香港螺絲業協會與香港表面處理學會
合辦

面處理講座課程 –
金屬腐蝕原理和防腐方法

金屬腐蝕的電化學原理和檢測
(METAL CORROSION PRINCIPLES & TESTING)

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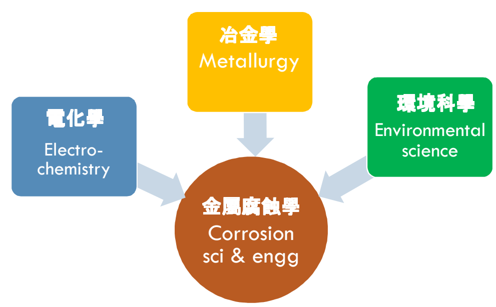
1. Introduction (簡介)
- Definitions (**定義**)

Definitions of corrosion (腐蝕的定義)

- Corrosion is defined as the deterioration of a material, usually a metal, that results from a reaction with its environment. ***- NACE International***
- Physico-chemical interaction between a metal and its environment which results in changes in the properties of the metal and which may often lead to impairment of the function of the metal, the environment, or the technical system of which these form a part. - ***ISO***
- *Corrosion cost to society (expensive, wasteful of natural resources and loss of life) : typical 3-4% GNP*

Corrosion – an interdisciplinary subject
(金屬腐蝕 - 一門融合多門學科的边缘科學)



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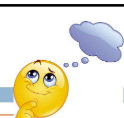
1. Introduction (簡介)
- **Electrochemical Aspect (電化學理論)**



- a. Electrochemical cells (電化學電池)
- b. Thermodynamics (熱力學)
- c. Kinetics (動力學)
- d. Passivity & passivation (鈍態與鈍化)
- e. Dry corrosion (乾腐蝕)

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1. Introduction (簡介)
- **Corrosion testing (腐蝕測試)**

- a. Electrochemical studies
- b. Metallurgical examination
- c. Other corrosion tests
- d. Corrosion monitoring
- e. Failure analysis

1. Introduction (簡介)

- Corrosion Forms (腐蝕類形)

- Classification based on reactions and mechanisms of the corrosion processes
  - Wet erosion (濕腐蝕)
  - Dry corrosion (干腐蝕)

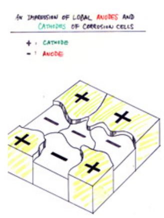
Corrosion Forms (腐蝕類形)

CORROSION

- Uniform or general corrosion (全面腐蝕)
- Localized corrosion (局部腐蝕)
  - (宏觀腐蝕) macroscopic
    - galvanic (電偶腐蝕)
    - erosion (磨耗腐蝕)
    - crevice (縫隙腐蝕)
    - pitting (點腐蝕)
    - selective (选擇性腐蝕)
    - cavitation (氣蝕)
  - microscopic (微觀腐蝕)
    - inter-crystalline (晶間腐蝕)
    - SCC (應力腐蝕開裂)
    - corrosion fatigue (腐蝕疲勞)
    - H embrittlement (氫脆腐蝕)
    - …

- **Corrosion forms (腐蝕類形)**
- ***Uniform (or general) corrosion*** **(全面腐蝕或均勻腐蝕)**
  - Corrosion attack dominated by uniform thinning due to even & regular loss of metal over the entire surface area.
  - Types - atmospheric corrosion and high temperature corrosion

- ***Localized corrosion*** **(局部腐蝕)**
  - Localized corrosion is common but sometimes catastrophic, and its occurrences and speed are hard to predicated.
  - Types: galvanic (bi-metallic); pitting; stress corrosion cracking; differential aeration (crevice corrosion); erosion-corrosion (cavitation); corrosion fatigue; selective corrosion

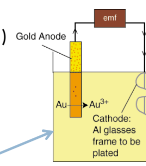


2. Corrosion theory (腐蝕理論)

2.1 Electrochemical Aspect (電化學理論)

a) Electrochemical cells (電化學電池)

- Composed of a pair of electrodes (電極) in contact with an electrolyte (電解液)
- 2 types
  - Electrolytic cell (電解電池)
    - e.g., electroplating system (電鍍)
  - Galvanic cell
    - e.g. batteries, corroding system(電池、 腐蝕系統)

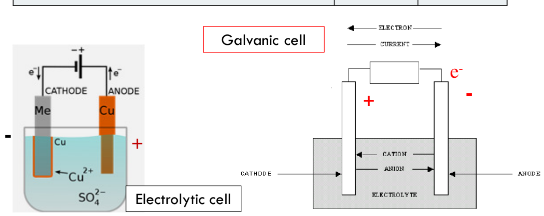


2. Corrosion theory (腐蝕理論)

2.1 Electrochemical Aspect (電化學理論)

a) Electrochemical cells (電化學電池) – sign convention

Sign convention	anode	cathode
Galvanic or Voltaic cell (corrosion, battery)	-	+
Electrolytic cell (electroplating)	+	-



2. Corrosion theory (腐蝕理論)

2.1 Electrochemical Aspect (電化學理論)

a) Electrochemical cells (電化學電池)

- Electrode potentials (電極電位)
  - Different metals (e.g., iron, zinc, copper) have different electrode potentials (called reduction potentials) due to their inherent different tendency toward electrochemical reaction
  - Metal having a more negative reduction potential tends to be more active (corroding) in an electrolyte

	Zn	*Fe*	*Cu*
E (V)	-0.76	-0.44	+0.34
		ACTIVE	

Standard electrode (reduction) potential

標準電極(還原)電位

TABLE 2.1 Standard Electromotive Force Potentials (Reduction Potentials)

