

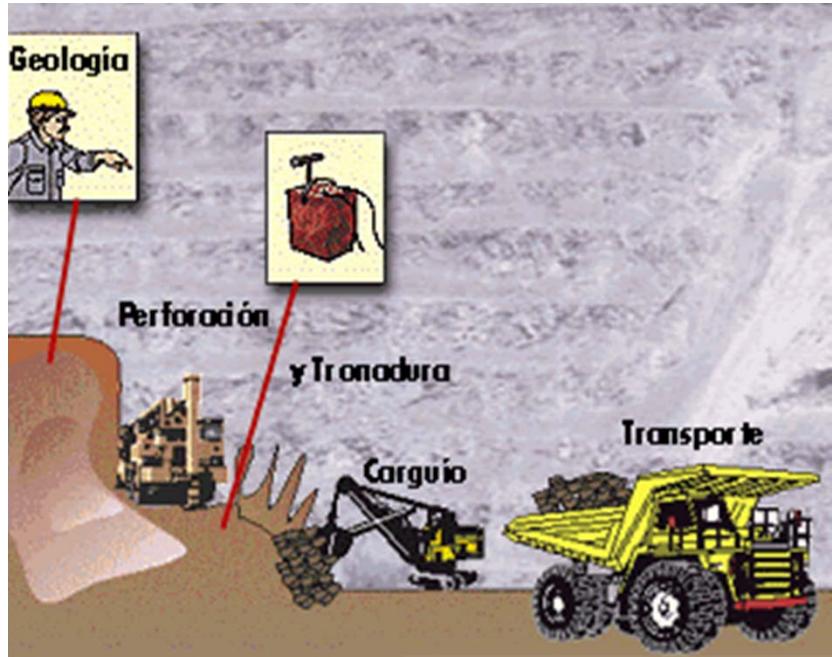
CURSO DE CORROSION



UNIVERSIDAD PEDAGOGICA Y
TECNOLOGICA DE COLOMBIA - UPTC

TUNJA - COLOMBIA
Ph.D. Enrique Vera

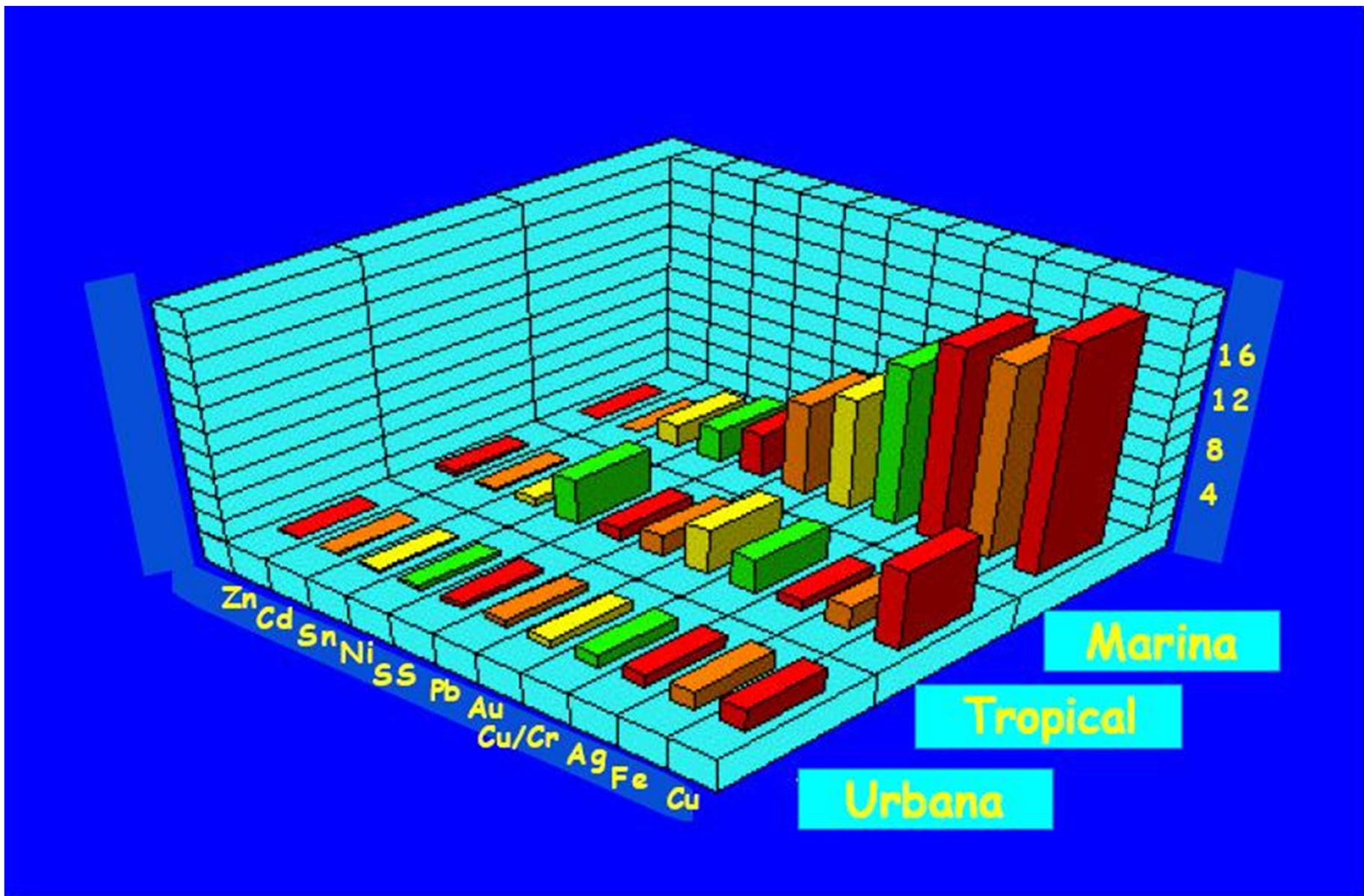
CONCEPTOS BASICOS DE ORIGEN DE LA CORROSION Y SU IMPACTO EN LA INDUSTRIA



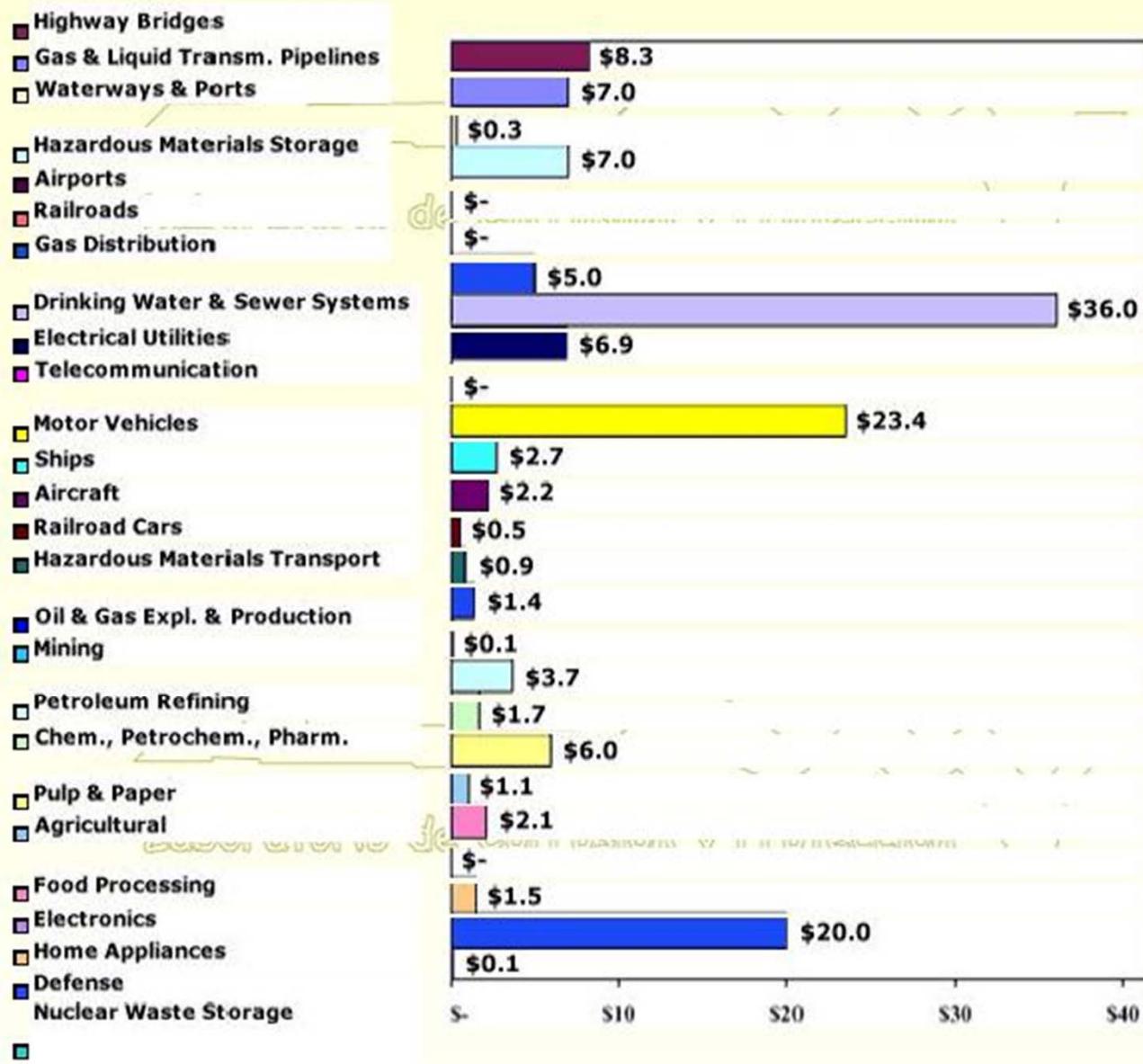
CICLO TERMODINAMICO DE LOS MATERIALES

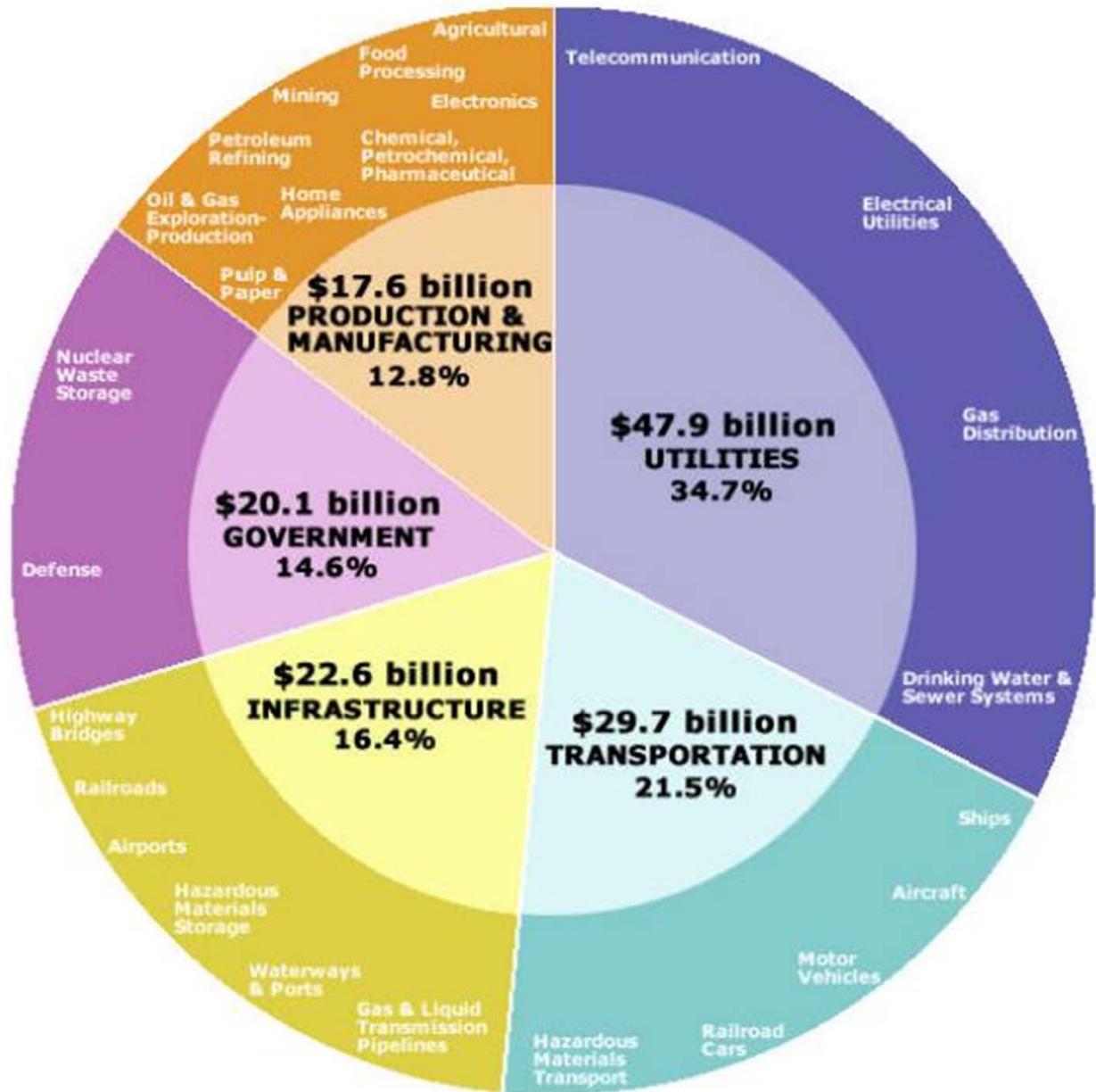


IMPACTO DEL MEDIO EN LA CORROSION



Cost of Corrosion Per Analyzed Economic Sector, (\$ x billion)





CONCEPTOS DEL POTENCIAL ELECTRICO

INTERFACE ELECTRIFICADA
ACERO / ELECTROLITO

Basics of Instrumentation

Electricity

Charge

Unit of charge the *Coulomb*, C (not to be confused with *C* for capacitance).

Charge on the electron (1.6×10^{-19} coulomb).

Current

Unit of current the *Amp*, A (= 1 coulomb/second).

Electronic and ionic current; conservation of charge.

Voltage (or Potential Difference)

Unit of voltage the *Volt*, V (1 joule required to move 1 coulomb through a potential difference of 1 volt).

Resistance

Ohm's Law (voltage = current x resistance, $V = IR$).

Unit of resistance the *Ohm*, W (that resistance which allows 1 amp to flow with a voltage of 1 volt).

Capacitance

Unit of capacitance the *Farad*, F (1 farad will absorb 1 coulomb when the voltage across it increases by 1 volt).

Charging of a capacitor, C ($I = C \frac{dV}{dt}$, $Q = C \square V$).

Inductance

Electrical Measurements

Measurement of current, effect of meter impedance (want $Z_{\text{meter}} = 0$).

Measurement of voltage, effect of meter impedance (want $Z_{\text{meter}} = \square$).

Noise

Interference Noise

Electronic Noise

Frequency Response or Filtering

Operational Amplifiers

Non-Inverting Buffer

Properties

7.2 UNIDADES Y EQUIVALENCIAS

JOULE: J ($M\ L^2\ T^{-2}$) Unidad de energía SI. $1J = 1V \cdot A \cdot s = 1CV = 1Kg \cdot m^2 \cdot s^{-2} = 10^7$ erg.

COULOMBIO: C (A T) Unidad de carga eléctrica SI. $1C = 1A \cdot s = 1J \cdot V^{-1}$.

VOLTIO: V ($M\ L^2\ T^{-3}\ A^{-1}$) Unidad de potencial eléctrico SI. $1\ V = 1W \cdot A^{-1} = 1\ J \cdot A^{-1} \cdot s^{-1}$.

VOTIO/METRO : V/m ($M\ L\ T^{-3}\ A^{-1}$) Unidad de campo eléctrico.

FARAD : F ($M^{-1}\ L^{-2}\ T^4\ A^2$) Unidad de capacidad SI.

$1F = 1\ C \cdot V^{-1}$ Unidades usuales nano, picofarad : nF, pF.

FARAD/METRO: F/m ($M^{-1}\ L^{-3}\ T^4\ A^2$) Unidad de permitividad.

