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2016

PRINCIPLES OF CORROSION

ELECTROCHEMICAL AND THERMODYNAMIC PRINCIPLES OF CORROSION

Content

1. Definition of corrosion.
2. Cost of corrosion.
3. Corrosion Cost Type
4. Classification of corrosion.
5. Expressions for corrosion rate.
6. Electrochemical principles of corrosion.
7. Thermodynamic principles of corrosion.

1. Definition of corrosion (1/3)

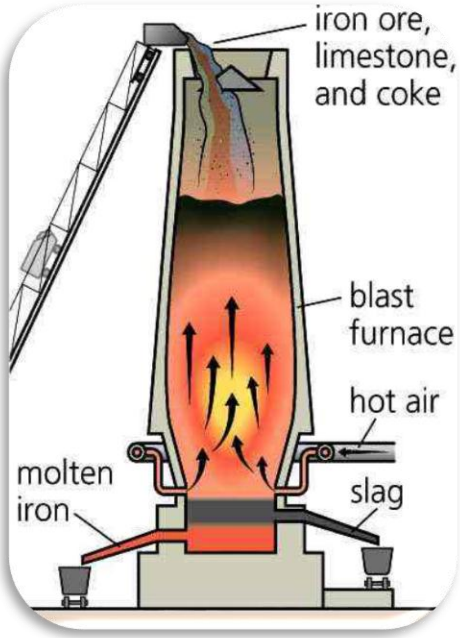
The loss of useful properties of material as a result of chemical or electrochemical reaction with its environment

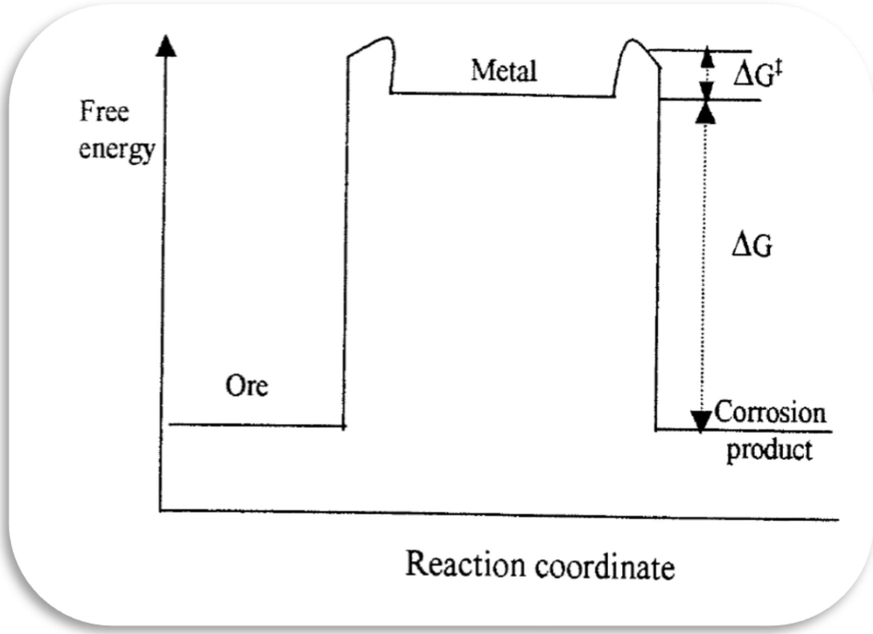
1. Definition of corrosion (2/3)

The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals.

1. Definition of corrosion (3/3)

A Thermodynamic energy profile for metals and their compounds.





