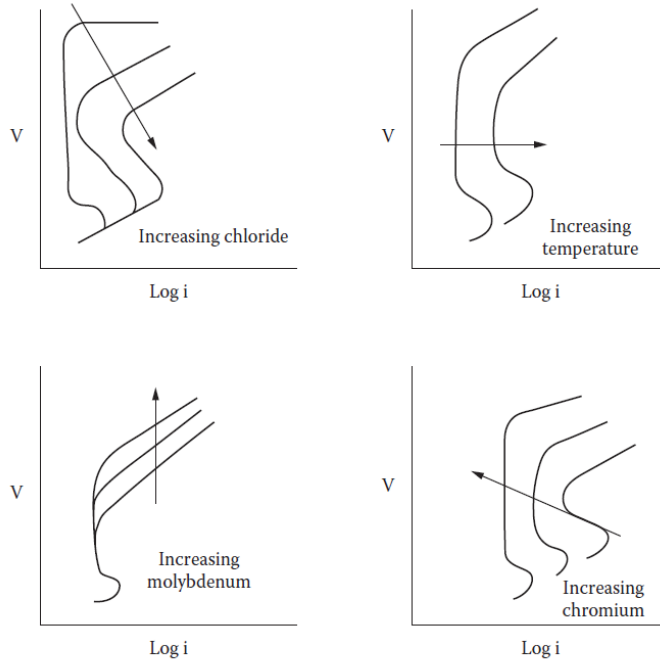


FIGURE 2.13
Effects of environment and alloy content on anodic polarization behavior.

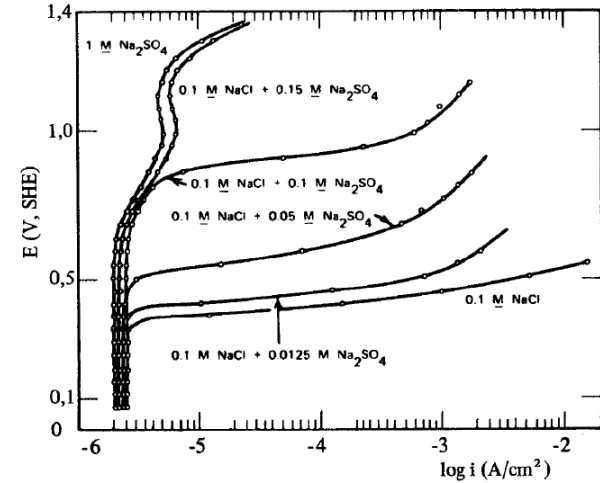
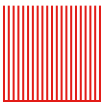


Figure 5.4 Anodic polarization curves for an 18-8 CrNi steel in a 0.1 M NaCl solution with different amounts of Na₂SO₄ added [5.3].