OHMIO : Ω ($M\ L^2\ T^{-3}\ A^{-2}$) Unidad de resistencia/impedancia SI. $1\ \Omega = 1\ V \cdot A^{-1}$.

SIEMIENS : S ($M^{-1}\ L^{-2}\ T^3\ A^2$) Unidad de conductancia SI.

$1\ S = 1\ \Omega^{-1} \gg$ Otro nombre " mho".

SIEMIENS/METRO : S/m ($M^{-1}\ L^{-3}\ T^3\ A^2$) Unidad de conductividad.

7.3 CONSTANTES

N_A : Número de Avogadro.

$$N_A = 6.0220943 \cdot 10^{23}$$

e : Carga elemental.

$$e = 1.602 \cdot 10^{19} \text{ C}$$

k : Constante de Boltzman.

$$k = 1.38041 \cdot 10^{-23} \text{ J.K}^{-1}.$$

F : Constante de Faraday.

$$F = N_A \cdot e = 96485 \text{ C.}$$

R : Constante de los gases.

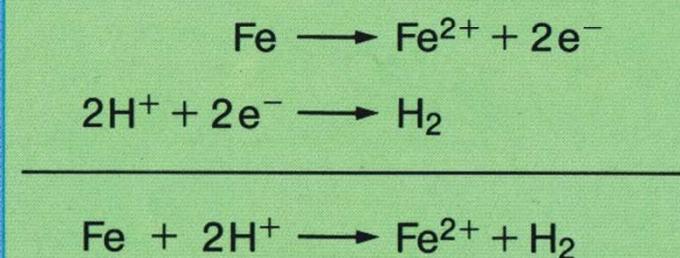
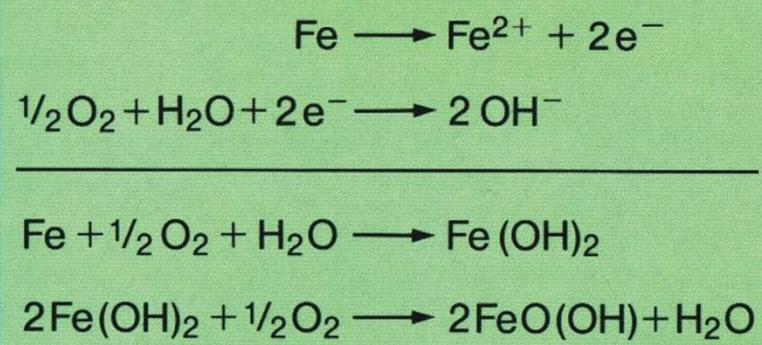
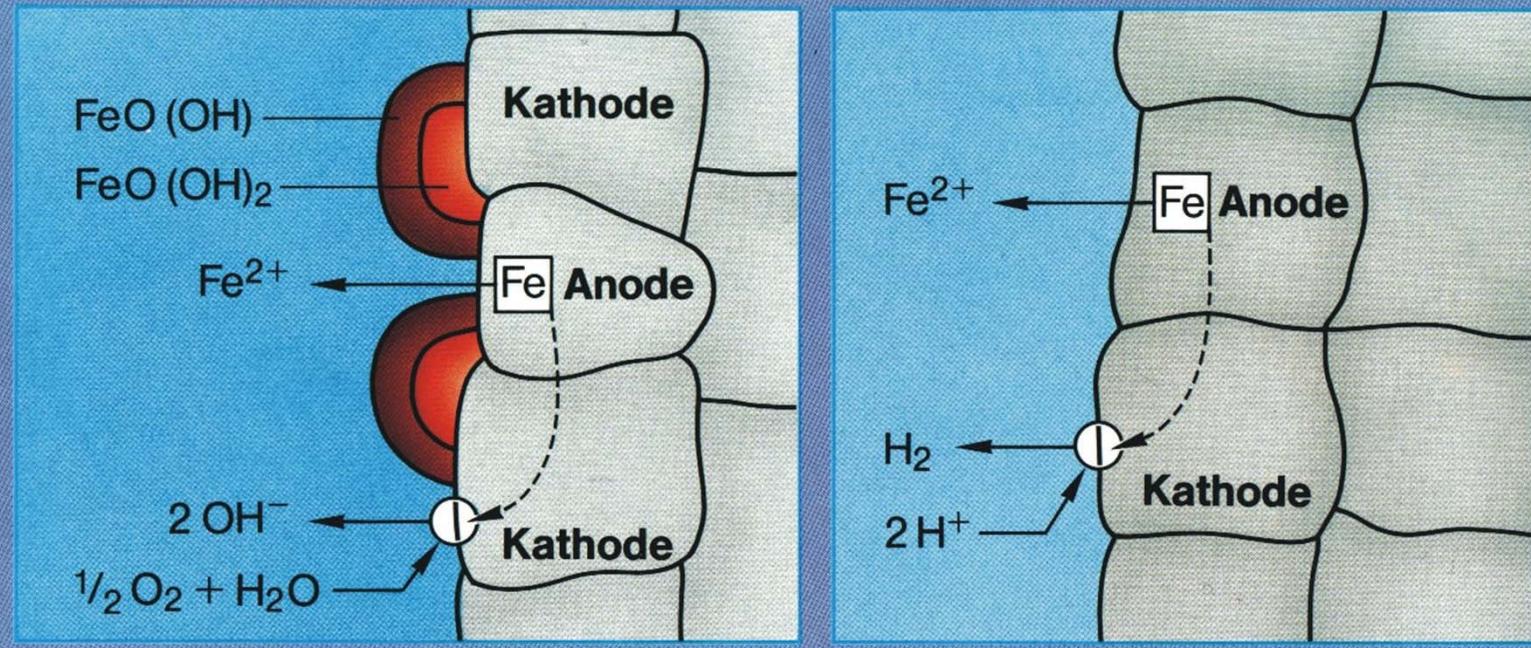
$$R = N_A \cdot k = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}.$$

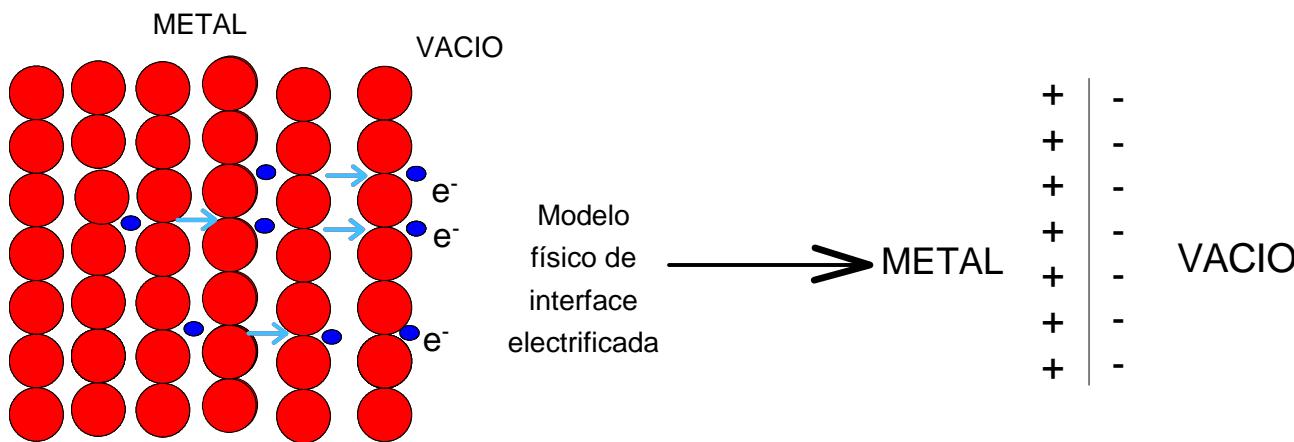
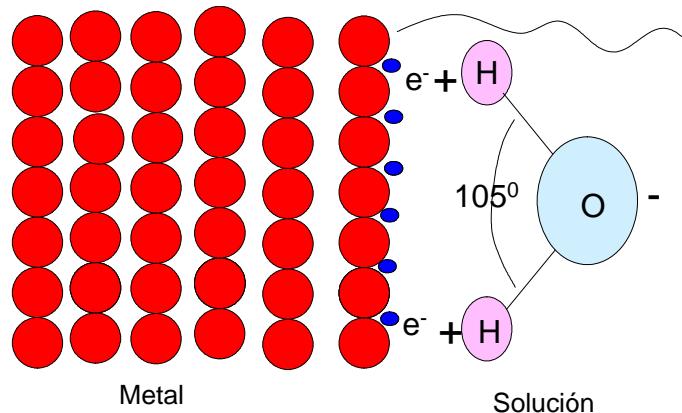
$$= 8.3144 \text{ J K}^{-1} \text{ mol}^{-1} (= \text{A.s.V.K}^{-1} \text{ mol}^{-1} = \text{C.V.K}^{-1} \text{ mol}^{-1})$$

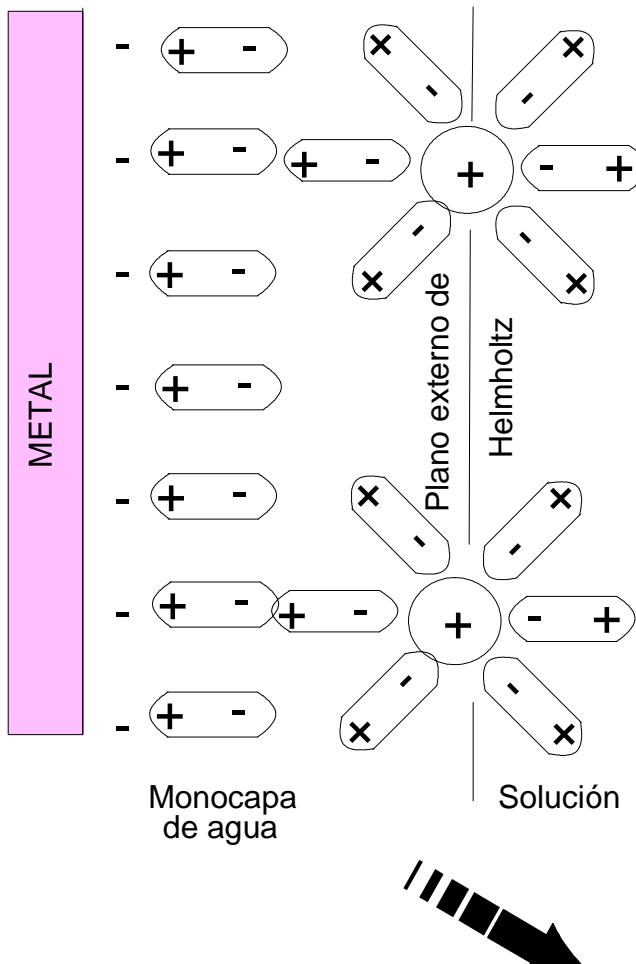
ϵ_0 : Permitividad del vacío.

$$\epsilon_0 = 8.854 \cdot 10^{-12} \text{ C.V}^{-1} \text{ m}^{-1} (\text{F.m}^{-1}).$$