2. Cost of Corrosion (1/4)

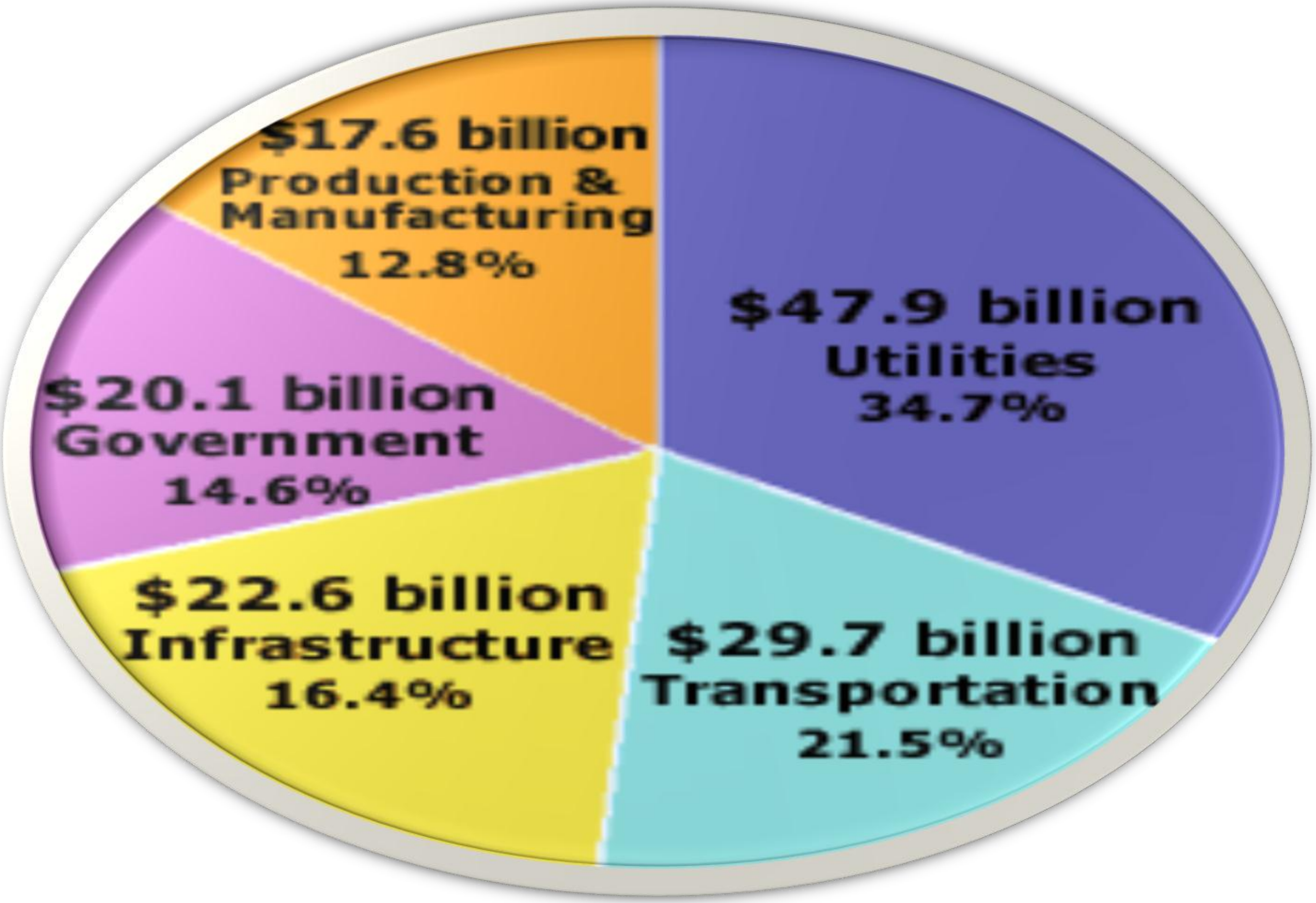
CC Technologies & NACE International

study shows the cost of corrosion in the U.S.A.