	Reaction	Standard Potential, e° (volts vs. SHE)
Noble	$Au^{3+} + 3e^- = Au$	+1.498
	$Cl_2 + 2e^- = 2Cl^-$	+1.358
	$O_2 + 4H^+ + 4e^- = 2H_2O$ (pH 0)	+1.229
	$Pt^{3+} + 3e^- = Pt$	+1.2
	$O_2 + 2H_2O + 4e^- = 4OH^-$ (pH 7)[a]	+0.82
	$Ag^+ + e^- = Ag$	+0.799
	$Hg_2^{2+} + 2e^- = 2Hg$	+0.788
	$Fe^{3+} + e^- = Fe^{2+}$	+0.771
	$O_2 + 2H_2O + 4e^- = 4OH^-$ (pH 14)	+0.401
	$Cu^{2+} + 2e^- = Cu$	+0.337
	$Sn^{4+} + 2e^- = Sn^{2+}$	+0.15
	$2H^+ + 2e^- = H_2$	0.000
	$Pb^{2+} + 2e^- = Pb$	−0.126
	$Sn^{2+} + 2e^- = Sn$	−0.136
	$Ni^{2+} + 2e^- = Ni$	−0.250
	$Co^{2+} + 2e^- = Co$	−0.277
	$Cd^{2+} + 2e^- = Cd$	−0.403
	$Fe^{2+} + 2e^- = Fe$	−0.440
	$Cr^{3+} + 3e^- = Cr$	−0.744
	$Zn^{2+} + 2e^- = Zn$	−0.763
	$2H_2O + 2e^- = H_2 + 2OH^-$	−0.828
	$Al^{3+} + 3e^- = Al$	−1.662
	$Mg^{2+} + 2e^- = Mg$	−2.363
	$Na^+ + e^- = Na$	−2.714
Active	$K^+ + e^- = K$	−2.925

[a] Not a standard state but included for reference.

Source: *A. J. deBethune and N. S. Loud,* Standard Electrode Potentials and Temperature Coefficients at 25C. *Clifford A. Hampel, Skokie, Ill., 1964.*

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2. Corrosion theory (腐蝕理論)

2.1 Electrochemical Aspect (電化學理論)

a) Electrochemical cells (電化學電池)

- Electrode potentials (電極電位)

Steel or iron corrodes in de-aerated acid

Anode (陽極)

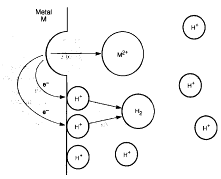
$Fe - 2e \text{ ---> } Fe^{2+}$ (E=0.44V)

Cathode (陰極) :

$2H^+ + 2e \text{ ---> } H_2$ (E=0.00V)

Overall :

$Fe + 2H^+ \text{ ---> } Fe^{2+} + H_2$



$\Delta E = E_{cell} = + 0.4$ V

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2. Corrosion theory (腐蝕理論)

2.1 Electrochemical Aspect (電化學理論)

a) Electrochemical cells (電化學電池)

- Electrode potential(電極電位)

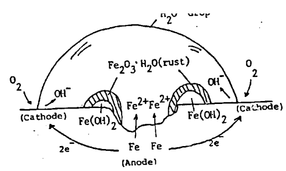
Steel or iron corrodes in contact with water drop (moisture)

at anode: $Fe - 2e \rightarrow Fe^{2+}$

at cathode: $½O_2 + H_2O + 2e \rightarrow 2OH^-$

overall reaction :

$Fe + ½O_2 + H_2O \rightarrow Fe(OH)_2$



$Fe + 1/2\ O_2 + H_2O \text{ ---> } Fe(OH)_2 \qquad \Delta E = E_{cell} = +0.84$ V

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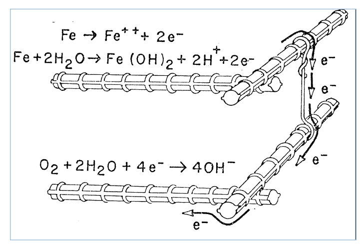
2. Corrosion theory (腐蝕理論)

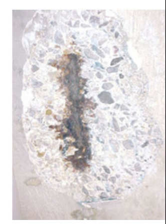
2.1 Electrochemical Aspect (電化學理論)

a) Electrochemical cells (電化學電池)

- Electrode potential (電極電位)

Rebar (鋼 筋) corrodes inside concrete (混凝土)





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a) Electrochemical cells (電化學電池)

- Electrode potential (電極電位)

Galvanic Series in Seawater (海水)

platinum (Noble end)
gold
graphite
titanium
zirconium
AISI 316, 317 stainless steel (passive)
AISI 304 (passive)
AISI 430 (passive)
nickel (passive)
copper-nickel (70-30)
bronzes
lead
AISI 316, 317 stainless steel (active)
AISI 304 (active)
steel or iron
aluminum alloy 2024
cadmium
zinc (Active end)

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b) Thermodynamics (熱力學)

- Provides an understanding of the *energy changes* involved in corrosion
- Some examples
  - Iron in contact with water drop
    $Fe + ½O_2 + H_2O \rightarrow Fe(OH)_2 \qquad \Delta E= +0.8V$
  - Copper in aerated acid
    $Cu + ½O_2 + 2H^+ \rightarrow Cu^{+2} + H_2O \quad \Delta E= +0.89V$
  - Copper in de-aerated acid
    $Cu + 2H^+ \rightarrow Cu^{+2} + H_2 \qquad \Delta E= -0.34V$
- Nernst equation
  - To calculate the half-potential E, of a couple where the reacting species are not at **unit activity**