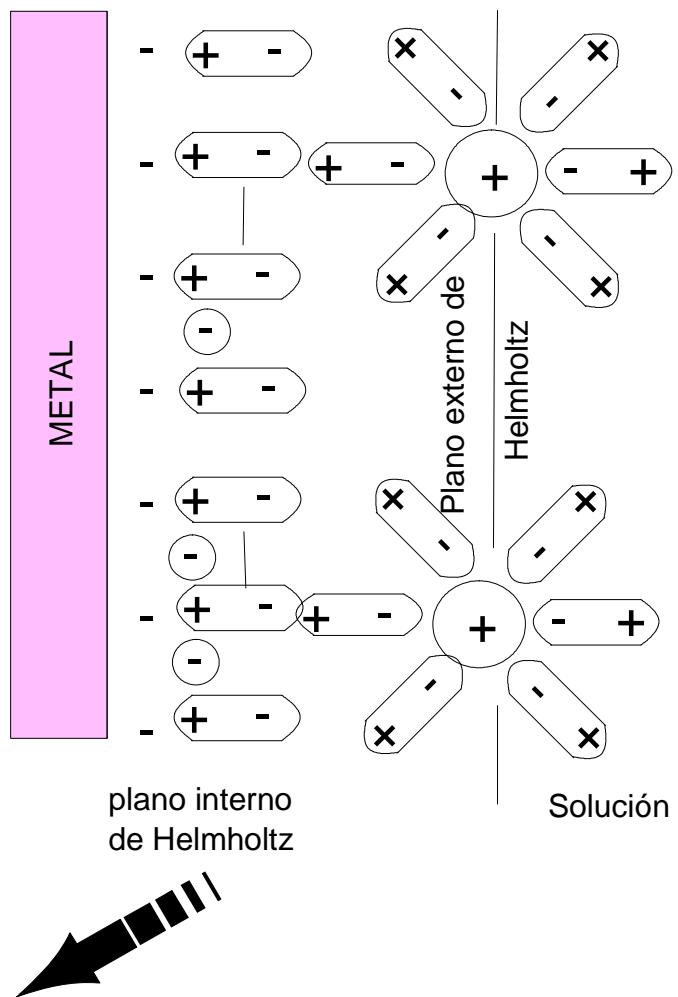
PRINCIPIO DE CORROSION POR OXIGENO Y CORROSION ACIDA

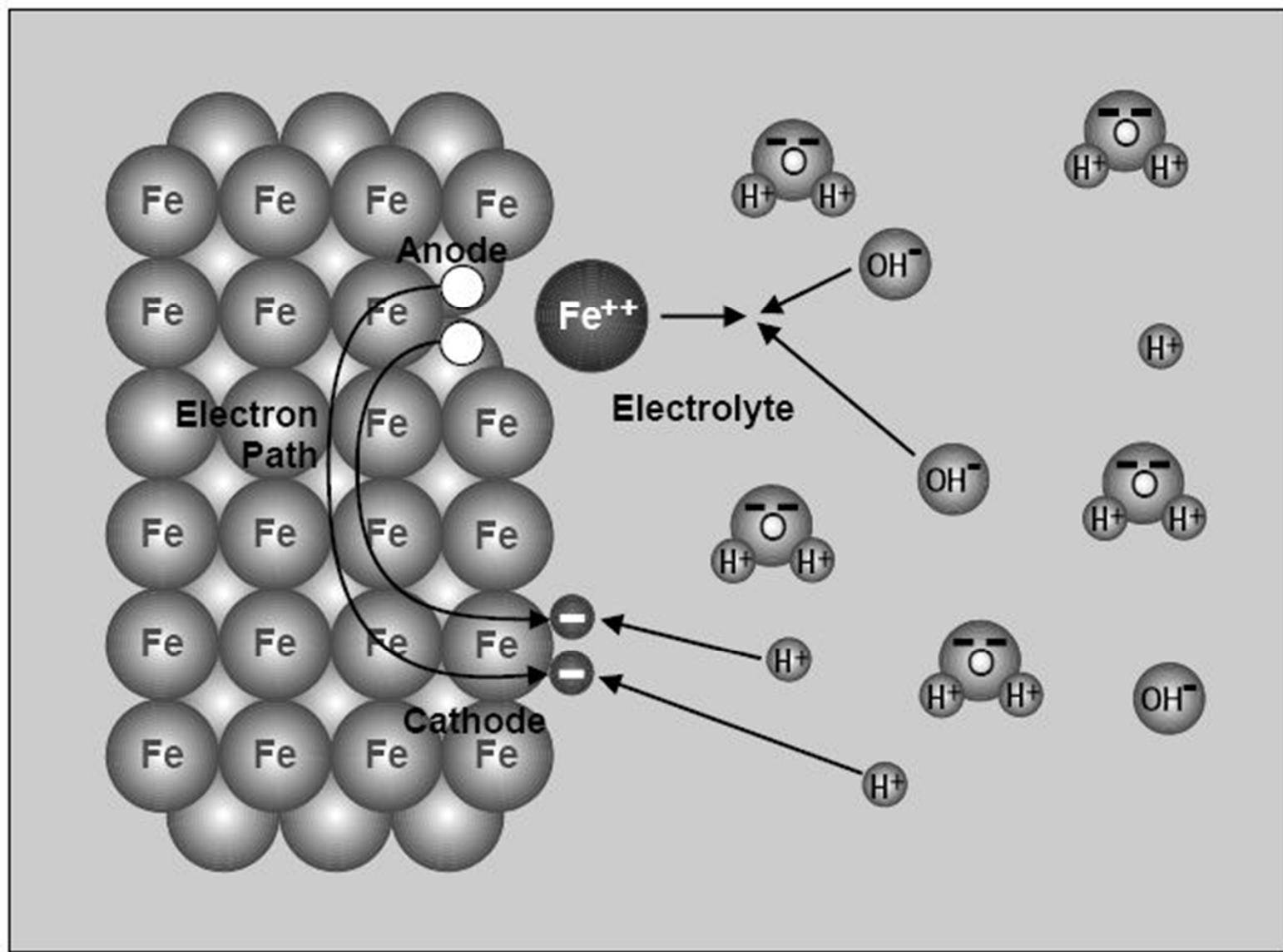


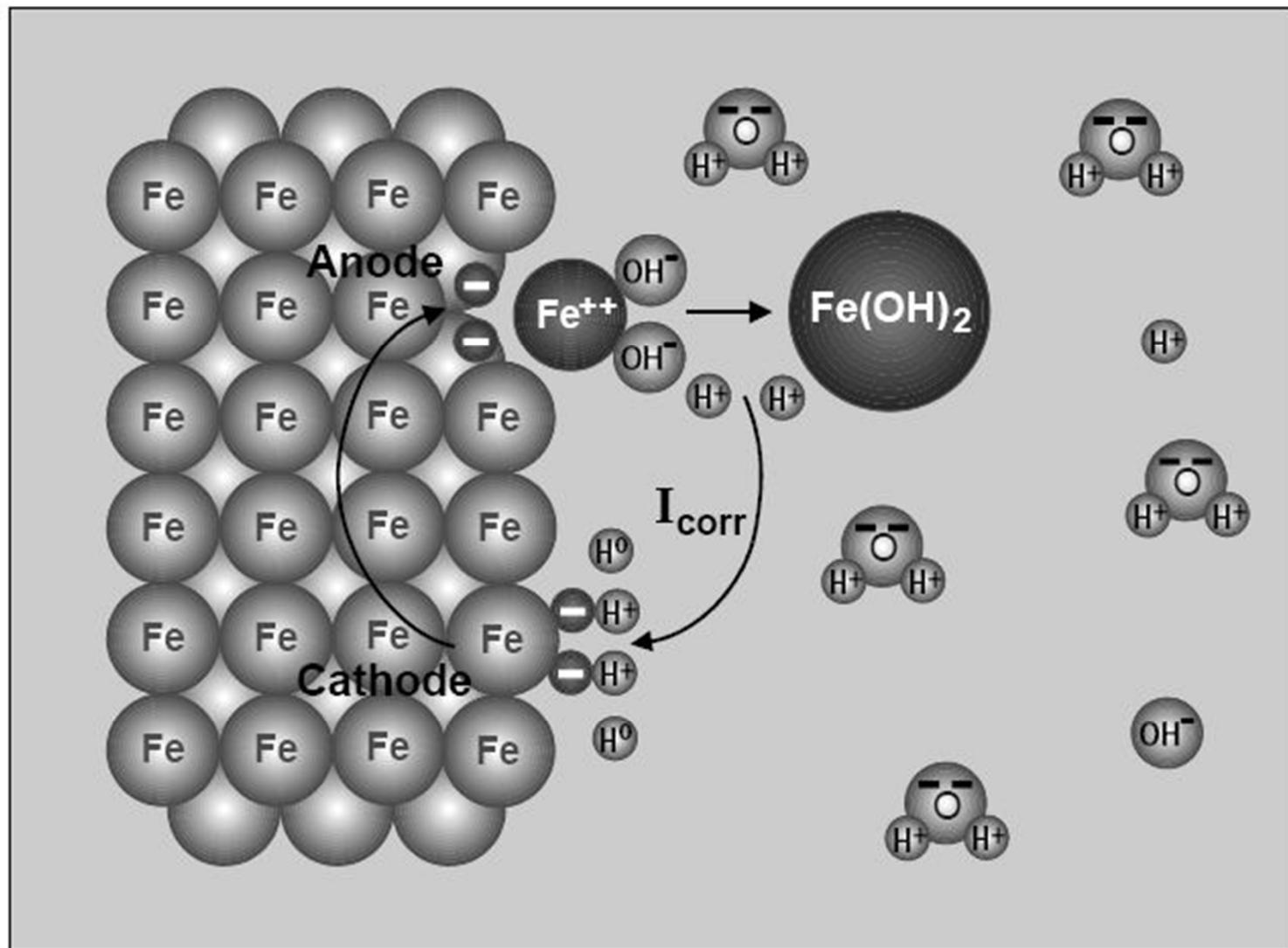




MODELO

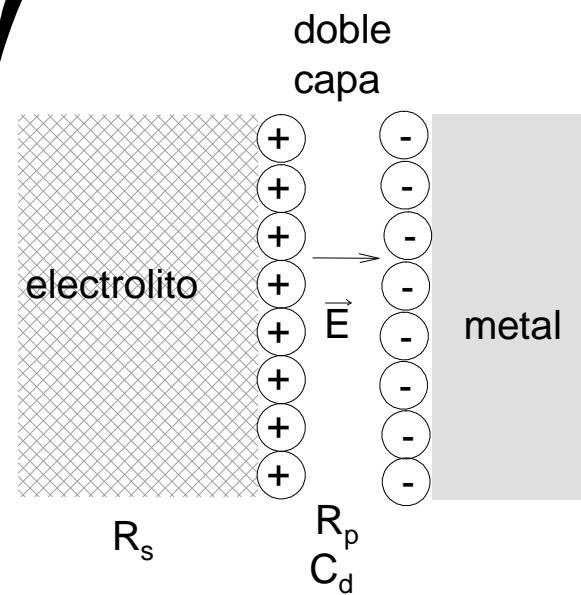




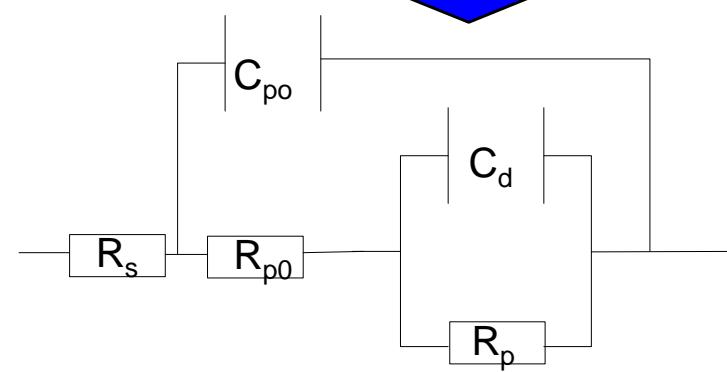
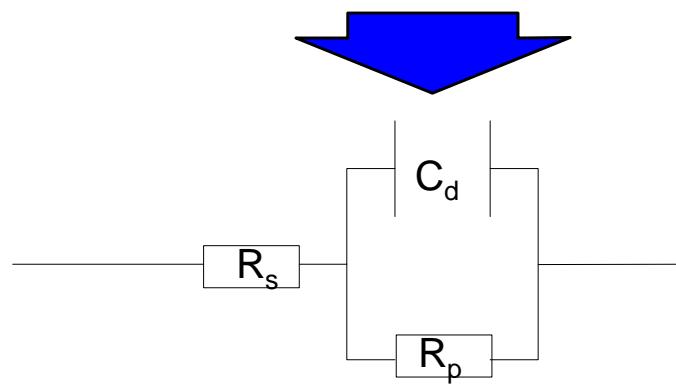
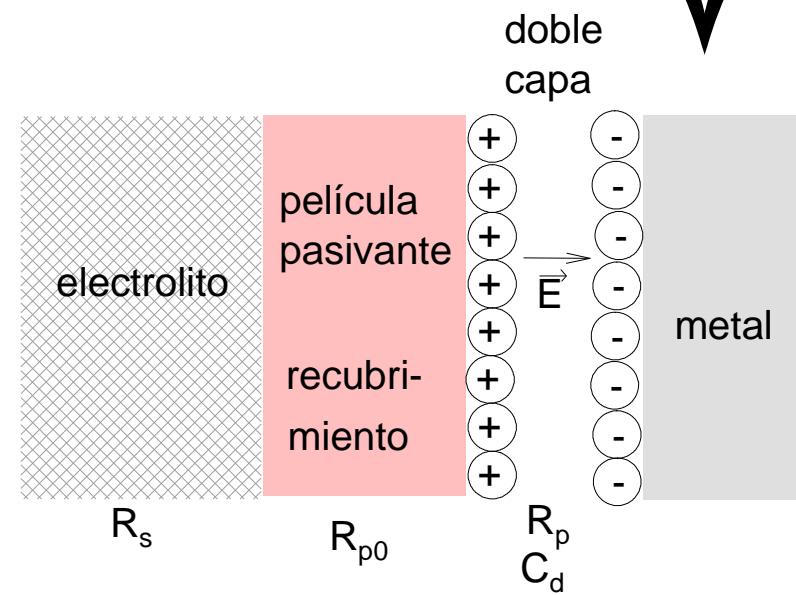


**Figure 1-13: Direction of Conventional Current
(positive charge flow)**

CASO SIMPLE: medio de relativa alta conductividad.



CASO COMPLEJO: adición de otros elementos

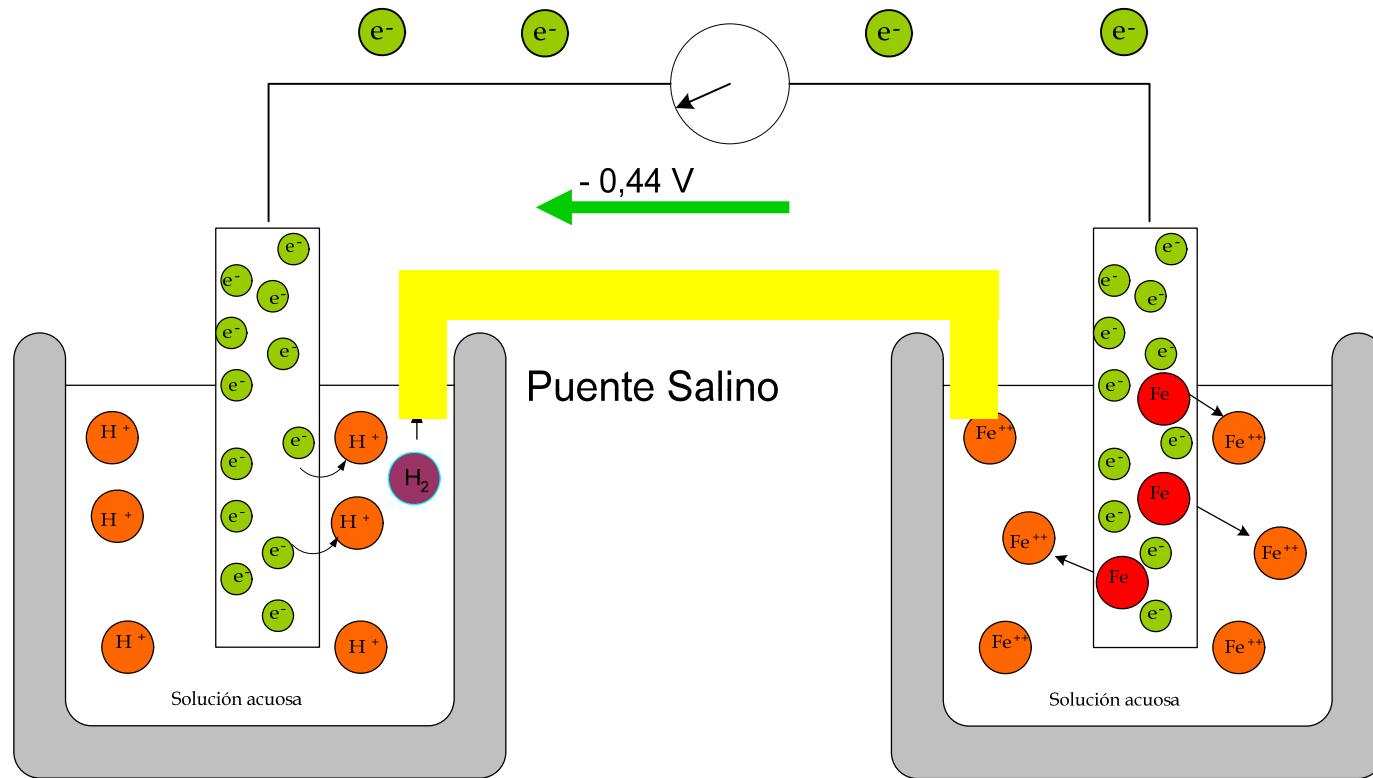


TERMODINAMICA DE LA CORROSION

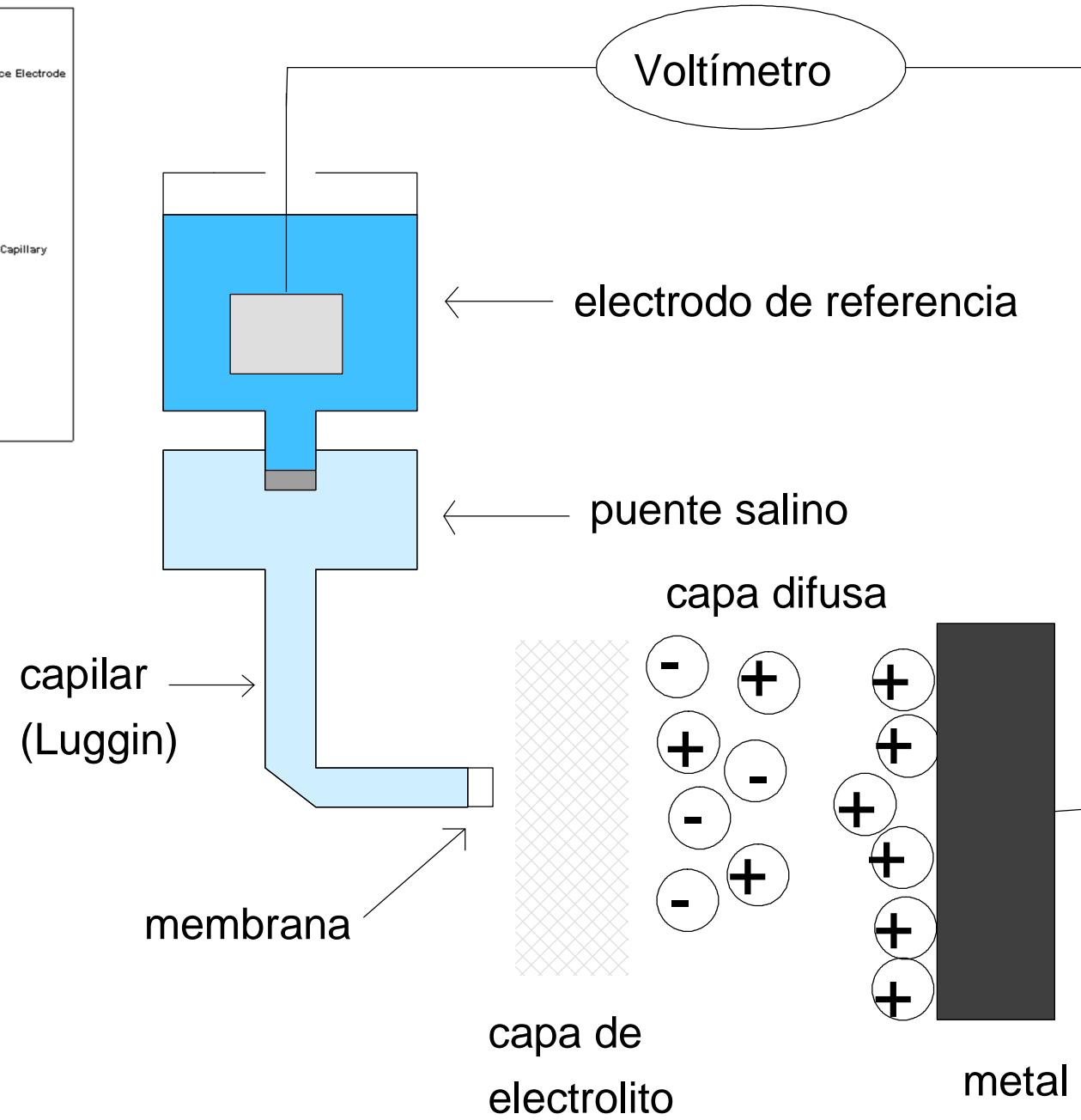
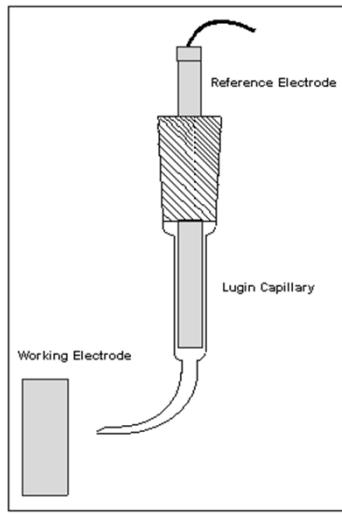
MEDICION DEL POTENCIAL ELECTROQUIMICO
O POTENCIAL DE ELECTRODO