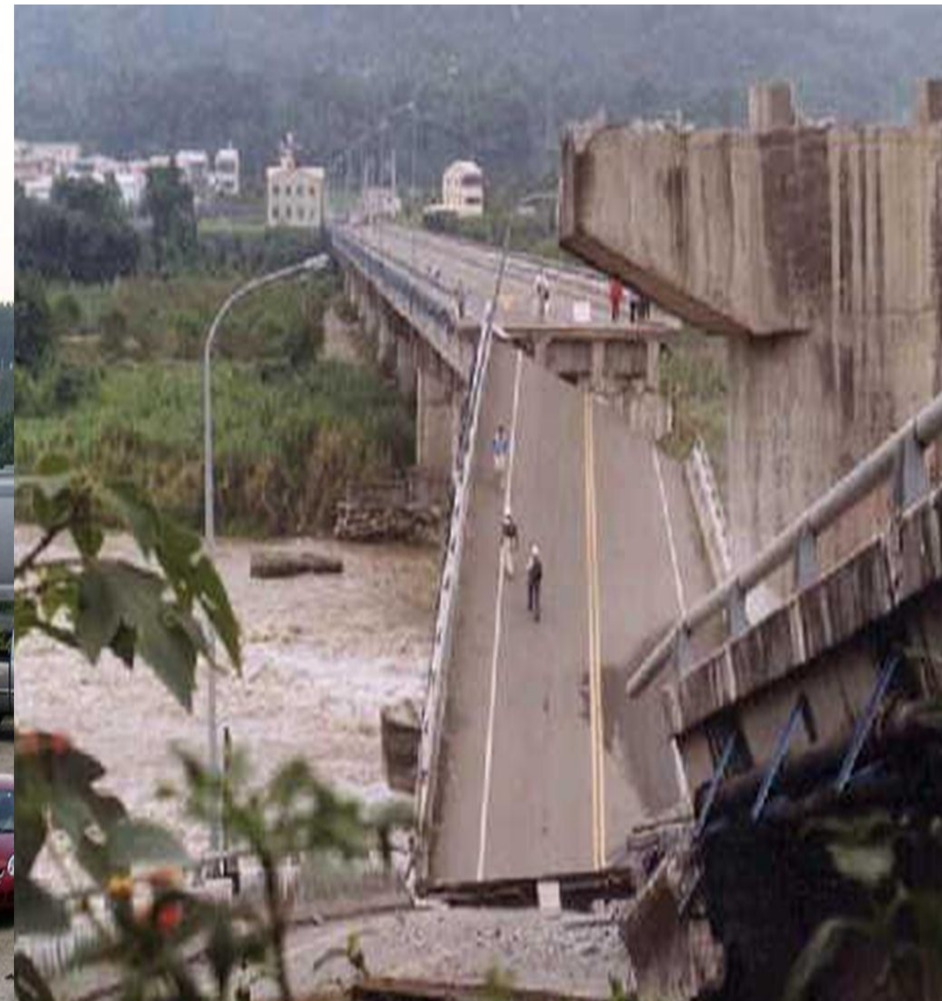
is $276 billion / year

Project funded by FHWA.

2. Cost of Corrosion (2/4)



Significance of Corrosion on Infrastructure



Utilities

2. Cost of Corrosion (3/4)

At US $2.2 trillion, the annual cost of corrosion Worldwide is over 3% of the world's GDP.

Yet, governments and industries pay little attention to corrosion except in high-risk areas like aircraft and pipelines.

Now is the time for corrosion professionals to Join together to educate industry, governments, and the public.

2. Cost of Corrosion (4/4)

Now is the time to work together to harmonize Standards and practices around the world and to communicate and share corrosion mitigation technologies.

Now is the time to make a major impact to protect The environment, preserve resources, and protect our fellow human beings

3. Corrosion Cost Type (1/3)

Cost of corrosion

- Direct losses
- Indirect losses

3. Corrosion Cost Type (2/3)

Direct losses

1. Inability to use otherwise desirable materials.
2. Over-design to allow for corrosion.
3. The cost of repair or replacement of the corroded component.
4. Cost of anti-corrosive painting or other protection methods.

3. Corrosion Cost Type (3/3)

Indirect losses

1. Contamination of the product.
2. Loss of valuable product from a container that corroded through.
3. Damage of equipment adjacent to that in which corrosion failure occurs.
4. Loss of product.
5. Safety, e.g., sudden failure of equipment may cause fire, explosion or release of toxic product.