RT/F = 0.0257V

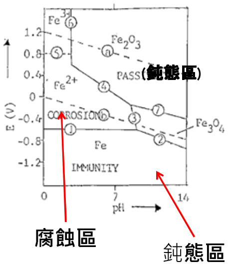
$$E = E^o + (RT/zF)\ \mathbf{ln}\ (a_{(ox)} / a_{(red)})$$

$Cu^{+2} + 2e \rightarrow Cu : E_{Cu} = E^\circ_{Cu\ 2+} + (0.059/2)\mathbf{log}\ a_{(Cu\ 2+)}$

b) Thermodynamics (熱力學)

E–pH diagram (圖) (also known as Pourbaix diagram)

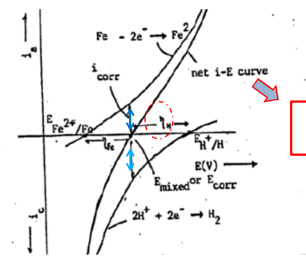
- "The conditions of a metal, that is, at different reduction potentials (E) and exposed to electrolytes of different pH, may determine the 3 regions of thermodynamic stability of species for metal/electrolyte system: Corrosion腐蝕區, Immunity免蝕區and Passivity鈍態區"
- **Limitation** (限制)
  - not all species may achieve equilibrium with others
  - pH varies from one point to another
  - passivity of oxides, hydroxides may not be necessarily protective
  - no information on corrosion rate (kinetic information)

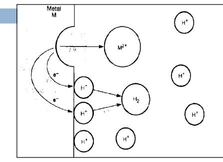


2. Corrosion theory (腐蝕理論)

2.1 Electrochemical Aspect (電化學理論)

c) Kinetics (動力學)

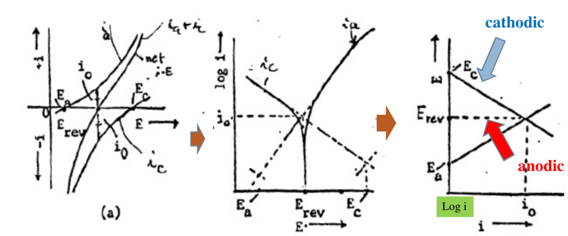




$$i = i_0\left(\exp\left(\alpha\frac{nF}{RT}\eta\right) - \exp\left(-(1-\alpha)\frac{nF}{RT}\eta\right)\right)$$

(Butler-Volmer equation)

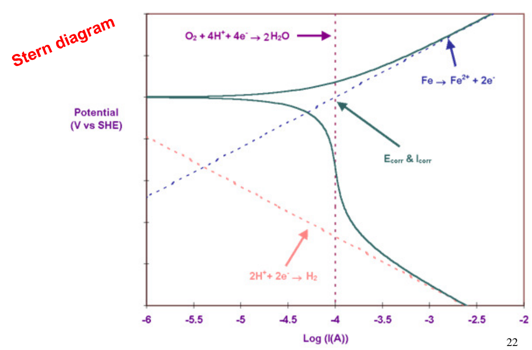
c) Kinetics - Measurement of corrosion potential and corrosion current density (腐蝕電位和電流密度的測量) using Tafel plot $\eta = a \pm b\log i$



Wagner-Traud diagram Stern diagram Evans diagram

Corrosion polarization diagrams (腐蝕極化圖)

Polarization diagram (極化圖) by potentiostatic scanning (電位掃描法)



2. Corrosion theory (腐蝕理論)

2.1 Electrochemical Aspect (電化學理論)

Corrosion rate (腐蝕速度) of mild steels (碳鋼)

抗腐蝕程度	腐蝕速度	
Outstanding	< 0.02 mmy	< 1 mpy
Excellent	0.02 - 0.1	1 - 5
Good	0.1 - 0.5	5 - 20
Fair	0.5 - 1	20 - 50
Poor	1 - 5	50 - 200
Unacceptable	>5	> 200

mmy = mm per year; mpy = mil per year

2. Corrosion theory (腐蝕理論)

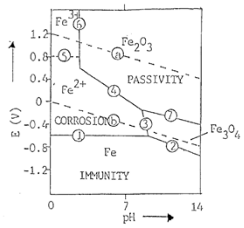
2.1 Electrochemical Aspect (電化學理論)

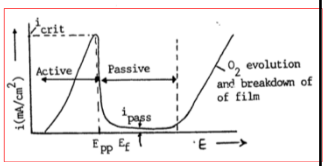
d) Passivity & Passivation (鈍態及鈍化)

- Certain metals and alloys are protected from corrosive solutions by forming very thin, oxidized and corrosion resistant films on their surfaces
- Passivity (鈍化) – a condition of corrosion resistance due to formation of thin surface films under **oxidizing** (**氧化**) conditions with high anodic polarization or highly oxidizing agent, such as "fuming" nitric acid (發煙硝酸)
- Metals able to form "passivity" film (鈍化膜)
  - Cr, stainless steels
  - Al, Si, Ti, Ta, Nb,

d) Passivity & Passivation (鈍態及鈍化)

- **Passivity (鈍態)**
  - Corrosion rate decreases when exceeding certain critical current density (i_{crit})
  - Passive current (鈍化電流) (i_{pass}) is very low
  - Stability of passivity may be disturbed by halide ion, causing unpredictable localized corrosion