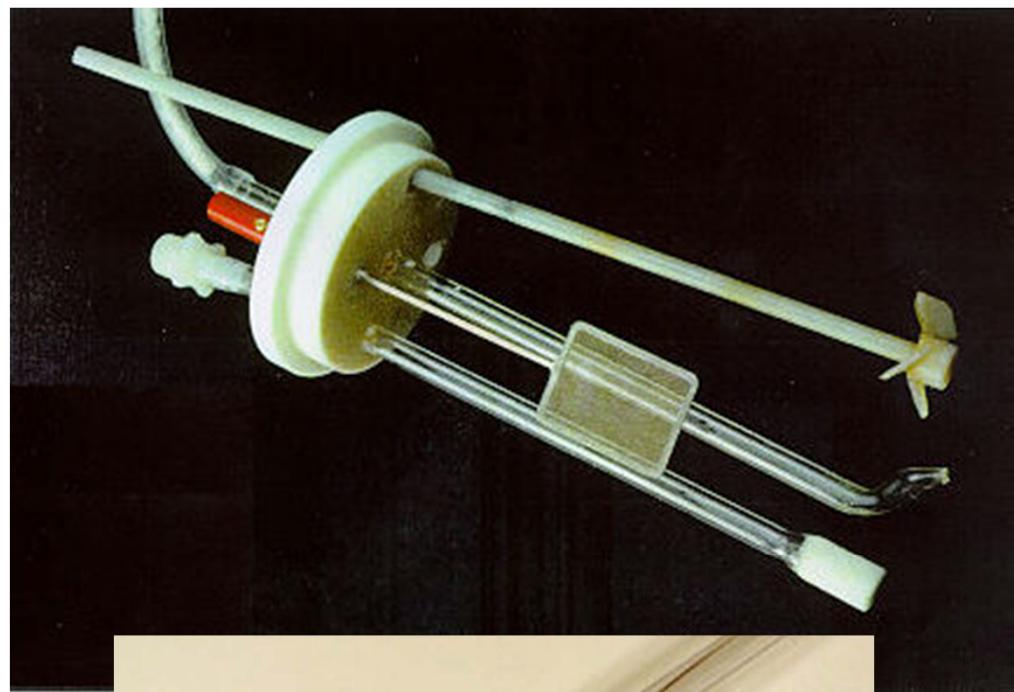
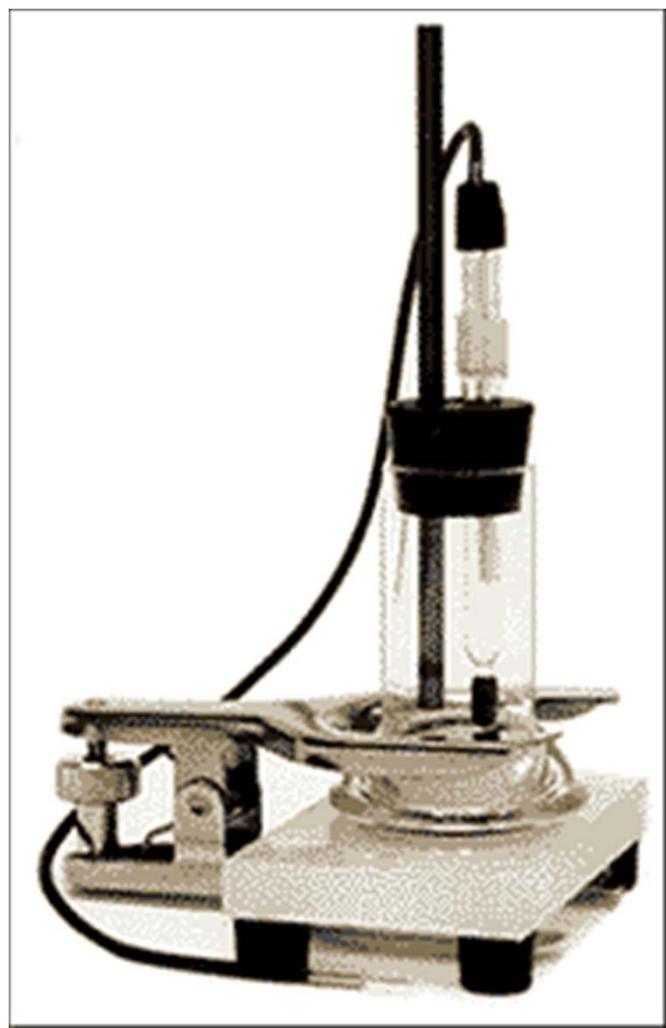
POTENCIAL (VOLTIOS)

Potencial de electrodo



En los casos prácticos, se mide una diferencia de potencial. Esta diferencia de potencial es la que existe entre dos electrodos metálicos.
En corrosión, uno de los electrodos es el material a examinar y el otro, es el llamado electrodo de referencia (que es un electrodo metálico)





ELECTRODO ESTANDAR DE HIDROGENO

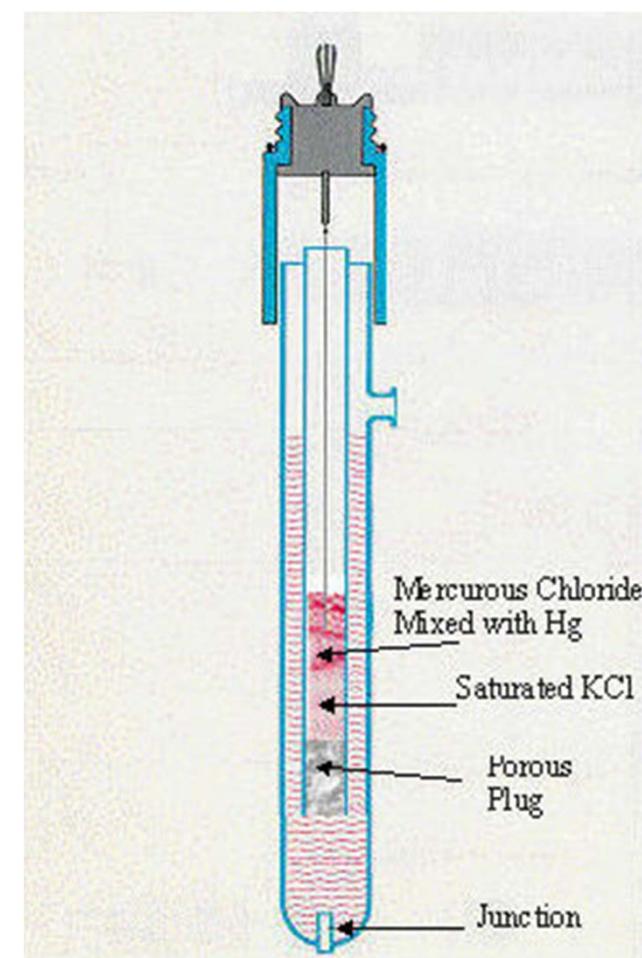
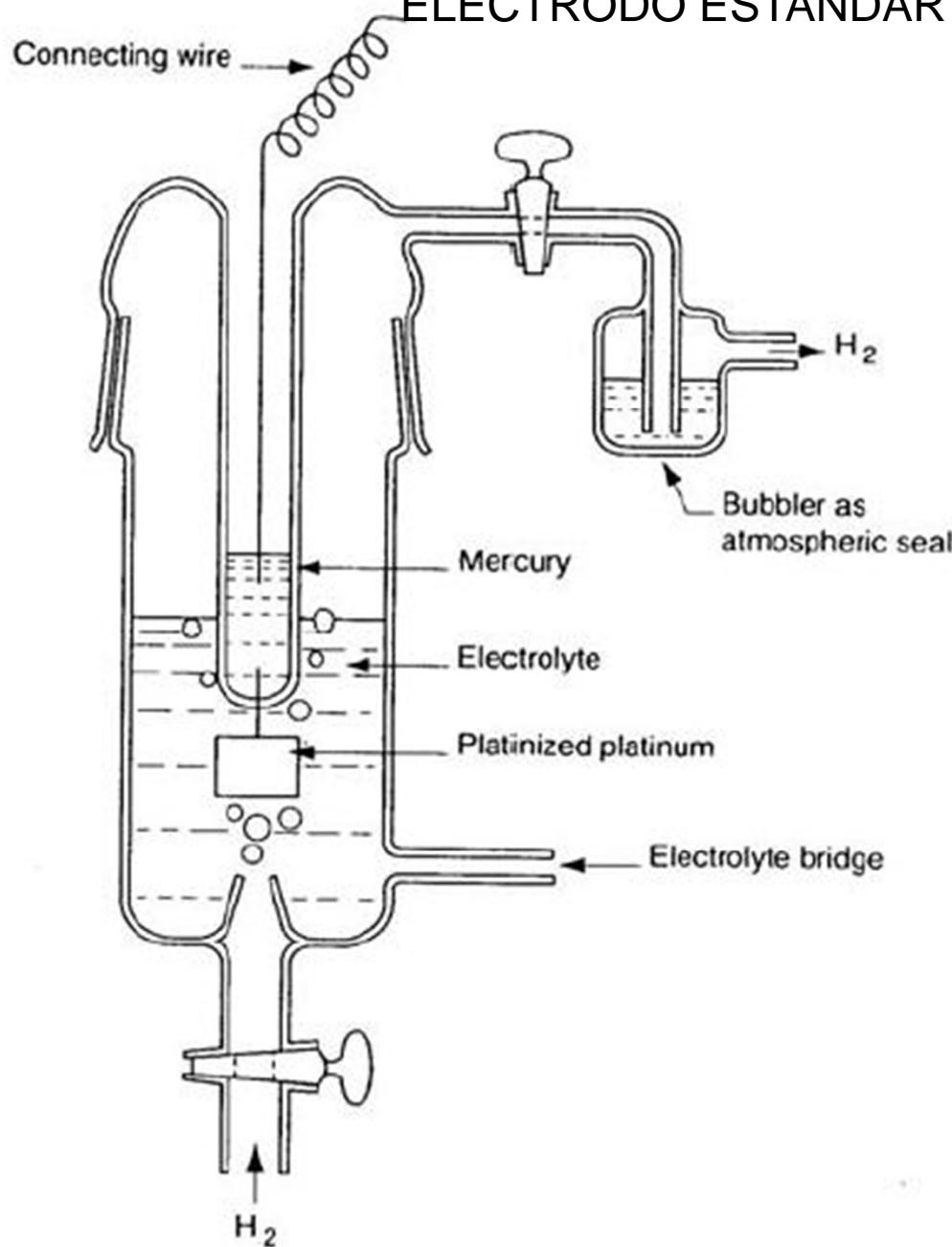


Table 1-3: Common Reference Electrodes and Their Potentials and Temperature Coefficients

Reference Electrode	Electrolyte Solution	Potential @ 25°C (V/SHE)	Temperature Co-efficient (mV/°C)	Typical Usage
Cu/CuSO ₄ (CSE)	Sat. CuSO ₄	+0.316 ⁽³⁾	0.9 ⁽⁵⁾	soils, fresh water
Ag/AgCl (SJ) (SSC)	0.6M NaCl (3 ½%)	+0.256 ⁽¹⁾	0.33 ⁽¹⁾	sea water, brackish ⁽⁴⁾
Ag/AgCl (LJ) (SSC)	Sat. KCl	+0.222 ⁽⁶⁾	1.00 ⁽²⁾	---
Ag/AgCl (LJ) (SSC)	0.1N KCl	+0.288 ⁽³⁾	0.43 ⁽³⁾	---
Sat. Calomel (SCE)	Sat. KCl	+0.241 ⁽⁶⁾	0.66 ⁽³⁾	water, laboratory
Zn (ZRE)	Saline Solution	-0.79±0.1 ⁽²⁾	---	sea water
Zn (ZRE)	Soil	-0.80±0.1 ⁽²⁾	---	buried

SJ – solid junction

LJ – liquid junction

⁽¹⁾ Peterson, M.H. and Groover, R.E., "Tests Indicate the Ag/AgCl Electrode Is Ideal Reference Cell in Sea Water", Materials Protection, Vol. 11(5), May 1972, p.19-22.

⁽²⁾ von Baeckmann, W., Schwenk, W., and Prinz, W., Handbook of Cathodic Protection, Gulf Professional Publishing, 1997, p.80.

⁽³⁾ Uhlig, H.H., Corrosion and Corrosion Control, John Wiley & Sons, 2nd Edition, 1971, p.33-36.

⁽⁴⁾ Potential becomes more electropositive with increasing resistivity. See monograph for correction in waters of varying resistivity in NACE RP0176, latest edition, or (1).

⁽⁵⁾ Ansuini, F., and Dimond, J., Factors Affecting the Accuracy of Reference Electrodes, Materials Performance, Vol. 33(11), Nov. 1994, p.14-17.

⁽⁶⁾ Jones, D., Principles and Prevention of Corrosion, MacMillan Publishing Co., 1992, p.65.

MEDICION PARA OBTENER LA SERIE ELECTROQUIMICA

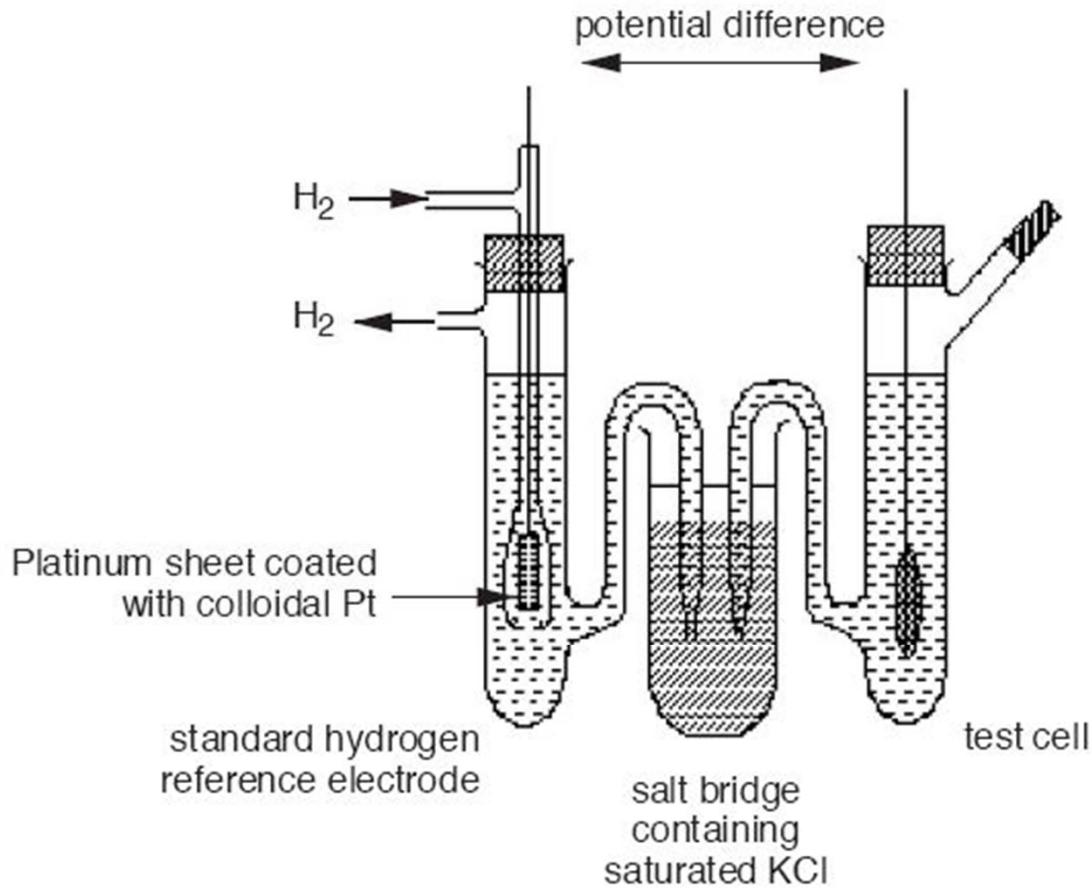


Figure 4: Cell for measurement of standard potentials

Table 1-2⁶
The Electromotive Series at 25°C (77°F)
(also called EMF Series)

Electrode	Standard Potential, E° (Referred to the SHE)	
	Volts	
K ⁺ K	-2.92	
Na ⁺ Na	-2.71	
Mg ⁺⁺ Mg	-2.34	
Al ⁺⁺⁺ Al	-1.67	
Zn ⁺⁺ Zn	-0.76	
Fe ⁺⁺ Fe	-0.44	
Pb ⁺⁺ Pb	-0.13	
Fe ⁺⁺⁺ Fe	-0.04	Less Noble Potentials
H ⁺ , H ₂ M* (SHE)	0.00	
KCl (sat.), Hg ₂ Cl ₂ Hg (SCE)	(0.245)**	More Noble Potentials
Cu ⁺⁺ Cu	+0.34	
I ⁻ , I ₂ M	+0.53	
Ag ⁺ Ag	+0.80	
Br ⁻ , Br ₂ M	+1.07	
H ⁺ , H ₂ O, O ₂ M	+1.23	
Cl ⁻ , Cl ₂ M	+1.36	
Au ⁺⁺⁺ Au	+1.50	
F ⁻ , F ₂ M	+2.87	

*M in this table denotes an inert metal electrode that acts merely as a donor or acceptor of electrons. Platinum is often used for that purpose.