4. Classification of Corrosion

1-Electrochemical corrosion

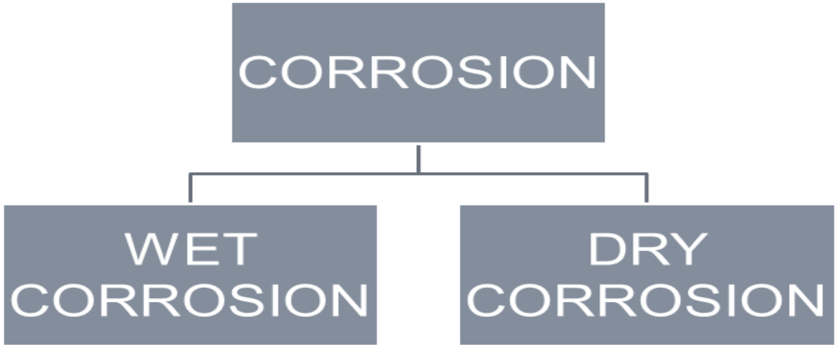
- Separable anode/cathode type.
- Interfacial anode/cathode type.
- Inseparable anode/cathode type.

2-Chemical Corrosion

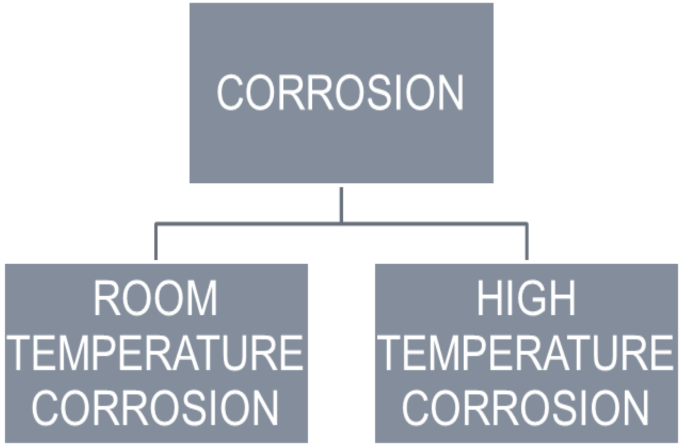
- Which involves direct chemical reaction of metal with its environment.