ELECTROCHEMICAL TEST

Current measurements : anodic reaction modified the surface reaction or itself

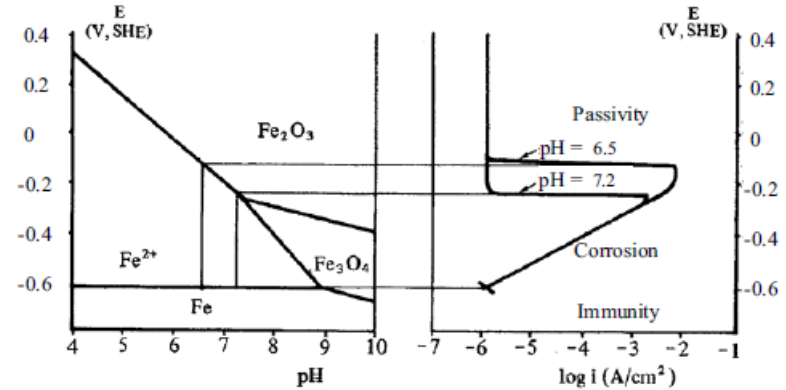
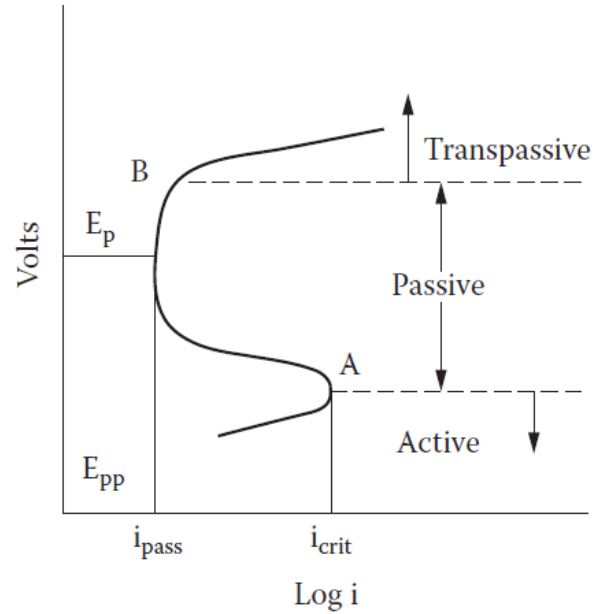
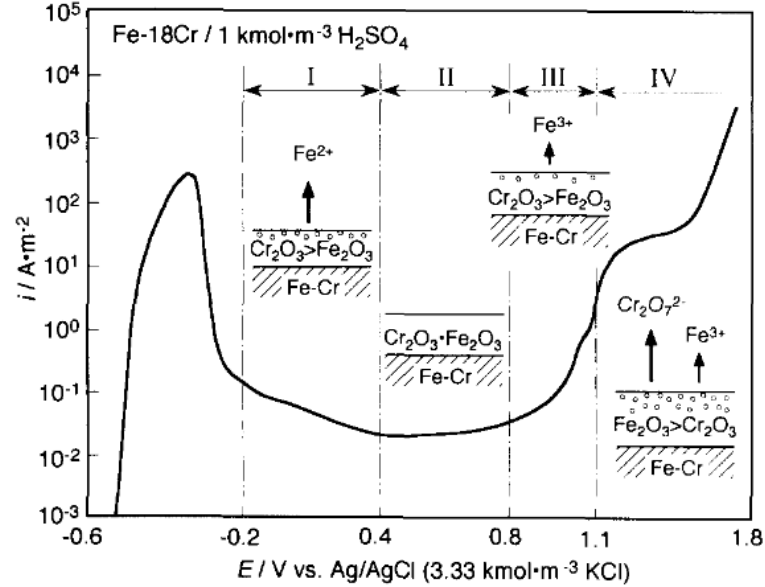
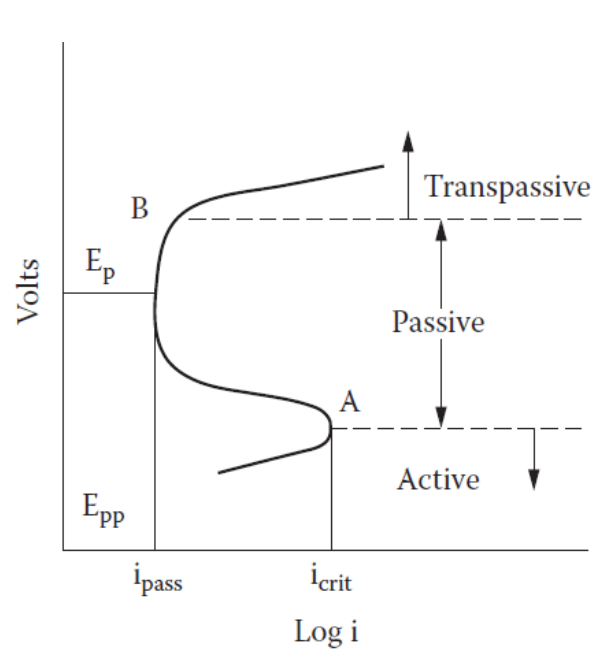


Figure 5.2 Pourbaix diagram and anodic overvoltage curves for iron in water.

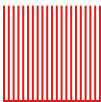
ELECTROCHEMICAL TEST

Current measurements : anodic reaction modified the surface reaction or itself



- I: Film is porous due to reduction dissolution of Fe₂O₃
- II: Film is compact without dissolution of both Cr₂O₃ and Fe₂O₃
- III: Film is slightly porous due to field-assisted dissolution of Fe₂O₃
- IV: Film is porous due to oxidation dissolution of Cr₂O₃

Fig. 14. Supposed structure of passive films on Fe-18Cr alloy in four potential ranges in 1 kmol m⁻³ H₂SO₄.



ELECTROCHEMICAL TEST

Current measurements : Electrochemical impedance measurements

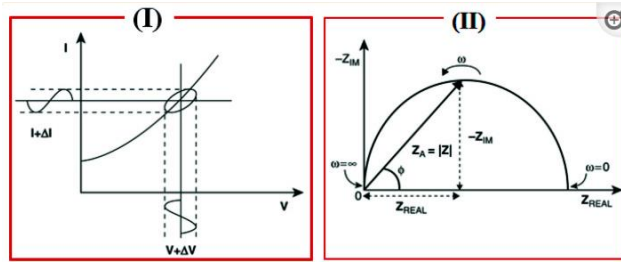


Table 4

Impedance fitting parameters for samples exposed to aerated synthetic groundwater solution as a function of the nickel content in the alloy.