**This is not a standard potential since the SCE is not a standard state electrode. The potential of the standard state calomel electrode is +0.268 volts.

Serie electromotriz

	E° (V)	
$\text{Au}^{+2} + 2\text{e}^- \rightarrow \text{Au}$	+1.498	
$\text{Pt}^{+2} + 2\text{e}^- \rightarrow \text{Pt}$	+1.2	
$\text{Pd}^{+2} + 2\text{e}^- \rightarrow \text{Pd}$	+0.987	
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.799	
$\text{Hg}^{+2} + 2\text{e}^- \rightarrow 2\text{Hg}$	+0.788	
$\text{Cu}^{+2} + 2\text{e}^- \rightarrow \text{Cu}$	+0.337	
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0,000	
$\text{Pb}^{+2} + 2\text{e}^- \rightarrow \text{Pb}$	-0.126	
$\text{Sn}^{+2} + 2\text{e}^- \rightarrow \text{Sn}$	-0.136	
$\text{Ni}^{+2} + 2\text{e}^- \rightarrow \text{Ni}$	-0.250	
$\text{Co}^{+2} + 2\text{e}^- \rightarrow \text{Co}$	-0.277	
$\text{Cd}^{+2} + 2\text{e}^- \rightarrow \text{Cd}$	-0.403	
$\text{Fe}^{+2} + 2\text{e}^- \rightarrow \text{Fe}$	-0.440	
$\text{Cr}^{+2} + 2\text{e}^- \rightarrow \text{Cr}$	-0.744	
$\text{Zn}^{+2} + 2\text{e}^- \rightarrow \text{Zn}$	-0.763	
$\text{Al}^{+3} + 3\text{e}^- \rightarrow \text{Al}$	-1.662	
$\text{Mg}^{+2} + 2\text{e}^- \rightarrow \text{Mg}$	-2.363	
$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.714	
$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.925	



Más Noble



Menos Noble

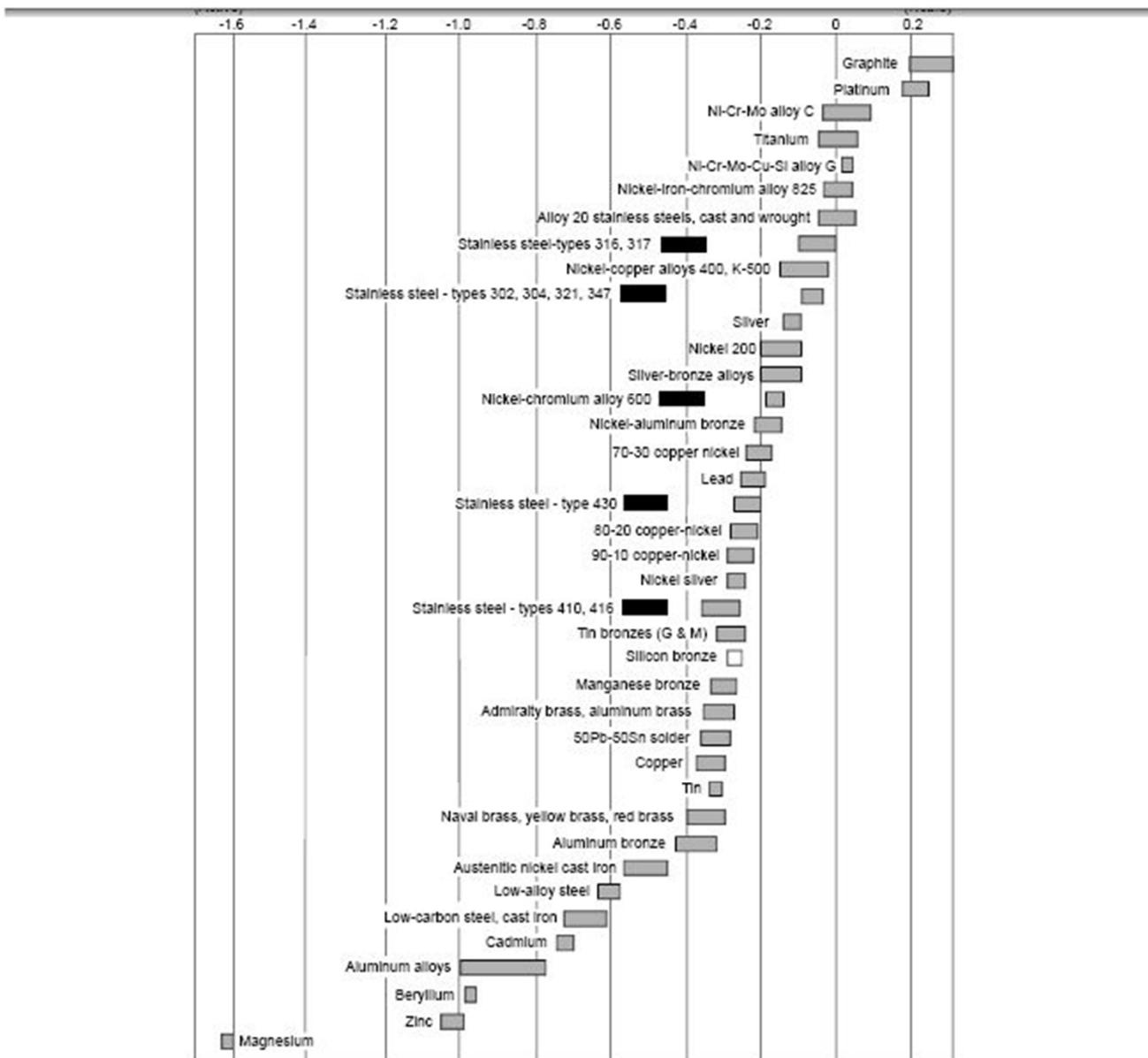


Figura 1-42: Serie Galvánica para el Agua de Mar
(Los rectángulos oscuros indican el comportamiento activo de las aleaciones activas-pasivas)

The effect of temperature on the reference potential can be expressed by the following equation:

$$E_t = E_{25^\circ\text{C}}^{\circ} + k_t(T - 25^\circ\text{C}) \quad [1-11]$$

where:

k_t = temperature coefficient

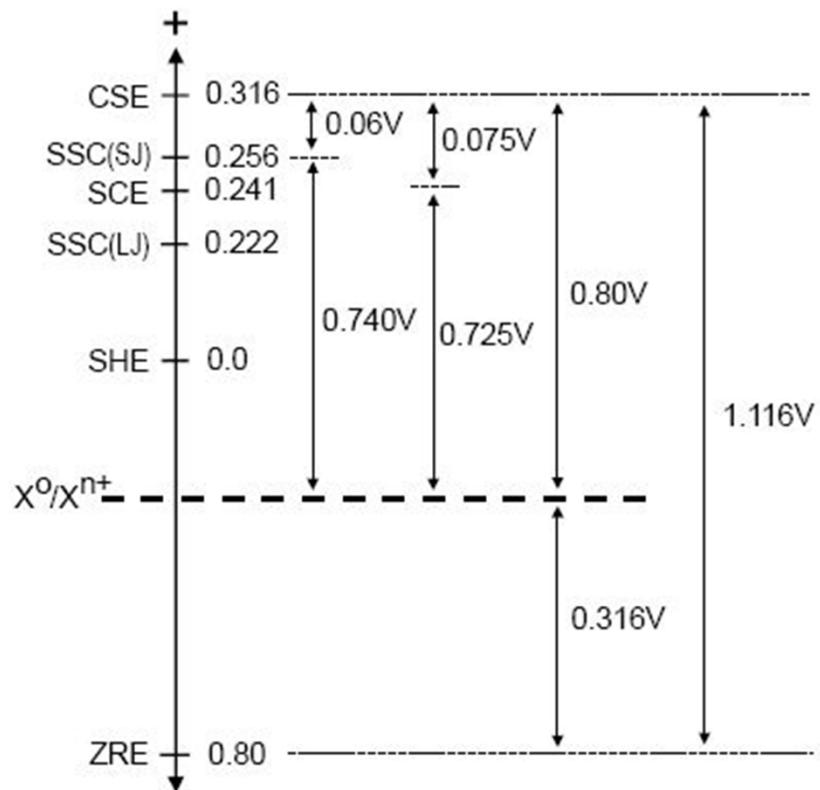
E_t = reference potential at temperature (t)

Therefore, for a copper-copper sulfate reference at 5°C , its potential would be:

$$\begin{aligned} E_{\text{CSE/SHE} @ 5^\circ\text{C}} &= +0.316 \text{ V}_{\text{SHE}} + 0.0009 \text{ V}/^\circ\text{C} (5^\circ\text{C} - 25^\circ\text{C}) \\ &= +0.316 \text{ V}_{\text{SHE}} - 0.018 \text{ V}_{\text{SHE}} \\ &= +0.298 \text{ V}_{\text{SHE}} \end{aligned}$$

or at 40°C , its potential would be:

$$\begin{aligned} E_{\text{CSE/SHE} @ 40^\circ\text{C}} &= +0.316 \text{ V}_{\text{SHE}} + 0.0009 \text{ V}/^\circ\text{C} (40^\circ\text{C} - 25^\circ\text{C}) \\ &= +0.316 \text{ V}_{\text{SHE}} + 0.014 \text{ V}_{\text{SHE}} \\ &= +0.330 \text{ V}_{\text{SHE}} \end{aligned}$$



(SJ) = only solid silver chloride (AgCl) over the silver wire.

(LJ) = a silver wire surrounded by a concentrated solution of KCl.

For a potential of $-0.800 \text{ V}_{\text{CSE}}$, the measurement of an unknown metal electrode $\text{X}^{\circ}/\text{X}^{n+}$ with respect to a CSE electrode converts to the following potentials with respect to other secondary reference electrodes:

$$\text{X}^{\circ}/\text{X}^{n+}/\text{SCE} \text{ is } -0.80 \text{ V}_{\text{CSE}} - (-0.075 \text{ V}_{\text{SCE}}) = -0.725 \text{ V}_{\text{SCE}} \quad [1-12]$$

$$\text{X}^{\circ}/\text{X}^{n+}/\text{SSC} \text{ is } -0.80 \text{ V}_{\text{CSE}} - (-0.060 \text{ V}_{\text{SSC}}) = -0.740 \text{ V}_{\text{SSC (SJ)}} \quad [1-13]$$

$$\text{X}^{\circ}/\text{X}^{n+}/\text{ZRE} \text{ is } -0.80 \text{ V}_{\text{CSE}} - (-1.116 \text{ V}_{\text{ZRE}}) = +0.316 \text{ V}_{\text{ZRE}} \quad [1-14]$$