4.1. Classification of Corrosion

- Corrosion may be classified in different ways

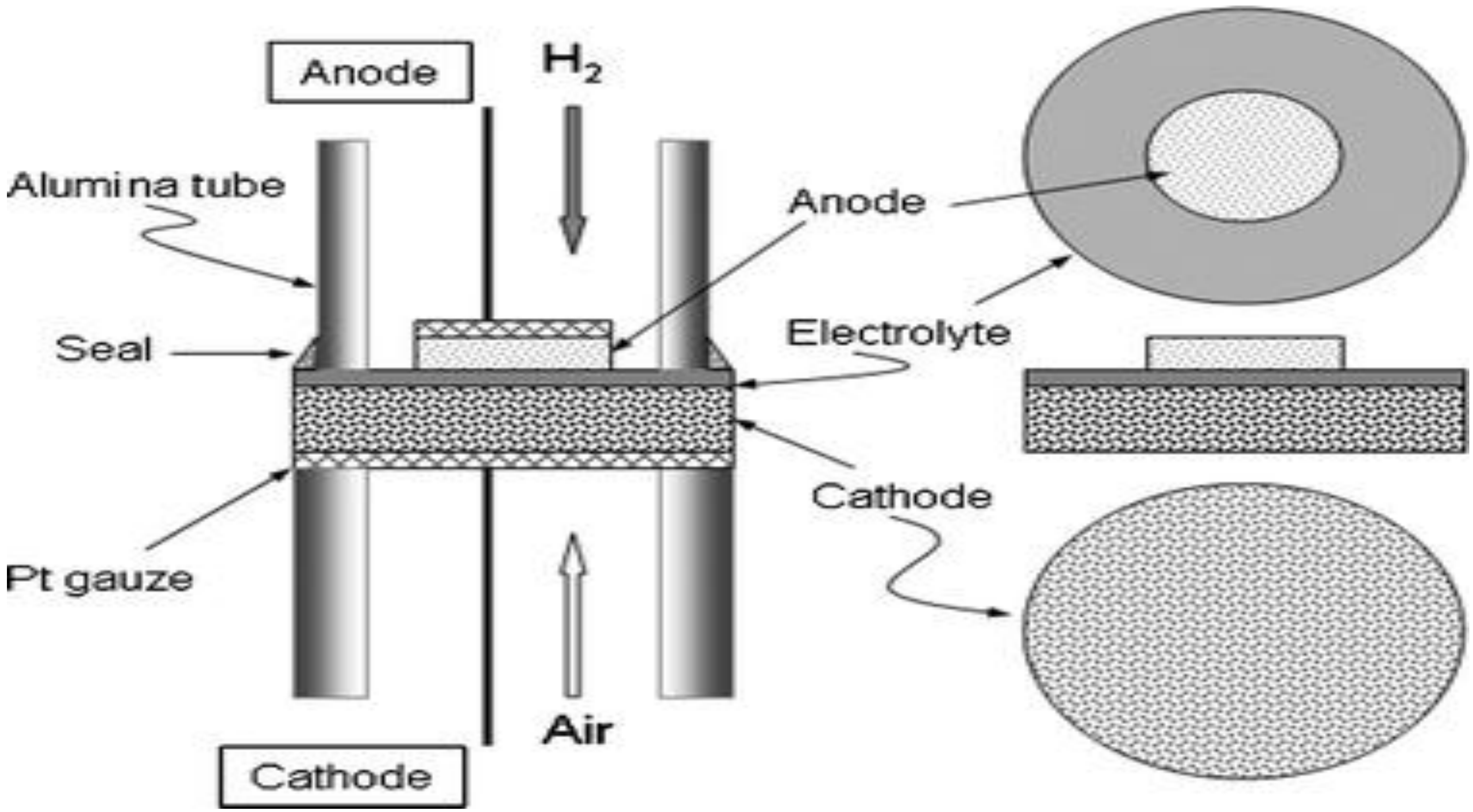


- Wet / Aqueous corrosion & Dry Corrosion



- Room Temperature/ High Temperature Corrosion

Separable anode/cathode type.



Interfacial anode/cathode type.