Parameters	Ni100	Ni70	Ni30	Cu100
EEC	$R_s \left[\begin{array}{c} Q_d \\ R_t \end{array} \right]$	$R_s \left[\begin{array}{c} Q_d \\ R_t W \end{array} \right]$	$R_s \left[\begin{array}{c} Q_f \\ R_f \\ R_t \end{array} \right]$	$R_s \left[\begin{array}{c} Q_d \\ R_t \end{array} \right]$
$R_s / \Omega \text{ cm}^2$	55.3	55.2	55.2	60.8
$C_{dl} / \mu\text{F cm}^{-2}$	21.5	17.3	72.2	199.9
$Q_{dl} / \text{S s}^n \text{ cm}^{-2}$	1.8×10^{-5}	1.6×10^{-5}	1.8×10^{-4}	9.1×10^{-5}
n_1	0.93	0.91	0.56	0.57
$R_f / \Omega \text{ cm}^2$	8.9×10^5	1.1×10^5	1.7×10^3	3.1×10^4
$W / \text{S s}^{1/2} \text{ cm}^{-2}$	-	5.3×10^{-5}	-	-
$C_f / \mu\text{F cm}^2$	-	-	36.4	11.6
$Q_f / \text{S s}^n \text{ cm}^{-2}$	-	-	7.3×10^{-5}	1.5×10^{-5}
n_2	-	-	0.87	0.92
$R_t / \Omega \text{ cm}^2$	-	-	1.0×10^2	1.9×10^3
χ^2	1.52×10^{-4}	8.03×10^{-4}	6.16×10^{-5}	9.49×10^{-5}

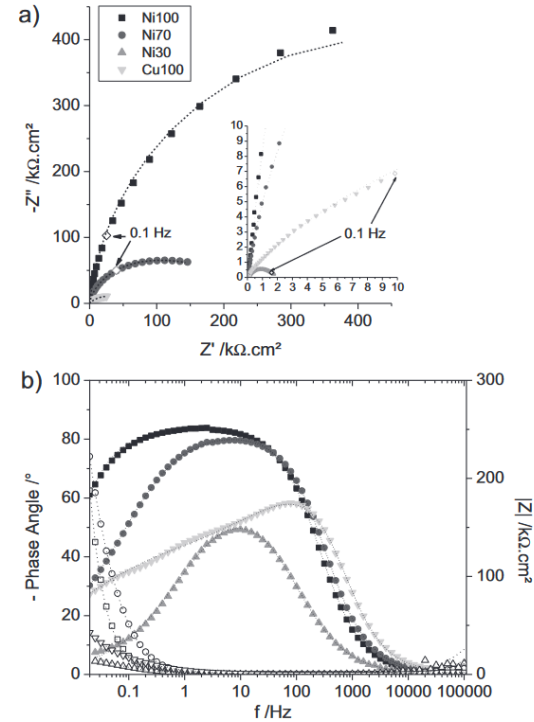


Fig. 5. (a) Nyquist and (b) phase impedance diagrams obtained for four alloy samples immersed in aerated synthetic groundwater. Temperature: 25 °C; pH 8.8, (●) exp, (—) fit.