EJEMPLOS DEL USO DEL POTENCIAL ELECTROQUIMICO

- SELECCIÓN DE MATERIALES PARA EVITAR PAR GALVANICO

Serie electroquímica

Au--> 1.70

Cu--> 0.521

0 V

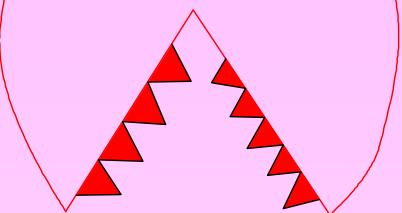
Fe--> -0.440

Mg--> -2.37

Agresividad

+ incremento de estabilidad metálica

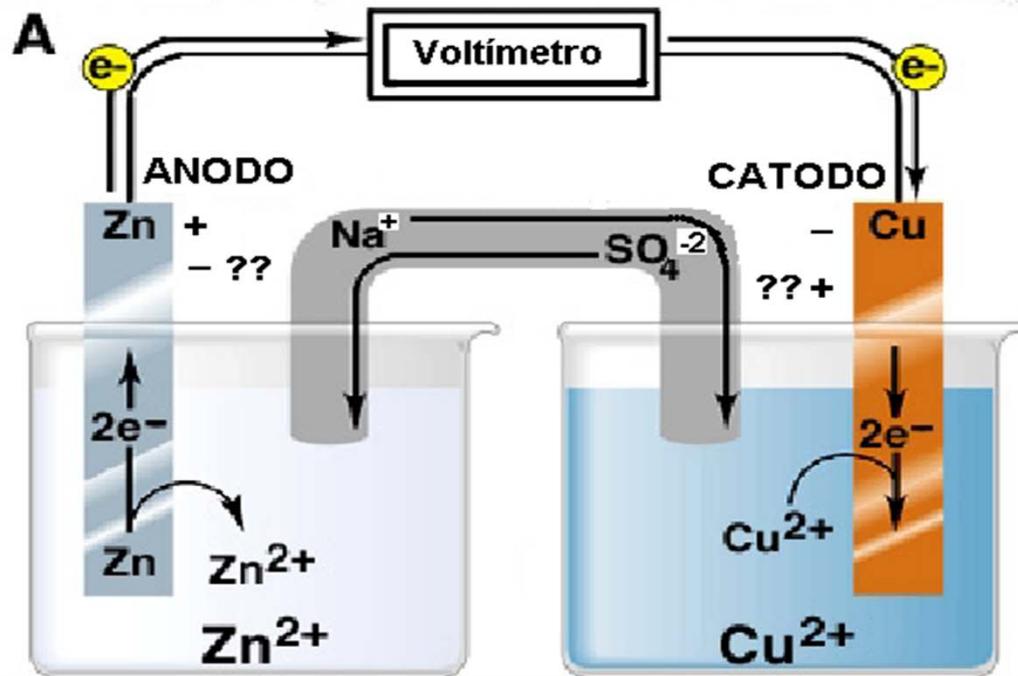
noble



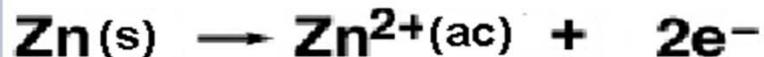
pobre

- disminución de la estabilidad metálica

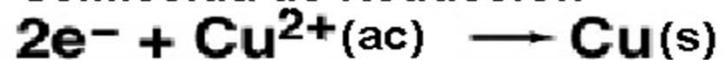
EJEMPLO DE PAR GALVANICO



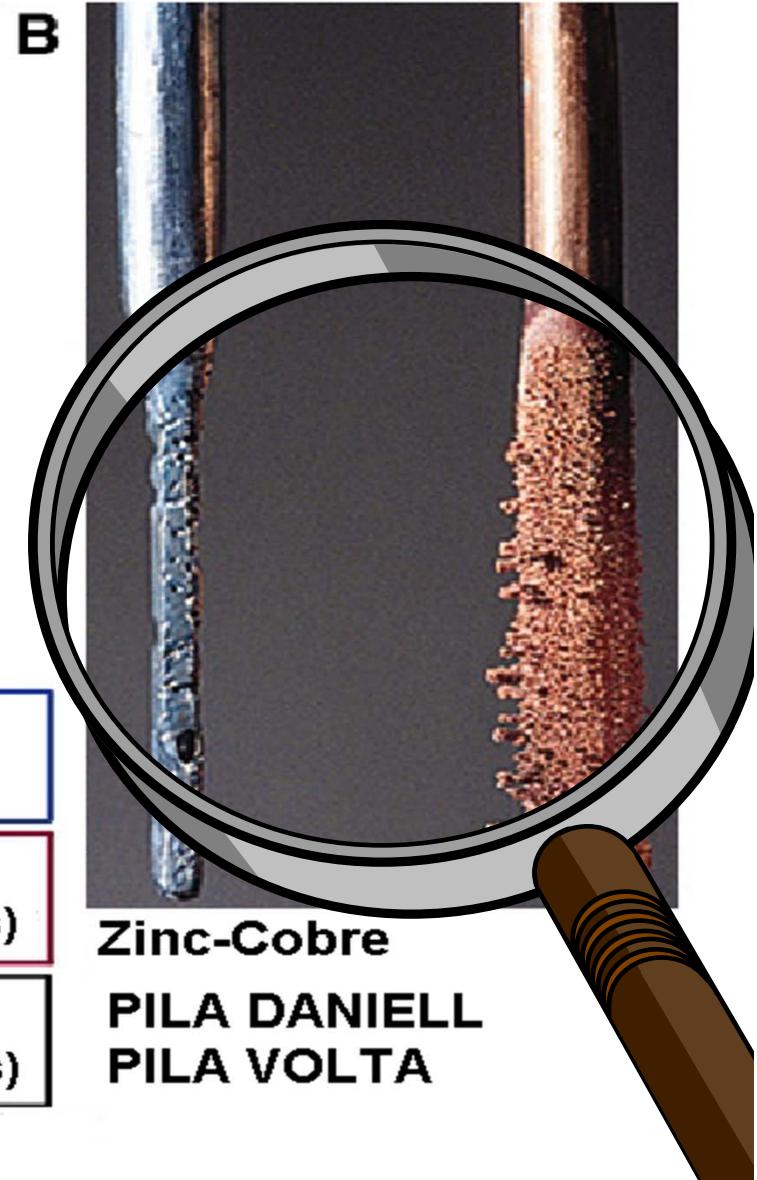
Semicelda de Oxidación



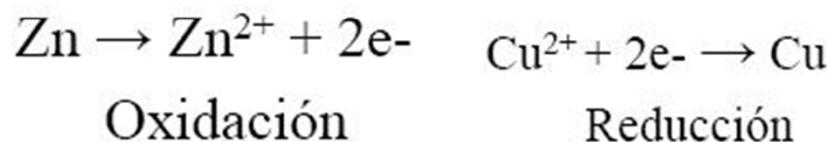
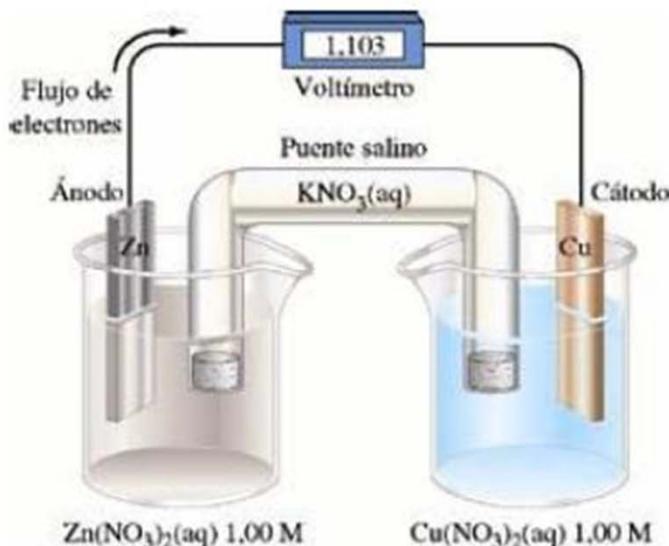
Semicelda de Reducción



Reacción Global



2.- TERMODINÁMICA DE SISTEMAS ELECTROQUÍMICOS. PILAS GALVÁNICAS.



Pila Daniell



John Frederic Daniell

(1790-1845)

Tabla : Serie galvánica práctica en agua de mar

METAL	VOLT Vs. Cu-CuSO ₄	VOLT Vs. Ag-AgCl
	Extremo activo o anódico	Extremo activo o anódico
Magnesio	-1.60 a – 1.75	-1.55 a – 1.70
Zinc	-1.10	-1.05
Aluminio	-1.05	-1.00
Acero al carbono limpio	-0.50 a – 0.80	-0.45 a – 0.75
Acero al carbono oxidado	-0.20 a – 0.50	-.015 a – 0.45
Acero ductil	- 0.50	- 0.45
Plomo	- 0.50	- 0.45
Acero en concreto	-0.20	-0.15
Cobre	-0.20	-0.15
Hierro de alto silicio	-0.20	-0.15
Carbono, grafito	+0.30	-0.35
	Extremo noble o catódico	Extremo noble o catódico

ECUACION DE NERNST
CONDICIONES NO ESTÁNDAR
VARIACION DEL POTENCIAL RESPECTO A LA CONCENTRACION



Walther Nernst (1864–1941; Nobel prize, 1920).

3.- FUERZA ELECTROMOTRIZ DE LAS PILAS. POTENCIALES DE ELECTRODOS.

$$\Delta G = -n F \Delta \varepsilon$$

- Reacción espontánea: $\Delta G < 0 \Rightarrow \Delta \varepsilon > 0$
 - Reacción no espontánea $\Delta G > 0 \Rightarrow \Delta \varepsilon < 0$
(la reacción espontánea será la inversa).
 - Equilibrio: $\Delta G = 0 \Rightarrow \Delta \varepsilon = 0$.
(no se produce energía eléctrica; la pila se ha agotado.)
- En condiciones estandar $\Delta G^\circ = -n F \Delta \varepsilon^\circ$.
(concentracion de los iones 1M)



Michael Faraday
(1791-1867)

$\Delta \varepsilon^\circ$ es una propiedad intensiva

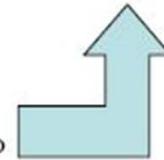
4.- DEPENDENCIA DE LA FEM CON LAS CONCENTRACIONES. ECUACION DE NERNST.

Si las condiciones no son estándar ¿Cuánto vale la fem?

$$\Delta G = \Delta G^\circ + RT \ln Q \quad [\text{Tema 5}]$$

$$\Delta G = -n F \Delta \varepsilon$$

$$\Delta G^\circ = -n F \Delta \varepsilon^\circ$$



$$-n F \Delta \varepsilon = -n F \Delta \varepsilon^\circ + RT \ln Q$$

$$\Delta \varepsilon = \Delta \varepsilon^\circ - \frac{RT}{nF} \ln Q$$

Ecuacion de Nernst

A 25°C:

$$\Delta \varepsilon = \Delta \varepsilon^\circ - \frac{0.0592}{n} \log Q$$

ECUACION DE NERNST

$$E_M = E_M^\circ + \frac{RT}{nF} \ln \frac{a^{(M^{z+})}}{a^{(M^\circ)}}$$

where:

E_M° = metal potential at standard conditions

R = gas constant (8.31 J/mol – °K)

T = absolute temperature

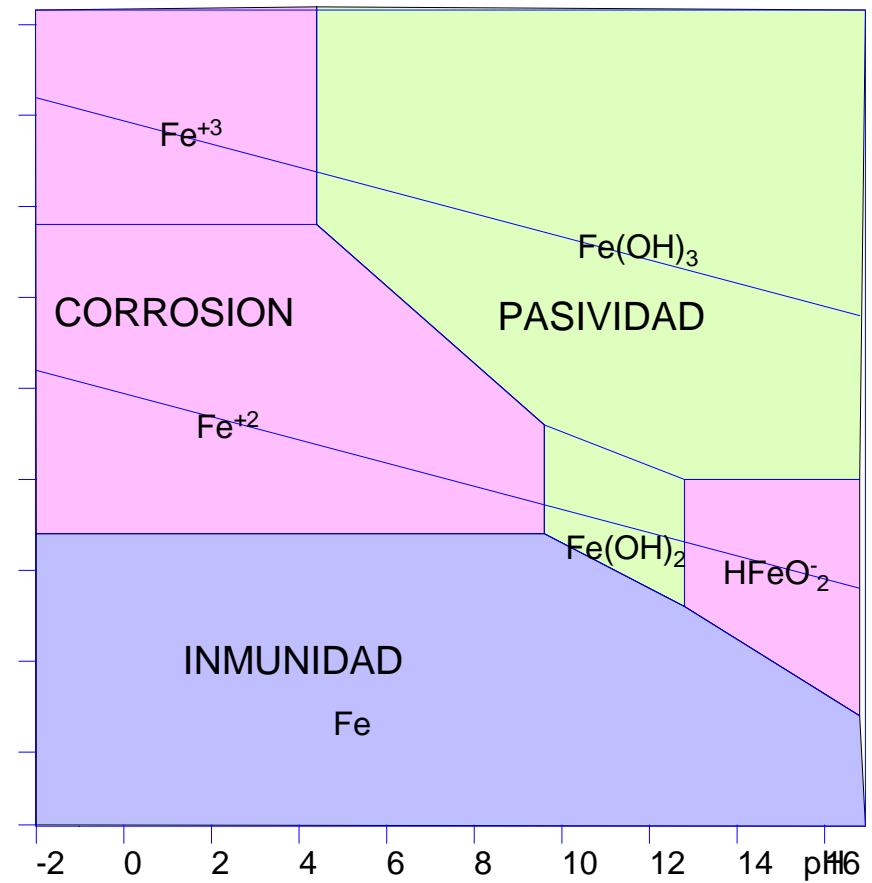
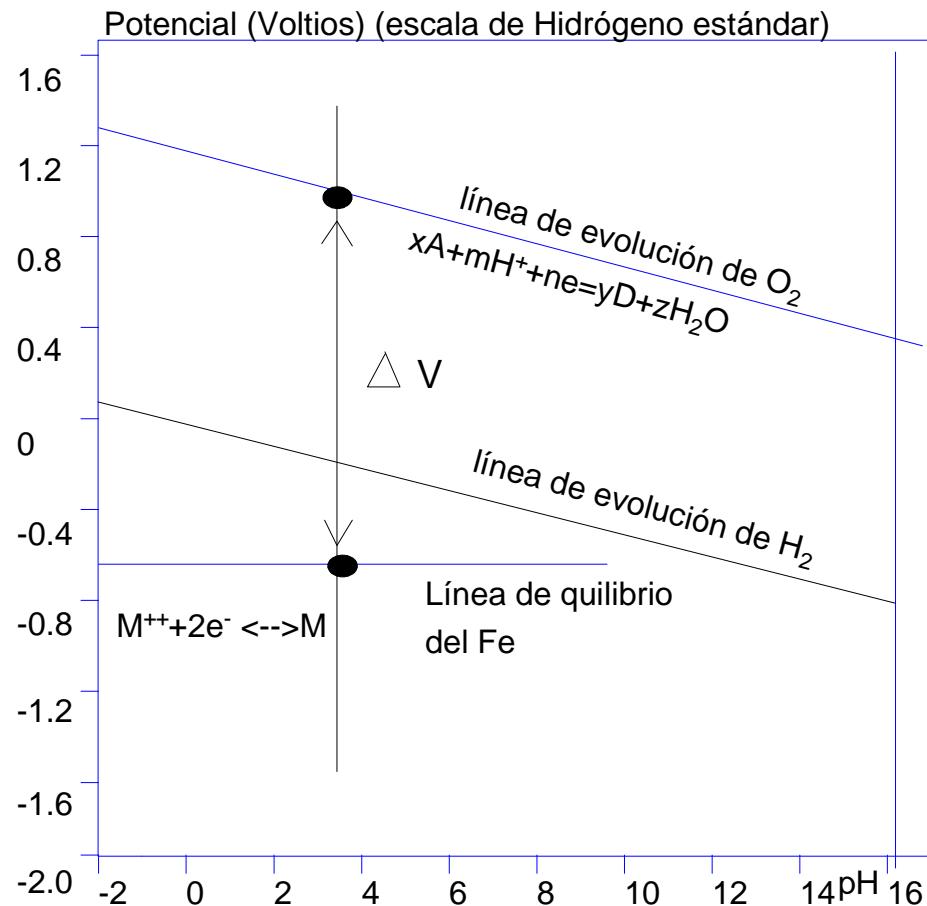
n = number of electrons transferred

F = Faraday's constant (96,500 coulomb)

$a^{(M^{z+})}$ = metal ion activity $a = \gamma m$, where γ is the activity coefficient
(always <1) and m is the molar concentration of the metal ion

$a^{(M^\circ)}$ = metal activity (assumed to be 1)