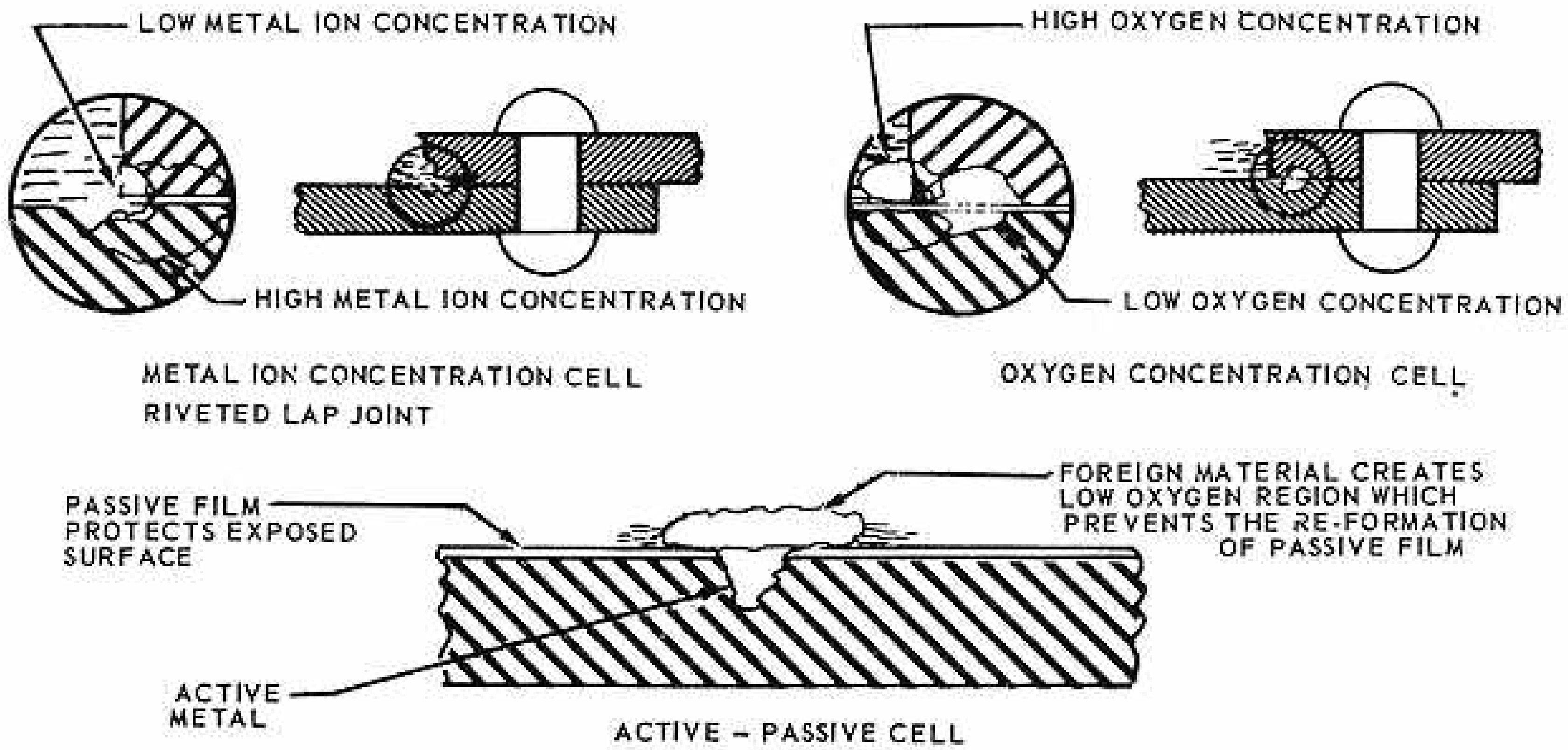
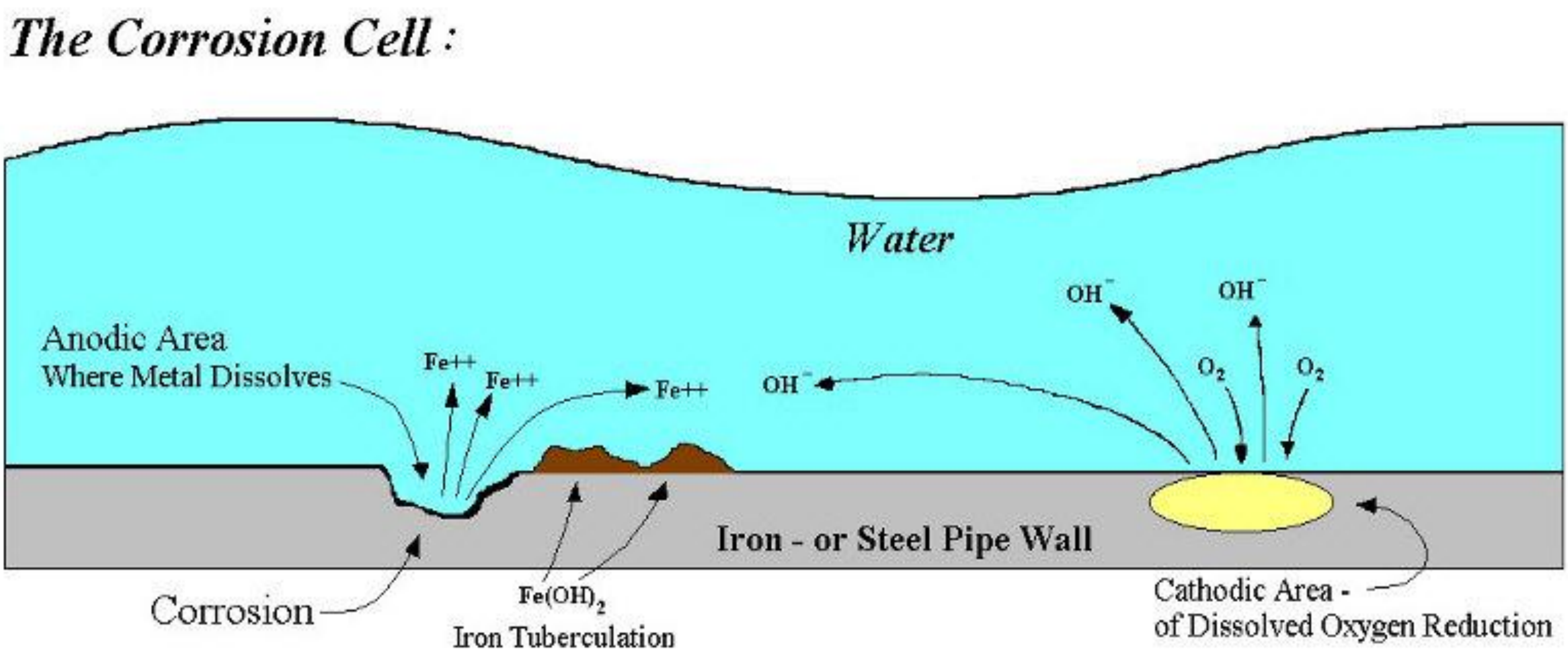


FIGURE 2-6. CONCENTRATION CELL CORROSION

Inseparable anode/cathode type.