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2. Corrosion theory (腐蝕理論)

2.1 Electrochemical Aspect (電化學理論)

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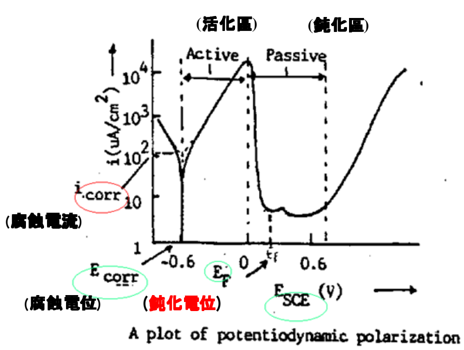
d) Passivity & Passivation (鈍態及鈍化)

- Chemical passivation (化學鈍化)
  - Caused by oxidants (Cr, Ni, Ti, Zr in air)
  - Examples
    - Iron in **dichromate** in circulating cooling water
    - Copper (bronze青銅) forms patina in air
    - Steel in **"fuming" nitric acid** (發煙硝酸)
- Anodic passivation (陽極鈍化)
  - Caused by anodic polarization, e.g., applying an external dc in aqueous media
  - Passivity forms as a result of a rate for cathodic reduction > i_{crit}
  - Alloys with lower i_{crit} and more active Epp are more easily passivated

d) Passivation (鈍化) - iron in sulfuric acid



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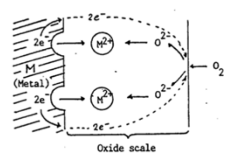
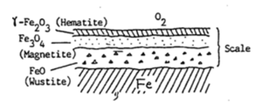
e) Dry corrosion (乾腐蝕)

- Corrosion may occur
  - in the absence of a liquid electrolyte (電解液) resulting in a corrosion product of film or scale formed on the metal surface and acting as an electrolyte as well as conductor (鍍電体)
  - when metal is exposed at room temperature to an oxidizing gas or vapour.
- Mechanism (機理)
  - adsorption of oxygen atom
  - formation of oxide nuclei
  - growth of a continuous film
- Example
  - Iron (Fe) exposed to temp >600°C





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2. Corrosion theory (腐蝕理論)

2.1 Electrochemical Aspect (電化學理論)

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e) Dry corrosion (乾腐蝕)

- Thermodynamics (熱力學)
- Kinetics (動力學)
  - Parabolic oxidation (拋物線氧化)
    - gives rise to an impervious adherent oxide layer, e.g., Ni (at all temp), Fe (>200°C), Cu (>800°C)
  - Linear oxidation (線性氧化) – catastrophic corrosion
    - gives rise to a non-impervious layer, e.g. Ca, Mg, Ta, Nb
  - Logarithmic oxidation (對數性氧化) (room temp)

2. Corrosion theory (腐蝕理論)

2.2 Metallurgical Aspect (冶金學理論)

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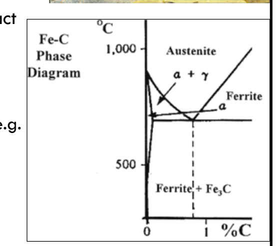
- **Composition (成份) (impurities, 雜質) and its effect**
  - C (graphite), Fe_3C (cementite) in Fe and unalloyed steels may act as cathodic (陰極) sites in corrosion
    - Ferrite acts as ***anode*** (陽極)
    - Slag (爐渣) inclusion in steels, e.g. oxides, sulfides, silicates act as ***cathode*** (陰極)



2. Corrosion theory (腐蝕理論)

2.2 Metallurgical Aspect (冶金學理論)

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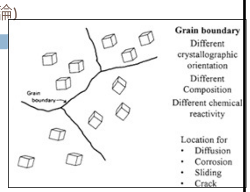
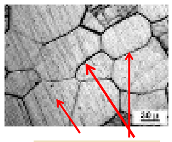
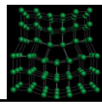
- **Metal structure (金屬結構) and its effects**
  - Metal structure - Imperfection or defects (缺陷)
  - Defects usually act as anodic site in metal dissolution
    - Grain boundary (晶間) – a discontinuity region with a width of several A (1A =10^{-10}m=0.1nm)
    - Dislocations (錯位) – step-like defect
    - Stacking faults (in fcc)





晶体 晶間



2. Corrosion theory (腐蝕理論)

2.2 Metallurgical Aspect (冶金學理論)

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- **Heat treatment (熱處理)**
  - Normalizing (正常化), hardening or quenching (淬火), tempering (回火), annealing(退火), sensitizing, welding (燒焊)
- **Effects of heat treatment (熱處理的效應)**
  - Change to phase (相)which may act as *cathodic sites*
  - Produce defect which may act as ***anodic sites***
  - Produce residual stress (殘餘應力) which may act as ***anodic sites***