γ = activity coefficient



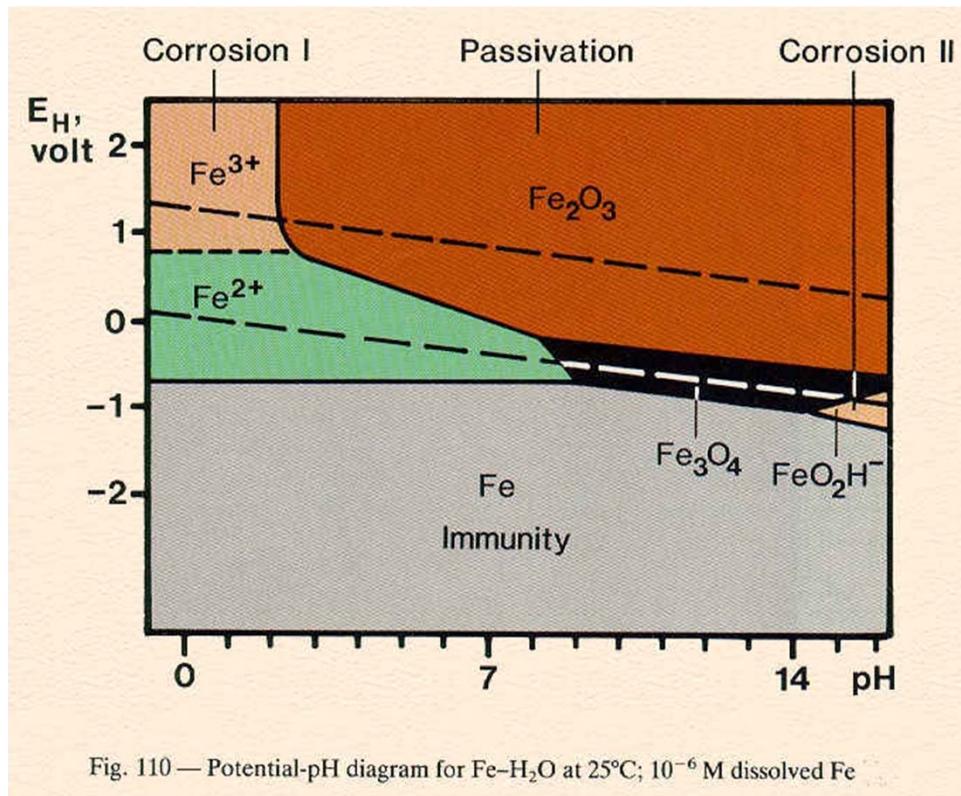


Fig. 110 — Potential-pH diagram for Fe-H₂O at 25°C; 10⁻⁶ M dissolved Fe

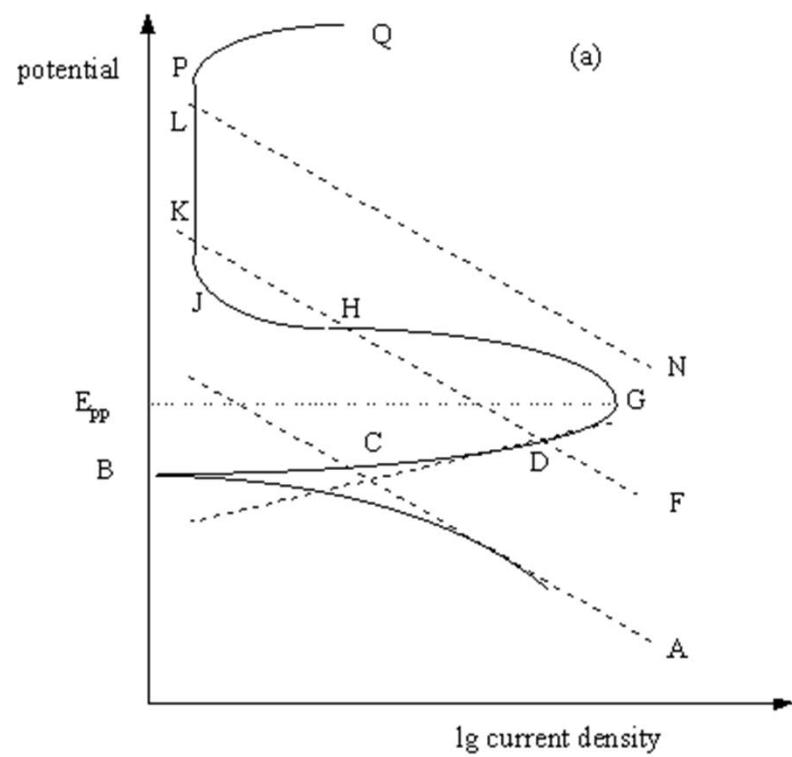


Diagrama de Pourbaix para Zinc

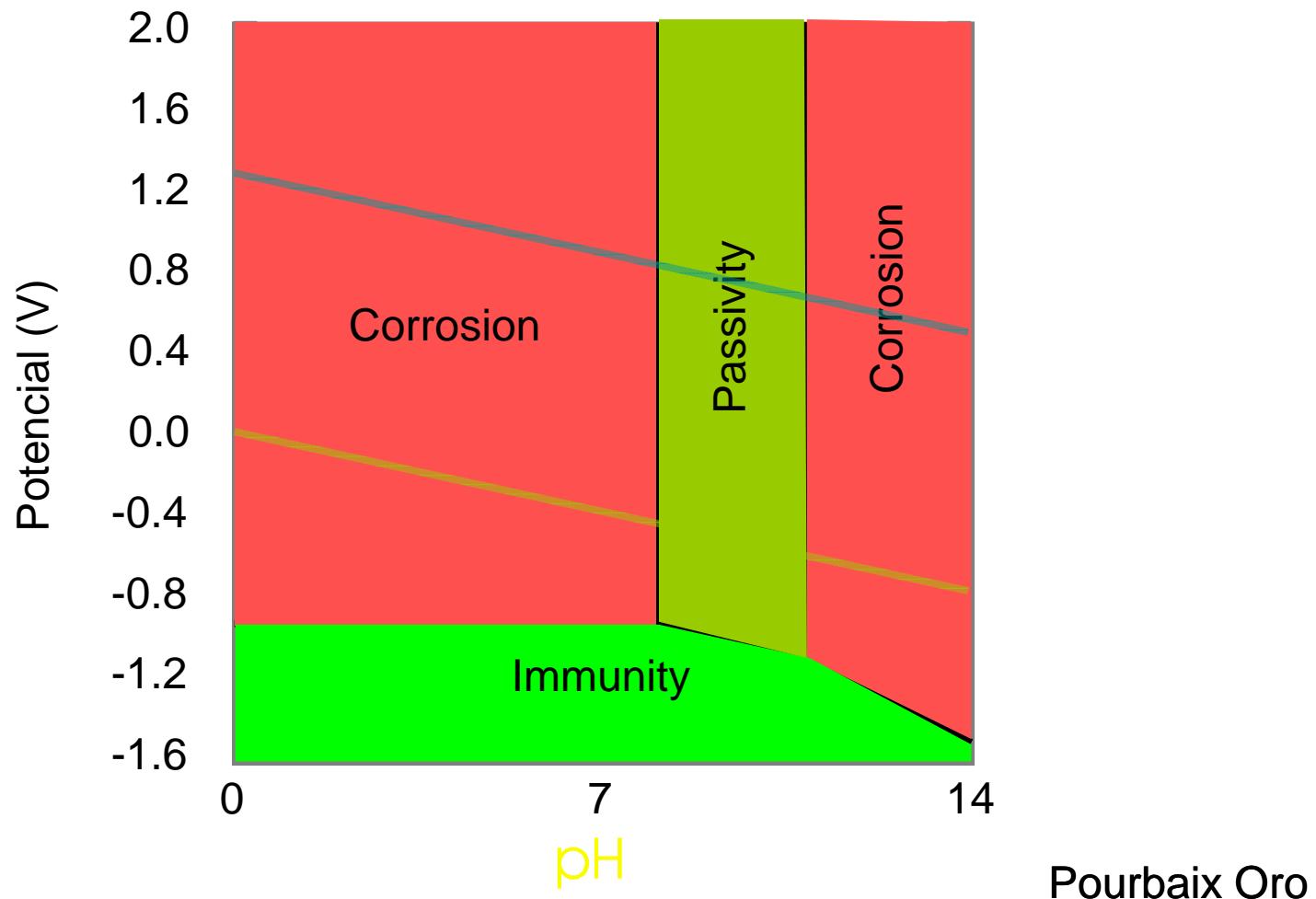


Diagrama Pourbaix para Oro

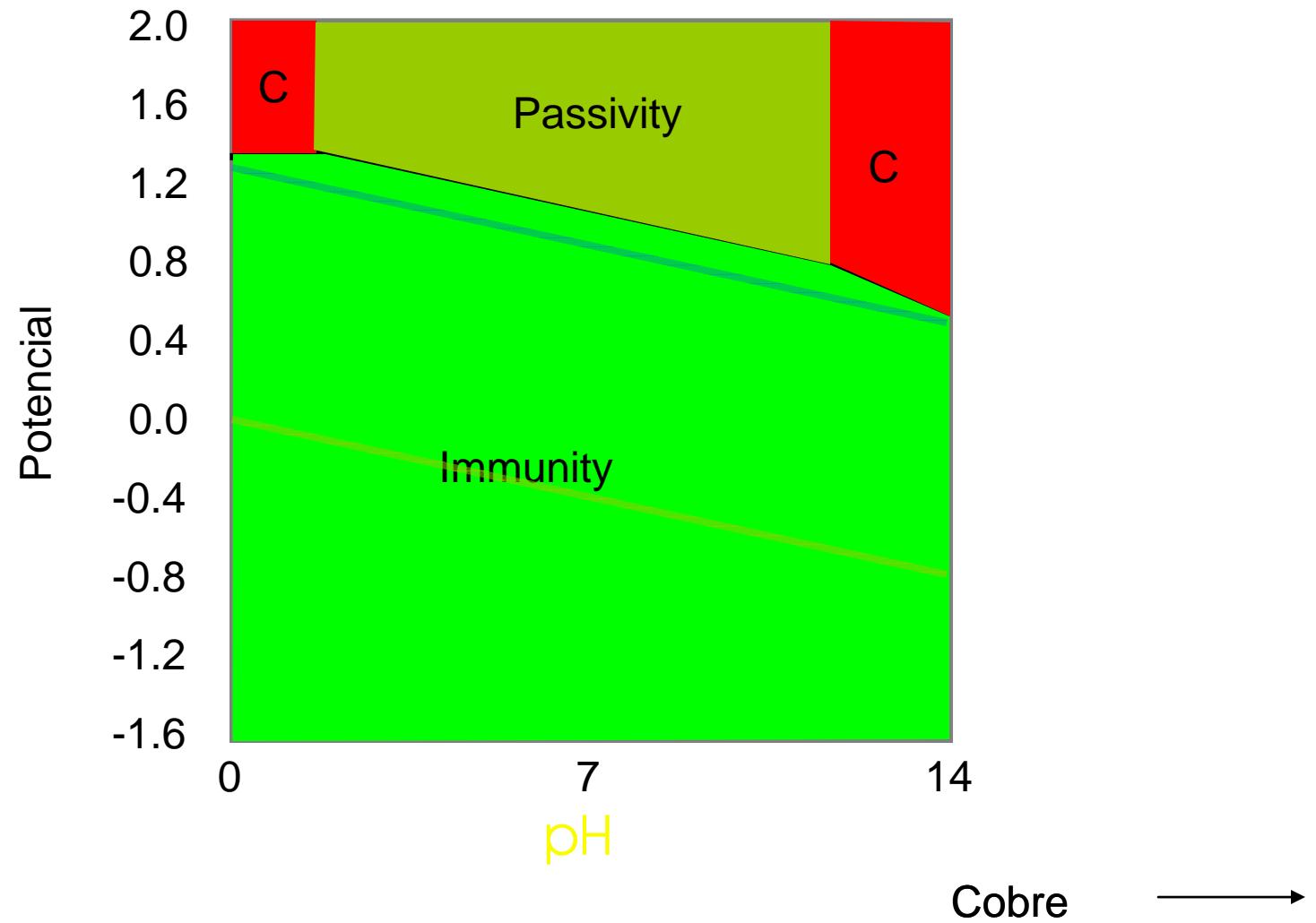
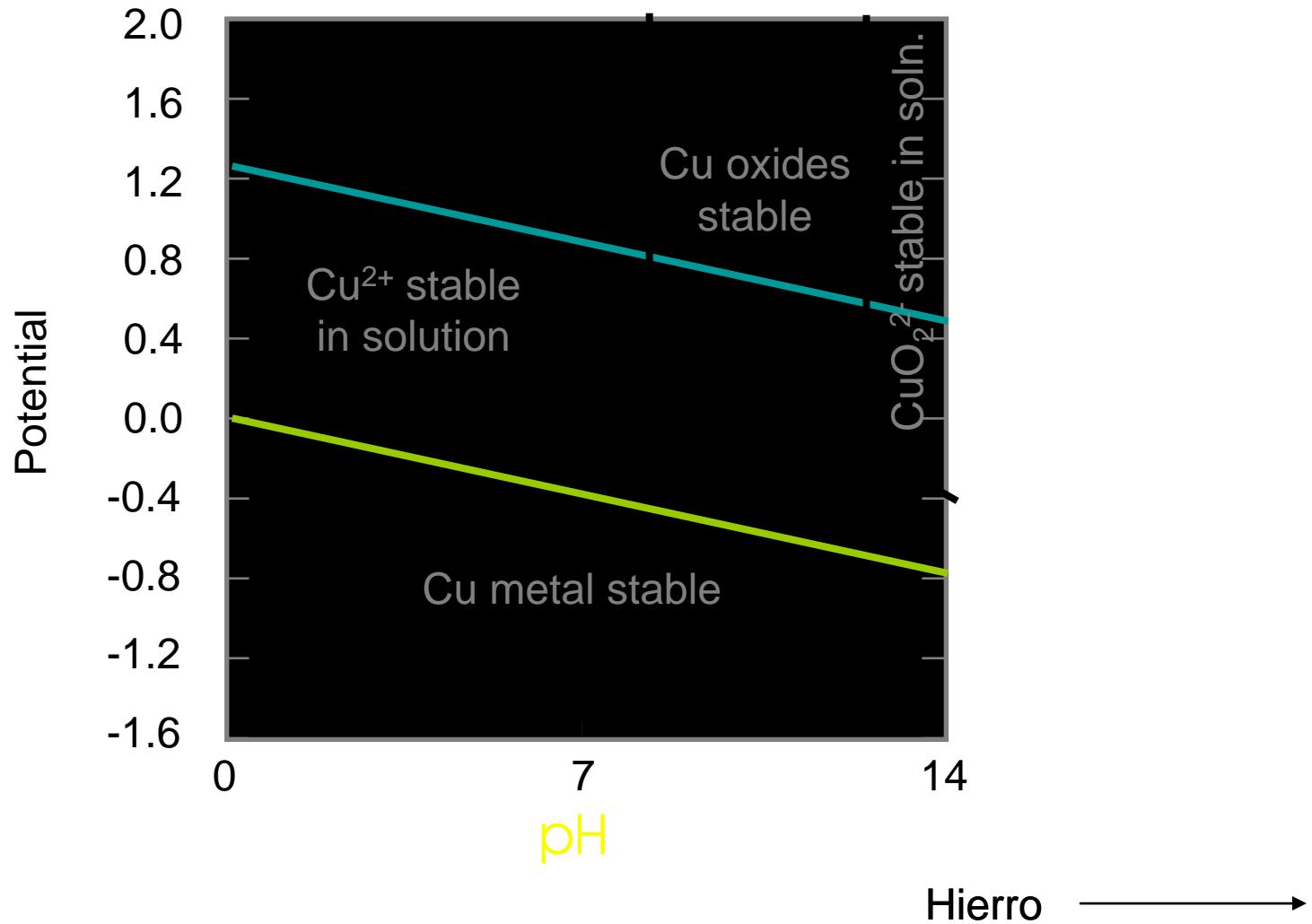
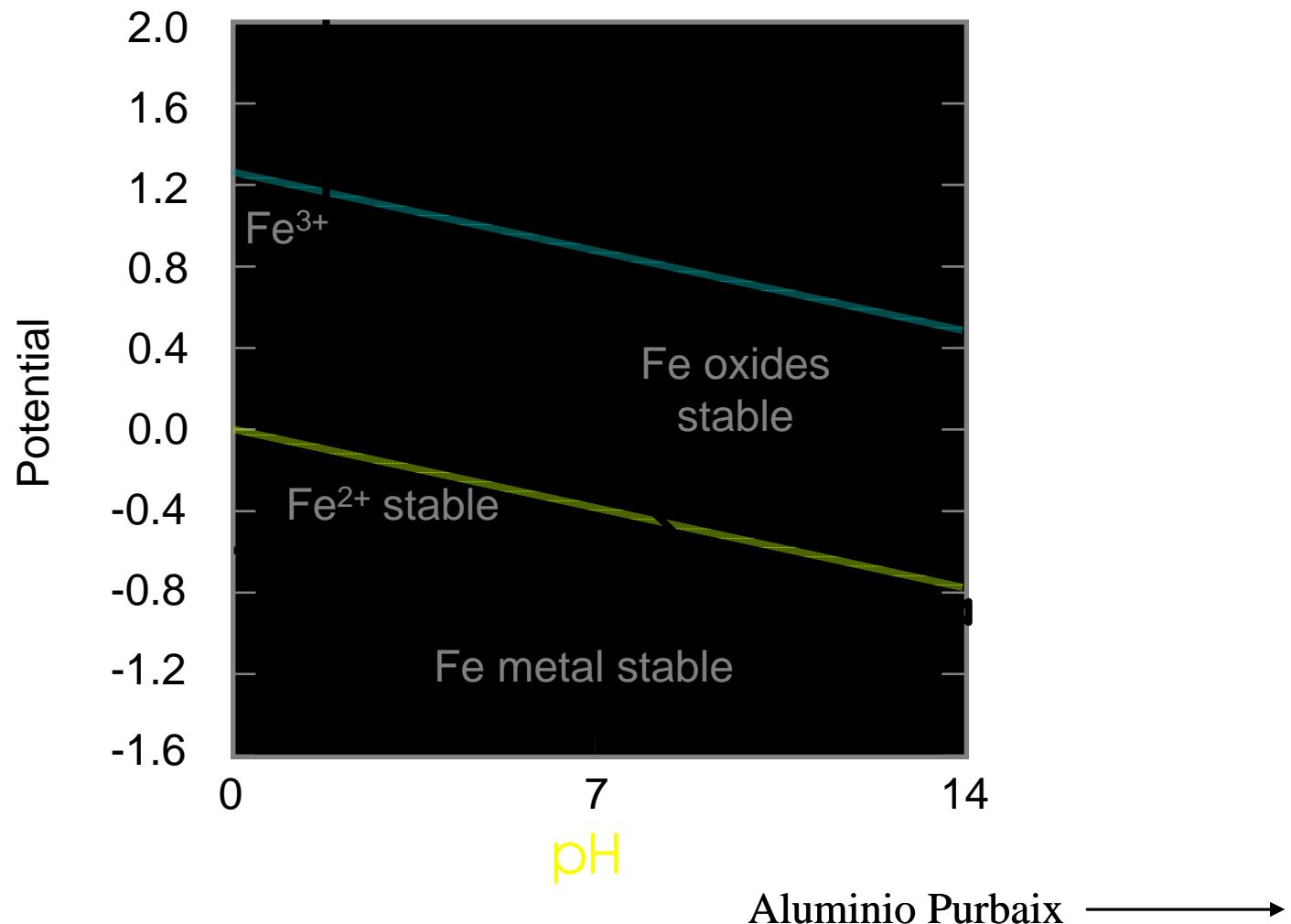