5. Expressions for corrosion rate (1/2)

- The calculator uses the following equation to estimate the corrosion rate:

$$R = \frac{K(m_b - m_a)}{A(\Delta t)\rho}$$

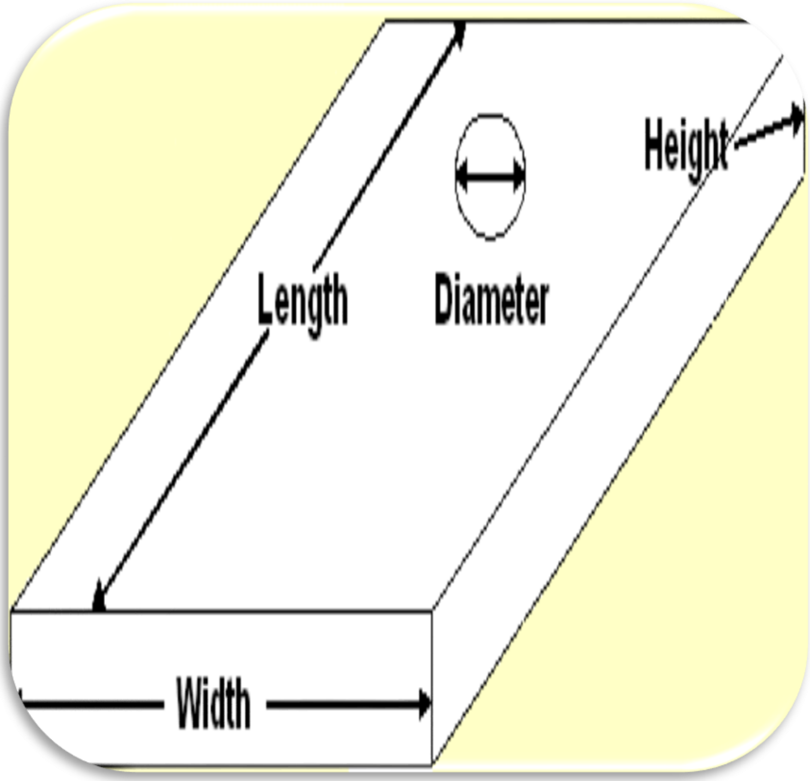
where:

R = penetration rate (mil/y or mm/y)
m_b = mass before exposure (gram)
m_a = mass after exposure (gram)
A = total exposed surface area (in^2 or mm^2)
Δt = total exposure time (hours)
ρ = density (g/cm^3) The units are those most commonly used and are those

5. Expressions for corrosion rate (2/2)

Assumed for this calculator. The information required to use the calculator for this type of corrosion coupon is

- Length (inch or millimeter)
- Width (inch or millimeter)
- Height (inch or millimeter)
- Diameter of bolt hole through coupon (inch or millimeter)
- Diameter of electrical isolation washers (inch or millimeter)
- Mass before exposure (gram)
- Mass after exposure (gram)
- Exposure time (hour)
- Density (gram/cm^3)