CORROSION RESISTANT MATERIALS **(抗腐蝕材料)**

American standard AISI	British standard BS	Cr (%)	Ni (%)	C (%)	Si Max. (%)	Mn Max. (%)	Others (%)
Martensitic: body-centred tetragonal, magnetic, heat treatable							
403	En 56B	11.5–13		<0.15	0.5	1.0	
410	En 56A	11.5–13.5		<0.15	1.0	1.0	
414	En 57	11.5–13.5	1.25–2.5	<0.15	1.0	1.0	
420	En 56D	12–14		0.3–0.4	1.0	1.0	
431	En 57	15–17	1.25–2.5	<0.20	1.0	1.0	
Ferritic: body-centred cubic, magnetic, heat treatable							
405	713	11.5–14.5		<0.08	1.0	1.0	Al 0.1–0.3
430	En 60	14.0–18.0		<0.12	1.0	1.0	
446	En 61	23–27		<0.2	1.0	1.5	N <0.25
Austenitic: face-centred cubic, non-magnetic, not heat treatable							
301	801A	16–18	6–8	<0.15	1.0	2.0	
302	En 58A	17–19	8–10	<0.15	1.0	2.0	
304	En 58E	18–20	8–12	<0.08	1.0	2.0	
304L	801C	18–20	8–12	<0.03	1.0	2.0	
309	En 55	22–24	12–15	<0.20	1.0	2.0	
310S	A 11	24–26	19–22	<0.08	1.5	2.0	
316	En 58H	16–18	10–14	<0.08	1.0	2.0	Mo 2.0–3.0
316Cb	A 12 Nb	16–18	10–14	<0.08	1.0	2.0	Mo 2–3, Nb >10C
316Ti	845 Ti	16–18	10–14	<0.08	1.0	2.0	Mo 2–3, Ti >5C
317	En 58J	18–20	11–15	<0.08	1.0	2.0	Mo 3–4
318	845	17–19	13–15	<0.08	1.0	2.0	Mo 1.75–2.75, Nb + Ta > 10C
321	En 58B	17–19	9–12	<0.08	1.0	2.0	Ti > 5C
347	En 58F	17–19	9–13	<0.08	1.0	2.0	Nb + Ta > 10C

In general, S < 0.03%, P < 0.045%. So-called easy machining, non-seizing grades have high contents of S (or Se) and P, which reduce their corrosion resistance considerably.

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2. Corrosion theory (腐蝕理論)

2.3 Environmental Aspect (環境學理論)

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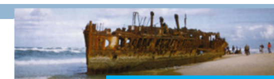

Marine environment

- **Water (水)**
  - Effects of
    - Oxidizers, aeration
    - Velocity of corrodants
    - Temperature
    - Galvanic coupling (bimetallic)
    - Air pollutants (SO_2, SO_3, NO_x, Cl_2, dusts…) & relative humidity and temperature
    - Soils
    - Water including natural rainfall, marine water…

2. Corrosion theory (腐蝕理論)

2.3 Environmental Aspect (環境學理論)

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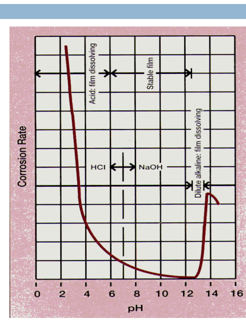
- **Water (水)**
  - Types
    - Aerated or de-aerated
    - Soft water or hard water
  - pH value
  - Dissolved oxygen
  - Total dissolved solids
    - Aggressive ions (chloride, sulfate)
    - Conductivity
  - Velocity (water flow)
  - Temperature



Effect of pH on corrosion rate of Zn in water

- **Soils (土壤)**
  - resistivity (dissolved salt and water)
  - pH value (acidity)
  - aeration (presence of oxygen)
  - texture (porosity) – sand, silt, clay
  - bacteria (microbial corrosion)
    - Anaerobic reduction: sulfate reducing bacteria
    - Aerobic oxidation: sulfur oxidizing bacteria

Soil resistivity (ohm cm)	Corrosivity rating
>20,000	Essentially non-corrosive
10,000 to 20,000	Mildly corrosive
5,000 to 10,000	Moderately corrosive
3,000 to 5,000	Corrosive
1,000 to 3,000	Highly corrosive
<1,000	Extremely corrosive

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- **Air (大氣)**
  - Air pollutants (大氣污染物)
    - $O_2 + H_2O + 2e^- \longrightarrow 2OH^-$
    - $SO_2 + H_2O \longrightarrow H_2SO_3$
    - $SO_3 + H_2O \longrightarrow H_2SO_4$
    - $2NO + O_2 \longrightarrow 2NO_2$; $2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$
    - Halides (鹵化物) ：chloride, fluoride
    - Dusts and particles: when condensed with moisture on metal, initiate corrosion by formation of galvanic cell or differential aeration cell
  - Relative humidity (RH, 相對濕度) and temperature
    - Critical RH – below which negligible corrosion is found at constant temperature
      - For steel (65%); cupper (65%); Al (75%)
  - Dew point (corrosion)
    - When the temperature drops below the dew point, water and acid will condenses on exposed surface, causing corrosion of the metal

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3. Corrosion testing (腐蝕測試)

3.1 Overview (概述)

- **Why corrosion testing?**
  - Evaluation of corrosion resistance of materials under performance conditions for the following pourposes
    - material and coatings development (材料和塗層的開發)
    - Corrosion monitoring (鑑控)
    - Quality control of materials (質檢)
    - Failure analysis (失效分析)
  - Find out preventive and protective measures, e.g. methods (方法), device(設備)

3. Corrosion testing (腐蝕測試)

3.2 Electrochemical studies (電化學方法)

Reference electrode (參攷或參比電極)

- A reference electrode provides a fixed potential which does not vary throughout the experiment
- Major types
  - Standard reference electrode (SHE)
  - Saturated Calomel electrode (SCE)
  - Silver chloride electrode
  - Saturated copper sulfate electrode

An electrode which measures -0.34V against an SCE would only measure -0.10V against SHE

Calculation of potential of reference electrodes (參比電極)