Diagrama Pourbaix para Cobre



Pourbaix Diagram for Iron



Limitaciones de los Diagramas de Pourbaix

- Se refiere a la probabilidad termodinámica que ocurrán los procesos. Nos dice que podría pasar, pero no lo que pasará.
- pueden ser obtenidos con certeza para metales puros y soluciones relativamente simples
- Es una ayuda. La información que provee debe considerarse en conjunto con evaluaciones cinéticas de los procesos eletroquímicos involucrados en corrosión

APLICACIONES DE MEDIDAS DE POTENCIAL

Corrosion Monitoring

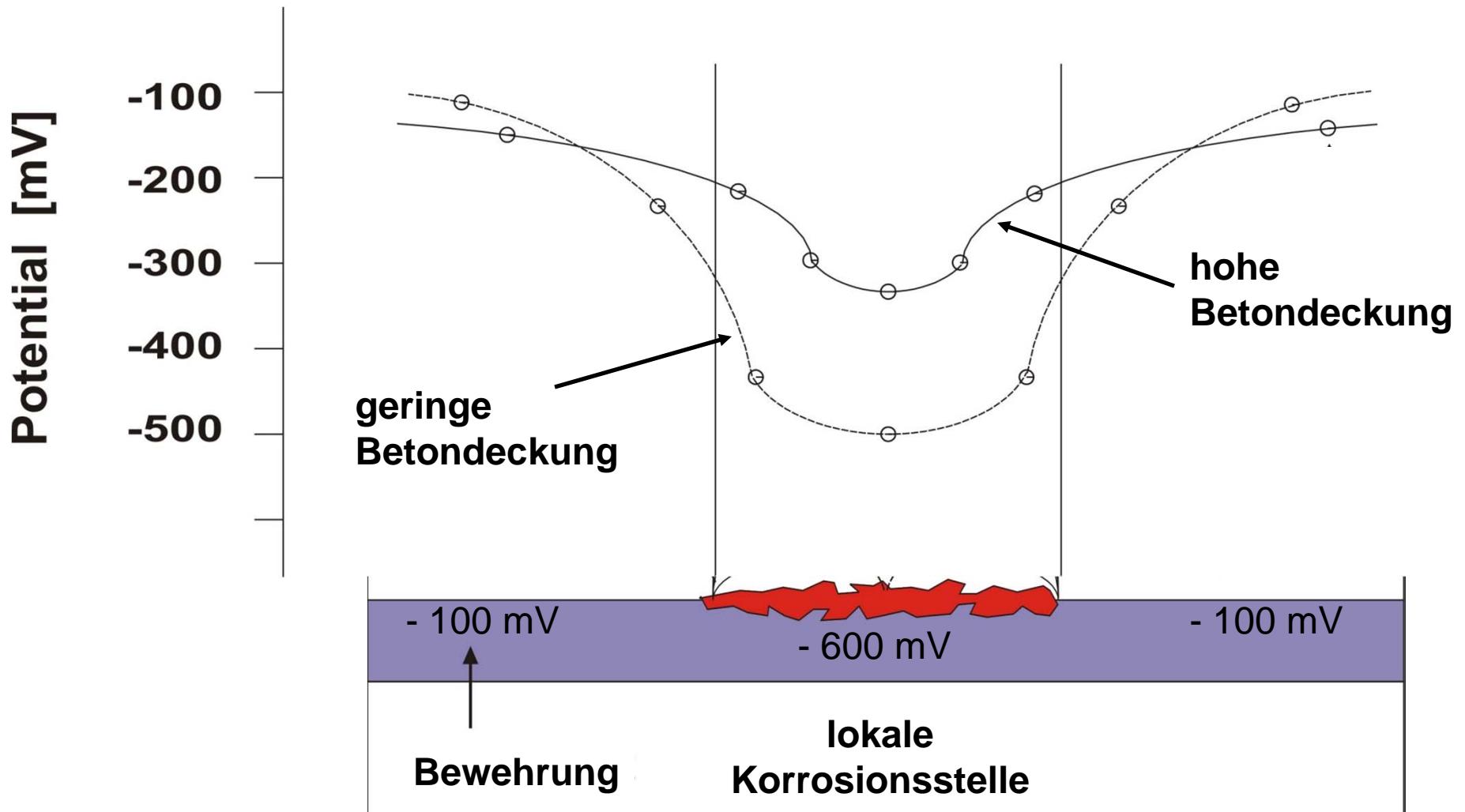
USO DE MONITOREO DE POTENCIALES



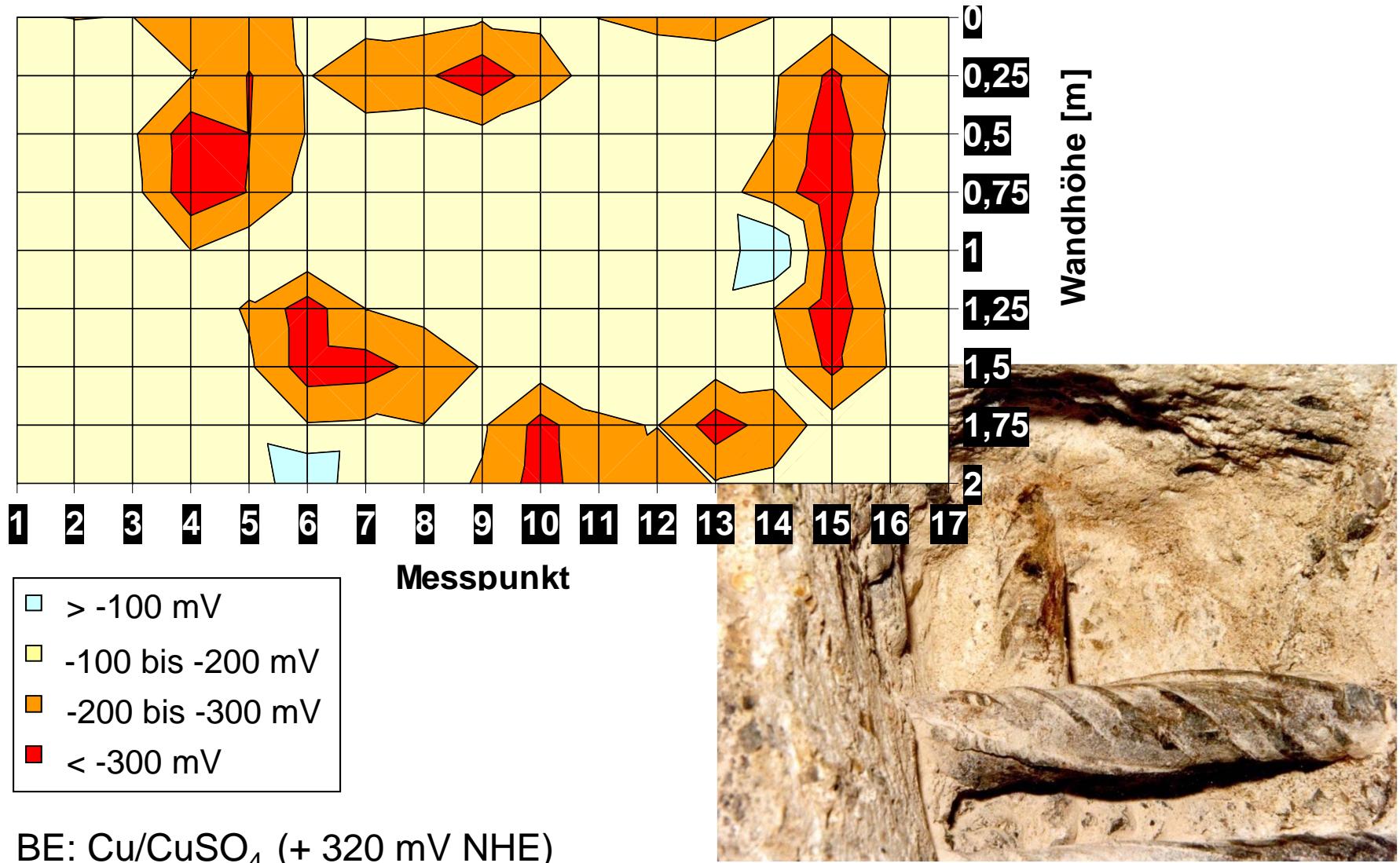
Potentialmessung, Technik



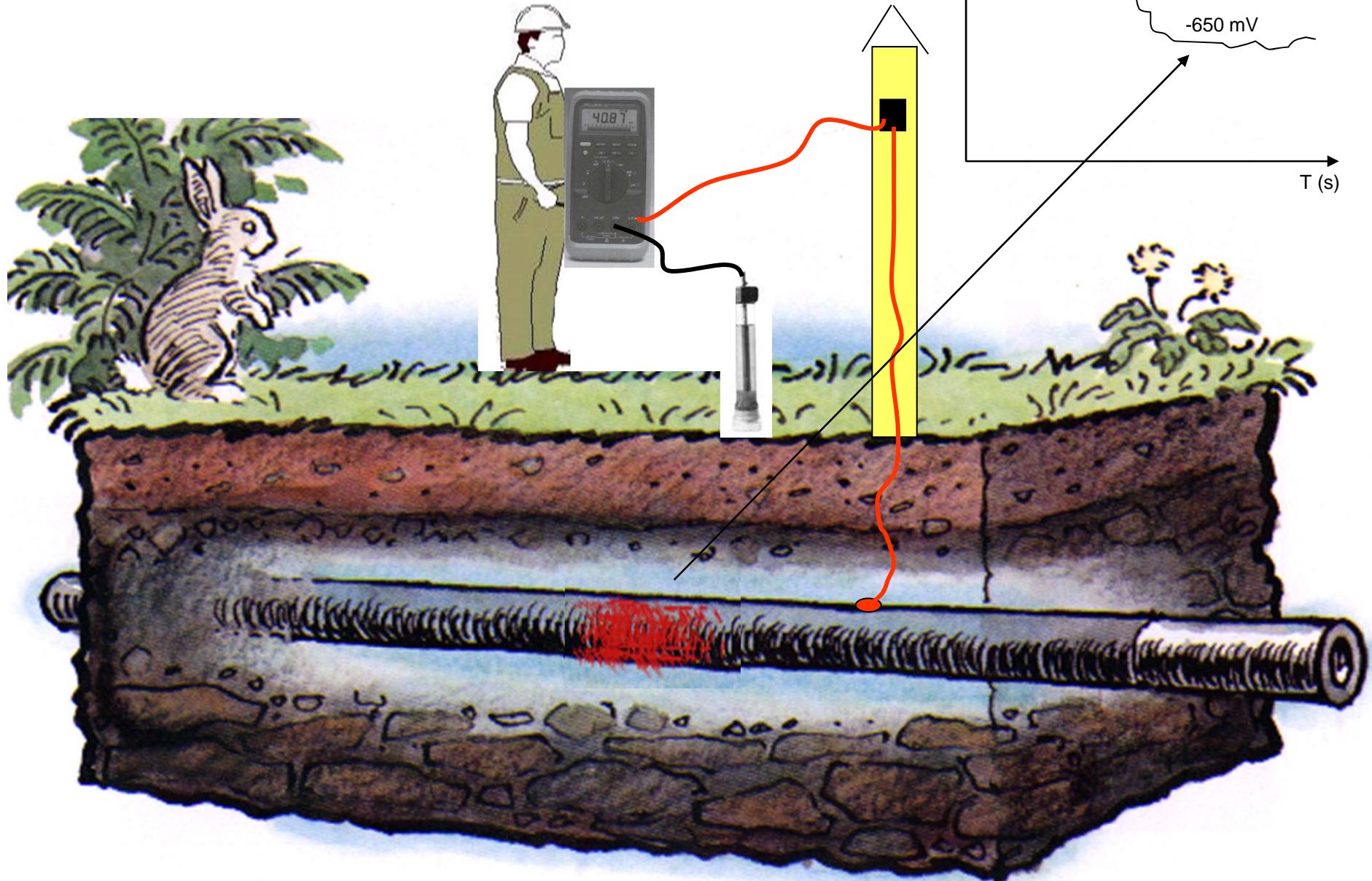
Einfluss der Betondeckung



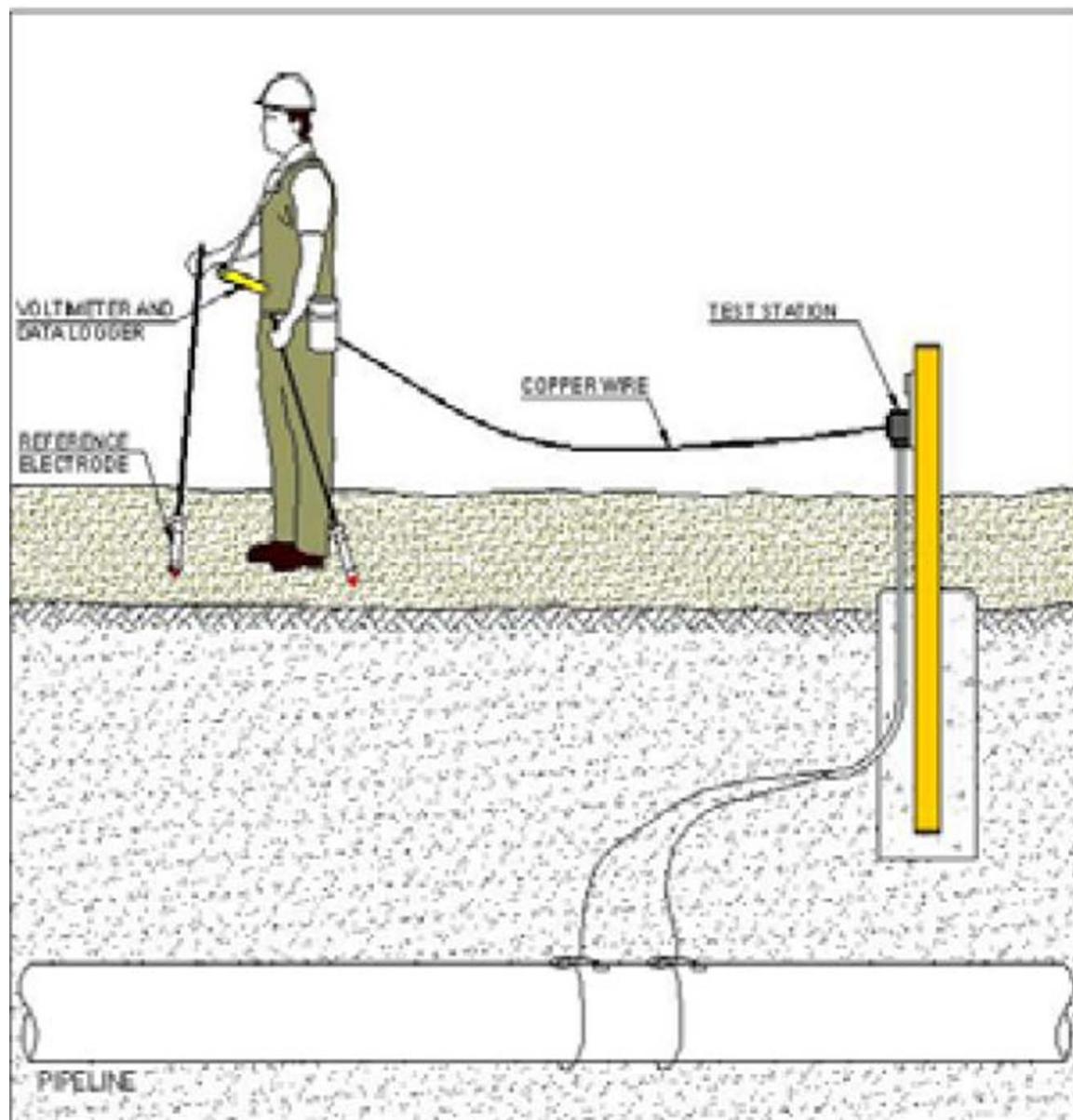
Potentialfeldmessung, Tunnel Rendsburg



MEDICION DE POTENCIALES



TECNICA CIS (CLOSE INTERVAL SURVEY)



Es una técnica que permite determinar el estado de los potenciales de un ducto paso a paso a lo largo del mismo.

Sus mediciones se realizan utilizando interruptores de corriente sincronizados en los respectivos rectificadores.

MEDIDAS DISCRETA DE POTENCIALES



POTENCIALES PC