ELECTROCHEMICAL TEST

Current measurements : Electrochemical impedance measurements

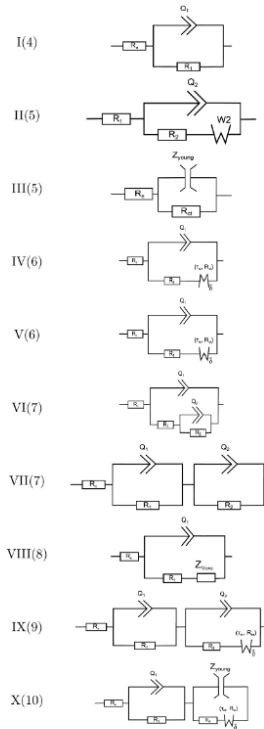
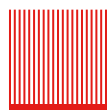
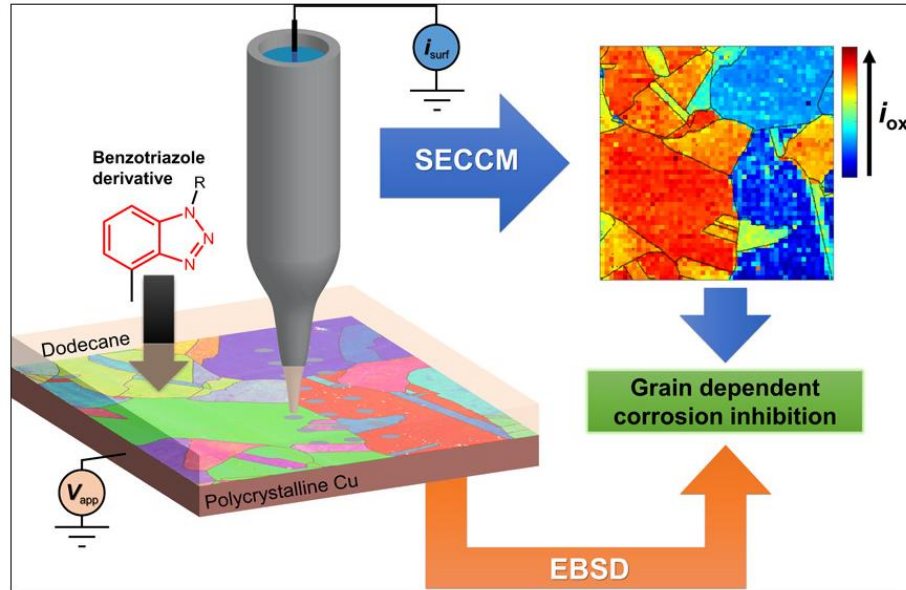


Fig. 3. The descriptive models used in the present methodology. Arabic numbers are the number of parameters used in the model.

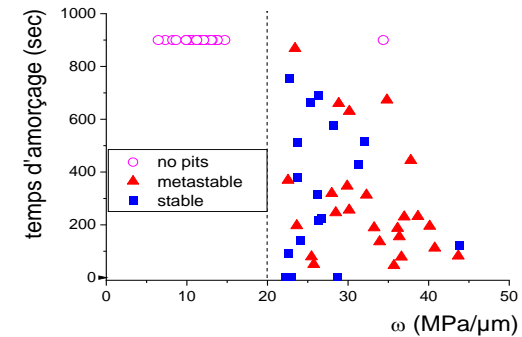
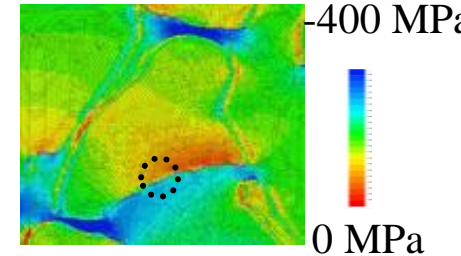
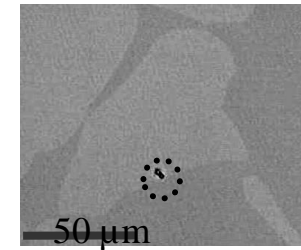
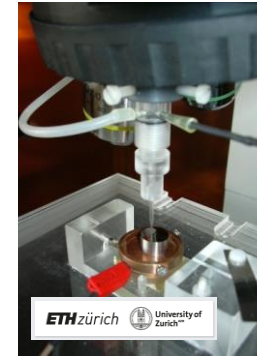
- I: the oxide layer is taken into account without any hydroxide [19].
- II: the faradic reactions are limited by migration processes. The PDM of D. D. Macdonald demonstrates that the migration in passive film can be described by Warburg diffusion [20].
- III: the evolution of stoichiometry through the film leads to the evolution of conductivity in the oxide following an exponential law (Young model) [21], this non-faradic behavior is in parallel with a charge transfer resistance [22].
- IV: faradic reactions are limited by diffusion with flow equal to zero as boundary condition. It also corresponds to model VIII if the transport number of electrons is equal to the transport number of considered ions [17].
- V: faradic reactions are limited by diffusion in a finite diffusion layer. This model corresponds to model VIII if the transport of the positive and negative species have the same boundary conditions [23].
- VI: similar to I with a porous hydroxide layer [24];
- VII: similar to I with a non-porous hydroxide layer [25];
- VIII: faradic reactions are limited by diffusion / migration processes according to Vorotyntsev's calculation [26].
- IX: similar than V with a non-porous hydroxide layer;
- X: the MCM, developed by M. Bojinov, takes into account an outer interface with two charge transport paths through the oxide [27].



TOWARD ELECTROCHEMICAL AT LOCAL SCALE



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SYNERGIES