- **Nernst equation** $E = E^o + (RT/zF) \ln (a_{(ox)} / a_{(red)})$

Calomel reference electrode **Hg/Hg_2Cl_2, KCl // M^+/M**

- Half cell reaction $Hg_2Cl_2 + 2e^- <=> 2Hg + 2 Cl^-$

Conc of KCl filled (M)	E (V)
0.1	0.336
1.0	0.283
Saturated (SCE)	0.242

Silver chloride reference electrodes Ag/AgCl, KCl // M^+/M

- Half cell reaction $AgCl + e- <=> Ag + Cl^-$

Conc of KCl filled (M)	E (V)
0.1	0.288
1.0	0.222

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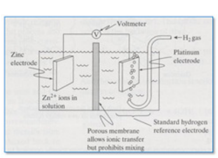
Measurement of half-cell potentials

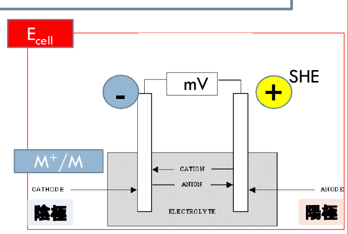
- The potential of an electrode (M^+/M) relative to a Standard Hydrogen Electrode (SHE) and expressed as

$Pt/H_2(atm)/HCl\ (a=1)\ //\ M^+\ (a=1)\ /M$

(Anode "+") 陽極 (Cathode "-") 陰極

$E_{cell} = E_{cat} - E_{an}$





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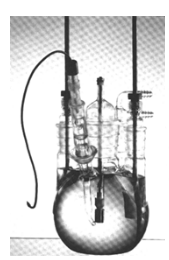
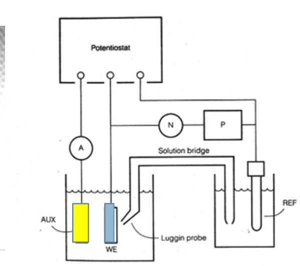
3. Corrosion testing (腐蝕測試)

3.2 Electrochemical studies (電化學方法)

Experimental setup

參比電極





tE 4.10 Controlled potential circuitry utilizing a potentiostat.

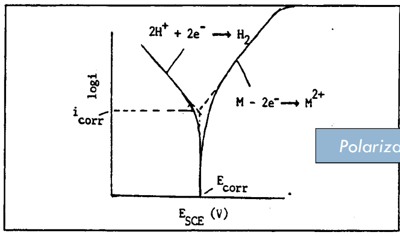
3. Corrosion testing (腐蝕測試)

3.2 Electrochemical studies (電化學方法)

Measurement techniques –

$\eta = a \pm b \log i$

(1) Polarization resistance measurement (Tafel plot)

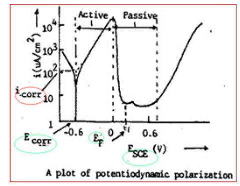


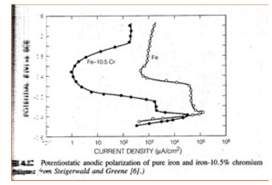
Polarization > 0.1V

Measurement techniques –

(2) Potentiodynamic polarization technique

- evaluation of corrosion resistance of various steels





Effect of scanning rate, **ν** on peak current i_p

$$\nu = dE/dt \quad (V/s)$$

$$i_p = 2.687 \times 10^5\ n^{3/2} A D^{1/2} c \nu^{1/2}$$

where i_p = peak current; A = area;

D = diffusion coefficient

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3. Corrosion testing (腐蝕測試)

3.2 Electrochemical studies (電化學方法)

Rating of metal's corrosion resistance

Corrosion Resistance	Corrosion rate (mmy)	Corrosion rate (mpy)
Outstanding	< 0.02	< 1
Excellent	0.02 - 0.1	1 - 5
Good	0.1 - 0.5	5 - 20
Fair	0.5 - 1	20 - 50
Poor	1 - 5	50 - 200
unacceptable	>5	> 200

mmy = mm per year; mpy = mil per year

3. Corrosion testing (腐蝕測試)

3.2 Electrochemical studies (電化學方法)

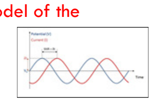
(3) Electrochemical Impedance Spectroscopy (EIS)

(電化學阻抗谱)

- Basic principle
  - Apply a small AC signal (5-50mV) to the across the corroding system. Measure the test electrode impedance and phase shift (θ) values over a wide range of frequencies of 0. 1 to 100kHz in a lock-in amplifier
  - Interpret the EIS results with help of a model of the interface

E = I x Z (Z is impedance in ohms)

($I_t = A \sin(\omega t + \theta)$)



Impedance response consists of 2 components:

Real resistance (Z') and Imaginary capacitance (Z")

(3) EIS (電化學**阻抗谱**)

- Application
  - Fit the EIS data (presented in a Nyquist or Bode plot) to a proposed circuit model used to indicate the electrochemical system of the coating and the metal substrate
  - For the study of corrosion of organic coating & oxides on steel surfaces with the assistance of a circuit model of the interface in respect of the following
    - Corrosion rate determination (electron transfer resistance or polarization resistance)
    - Study of inhibitor, coatings
    - Investigation of passive layers, e.g. anodizing of aluminium

BS EN 16128:2015 Ophthalmic optics – reference method for the testing of spectacle frames and sunglasses for nickel release

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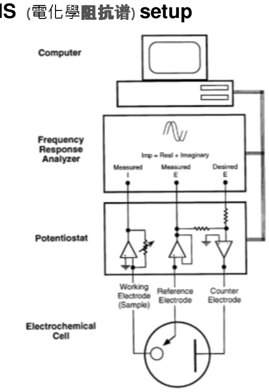
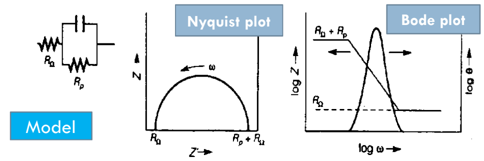
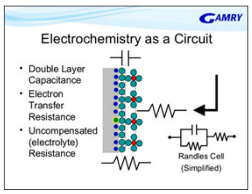
EIS (電化學**阻抗谱**) **setup**



48 NIST SP861, W. L. Grosshandler, et al., Editors

EIS : Nyquist and Bode plot (圖)





C_{dl} = double layer capacitance
R_Ω = solution resistance
R_p = metal polarization resistance
Z = imaginary impedance
Z' = real impedance
ω= frequency
θ = phase shift

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(3) EIS (電化學阻抗谱)

- Corrosion rate of uncoated metal:

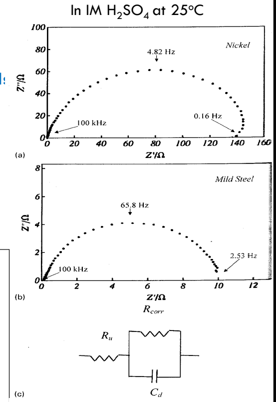
Material	E_{corr}/mV (Hg/HgSO$_4$)	R_{ct}/Ω cm^2
Mild steel	−900	55
Solid nickel	−660	755
Polished mild steel	−880	110

Measurement of corrosion rate of aluminum

$$I_{(corr)} = B/R_{ct}$$

B: proportional constant, B=24 mV for Al
R_{ct}(kΩ cm^2): resistance of charge transfer (ct) calculated from EIS at low frequency

In IM H_2SO_4 at 25°C



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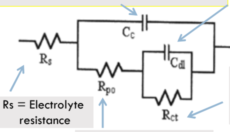
(3) EIS

- for modelling of organic coating (porous, non-conductive film) on metals → a **damaged** coating model (shown below)

C_c = Capacitance of the intact coating

C_{dl} = Double layer at metal surface (~40F)

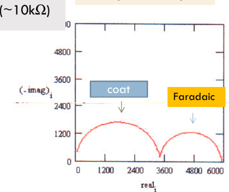


Rs = Electrolyte resistance

Rpo = Pore resistance in the coating (~100Ω)

Rct = Metal charge transfer or polarization (~10kΩ)

Nyquist plot for the equivalent model of damaged coating



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Reliable Corrosion Measurements via Electrochemistry

Electrochemistry Techniques	Parameters of Interest	ASTM Reference Methods
DC Techniques • Linear sweep voltammetry • Tafel slope analysis • Potentio-dynamic polarization (LPR)	• Polarization Resistance (Rp) • Corrosion Rate (mm/Year) • Corrosion Current • Corrosion Potential	• ASTM G102-89 (2015) • ASTM G59-97 (2014)
AC Techniques • Electrochemical impedance analysis (EIS)	• Film Resistance & Conductivity • Charge-transfer resistance • Solution Resistance • Polarization Resistance	• ASTM G59-97 (2014) • ASTM G106-89 (2015)
Chrono & other Techniques • Electrochemical noise (ECN) • Critical pitting technique (CPT) • Hydrogen Permeation study • Cyclic polarization • Hydrodynamic linear sweep	• Redox Kinetics • Pit initiation • Crevice progression • Hydrogen resistance • Surface morphology	• ASTM G150-99 (2010) • ASTM G148-97 (2003) • ASTM G100-89 (2015) • ASTM G61-86 (2014) • ASTM F746-04 (2014) • ASTM F2129-15

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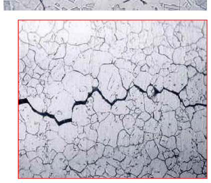
Source: Metrohm, Switzerland

3. Corrosion testing(腐蝕測試)

3.3 Metallographic examination (金相檢驗)

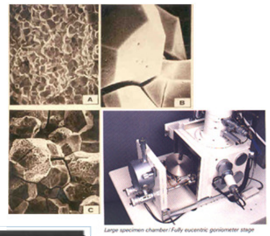
- Morphological studies and surface chemical analysis
- Metallographic studies (金相检验) of cross-section of corroded metal
- Instrumentation & techniques (儀器與技術)
  - Optical microscopy (光學顯微鏡)
  - Scanning/transmission electrode microscopy (STEM) equipped with EDX or WDX (for elemental analysis) (素描電子顯微鏡+能量扩散光谱仪)
  - X-ray diffraction (XRD) (X光射线衍射法)
  - X-ray fluorescence (XRF) (射线荧光(检查)法)
  - **X-ray induced photo-electron spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA)**
  - **Auger electron spectroscopy (AES)**
  - **ISS (ion scattering spectroscopy)**
  - **SIMS (secondary ion mass spectrometry) – for studying the chemical state of solid surfaces**

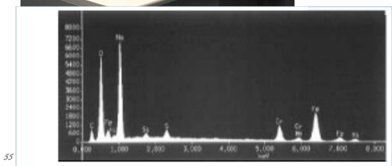
Optical microscopy(光學顯微鏡)



Scanning electron microscope (SEM) + EDX

(素描電子顯微鏡 + 能量扩散光谱仪)





SEM-EDXA of corrosion product on expansion joint fracture surface.

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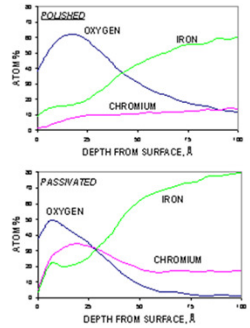
3. Corrosion testing(腐蝕測試)

3.3 Metallographic examination (金相檢驗)

Application of XPS or ESCA

- elemental composition of the surface (top 0–10 nm usually)
- empirical formula of pure materials
- elements that contaminate a surface
- chemical or electronic state of each element in the surface
- uniformity of elemental composition across the top surface (or line profiling or mapping)
- uniformity of elemental composition as a function of ion beam etching (or depth profiling)



3. Corrosion Testing

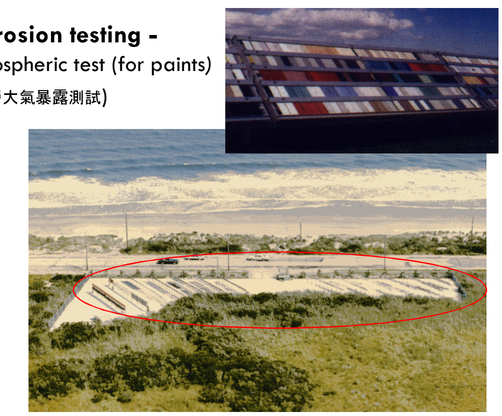
3.4 Other tests (其他檢測方法)

- 3 main types
  - Immersion tests
  - Atmospheric tests
  - High temperature tests
    - Elevated temperature and high humidity tests
- Special tests
  - Intergranular corrosion test 晶間腐腐蝕測試 (ASTM A-262)
  - Pitting corrosion test 點蝕測試 (ASTM G48-11)
  - Hydrogen induced cracking test
  - Chloride stress corrosion test
  - …

Corrosion testing -

Atmospheric test (for paints)

(塗層大氣暴露測試)



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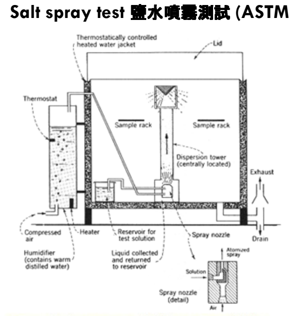
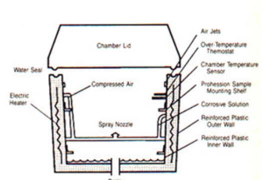
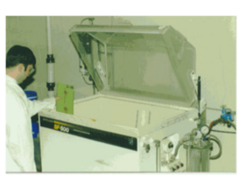
Salt spray test 鹽水噴霧測試 (ASTM B117)







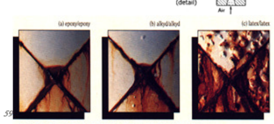


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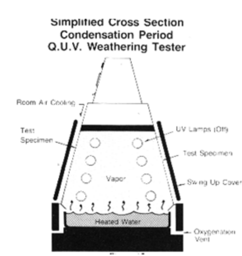
Fig. 1 Scribed regions of panels after 2,000 hours' salt spray testing (1,000 hours for latex)

Atmospheric tests - QUV Weathering Test 人工氣候測試 (ASTM G53-88)



Cyclic wet/dry testing of paints

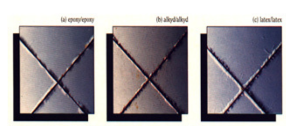


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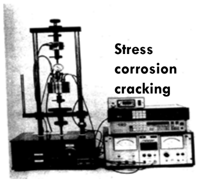
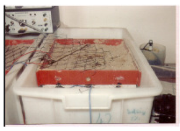
Fig. 2 Scribed regions of panels after cyclic wet/dry corrosion testing (2,000 hours)

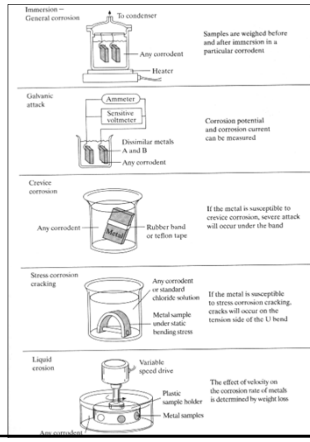
實驗室測試

Corrosion testing - Other lab tests





Corrosion study of re-bar in concrete



3. Corrosion testing (腐蝕測試)

3.5 Corrosion monitoring (腐蝕監察)

- A systematic measurement of metal corrosion in order to help understand the corrosion process and/or obtain information for use in controlling corrosion and its effectiveness
- Requires knowledge of corrosion mechanism and sophisticated electronic measuring devices
- Applications in chemical and petrochemical industries, bridges, highways, oil refining, power generation, food industries

3. Corrosion testing (腐蝕測試)

3.6 Failure analysis (破損分析, 失效分析)

- Failure of components of devices in service is not uncommon despite the introduction of a factor of safety in design
- Operating conditions can produce the following phenomena, which if ignored, will ultimately lead to failure:
  - Fracture (斷裂) - usually associated with overload
  - Fatigue (疲勞) - caused by repeatedly change stress)
  - Creep (蠕變) - usually occur under high temp)
  - Corrosion - environmental attack to the component materials associated with chemical and mechanical effects

THANK YOU FOR LISTENING

Corrosion Never Sleeps!
- B.M. Gordon, USA