CORROSION PRINCIPLES

Thermodynamic Principles

Metallurgical Principles

CORROSION PRINCIPLES

Physical and chemical Principles

Electrochemical Principles

CORROSION PRINCIPLES

ELECTROCHEMICAL AND THERMODYNAMIC PRINCIPLES OF CORROSION

Basic Corrosion Theory

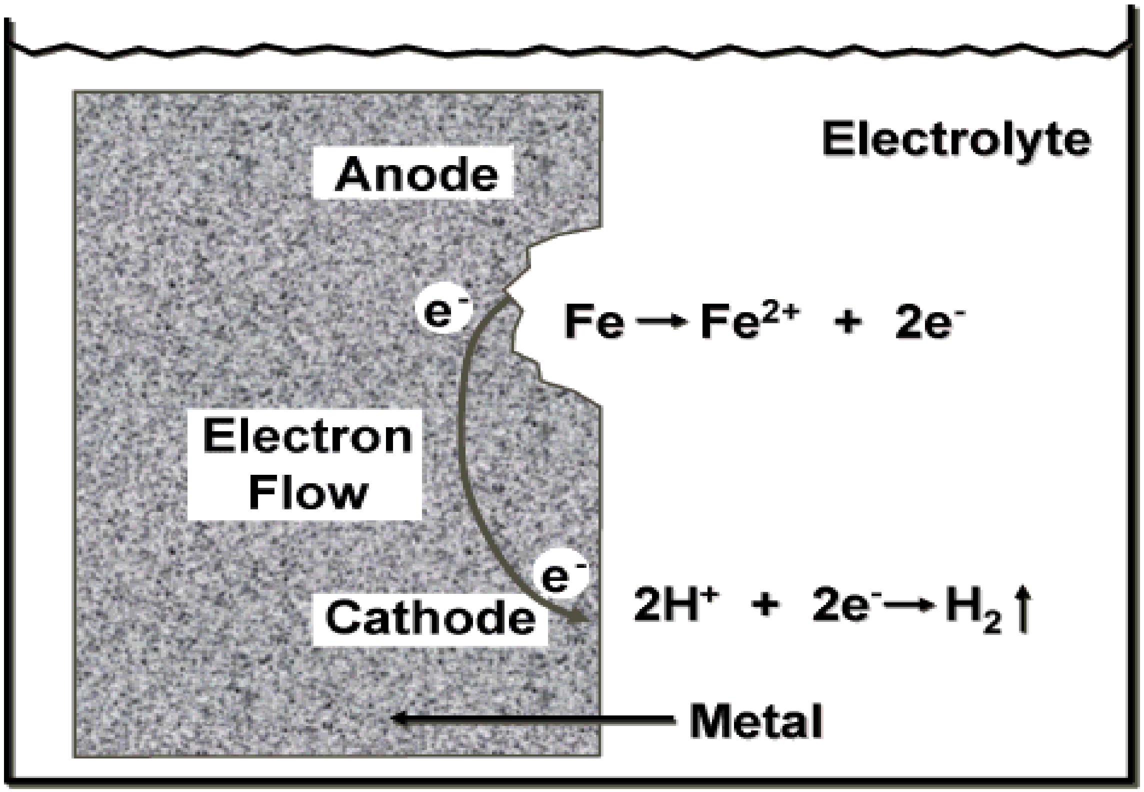
Corrosion is an electrochemical reaction composed of two half cell reactions, an anodic reaction and a cathodic reaction. The anodic reaction releases electrons, while the cathodic reaction consumes electrons . There are three common cathodic, reactions, oxygen reduction (fast), hydrogen evolution from neutral water (slow), and hydrogen evolution from acid (fast).

The Corrosion Cell (1/3)

- **Anodic reaction:**
  $M \rightarrow M^{n+} + ne^-$
- ***M stands for a metal and n stands for the number of electrons that an atom of the metal will easily release.***
- i.e. for iron and steel: $Fe \rightarrow Fe^{2+} + 2e^-$
- **Cathodic reactions:**
- $O_2 + 4\,H^+ + 4e^- \rightarrow 2H_2O$ (oxygen reduction in acidic solution)
  $1/2\,O_2 + H_2O + 2e^- \rightarrow 2\,OH^-$ (oxygen reduction in neutral or basic solution)
  $2\,H^+ + 2e^- \rightarrow H_2$ (hydrogen evolution from acidic solution)
  $2\,H_2O + 2e^- \rightarrow H_2 + 2\,OH^-$ (hydrogen evolution from neutral water)
- Each half-cell reaction has an electrical potential, known as the half-cell electrode potential. The anodic reaction potential, E_a , plus the cathodic reaction potential, E_c , adds up to E, the cell potential. If the overall cell potential is positive, the reaction will proceed spontaneously.

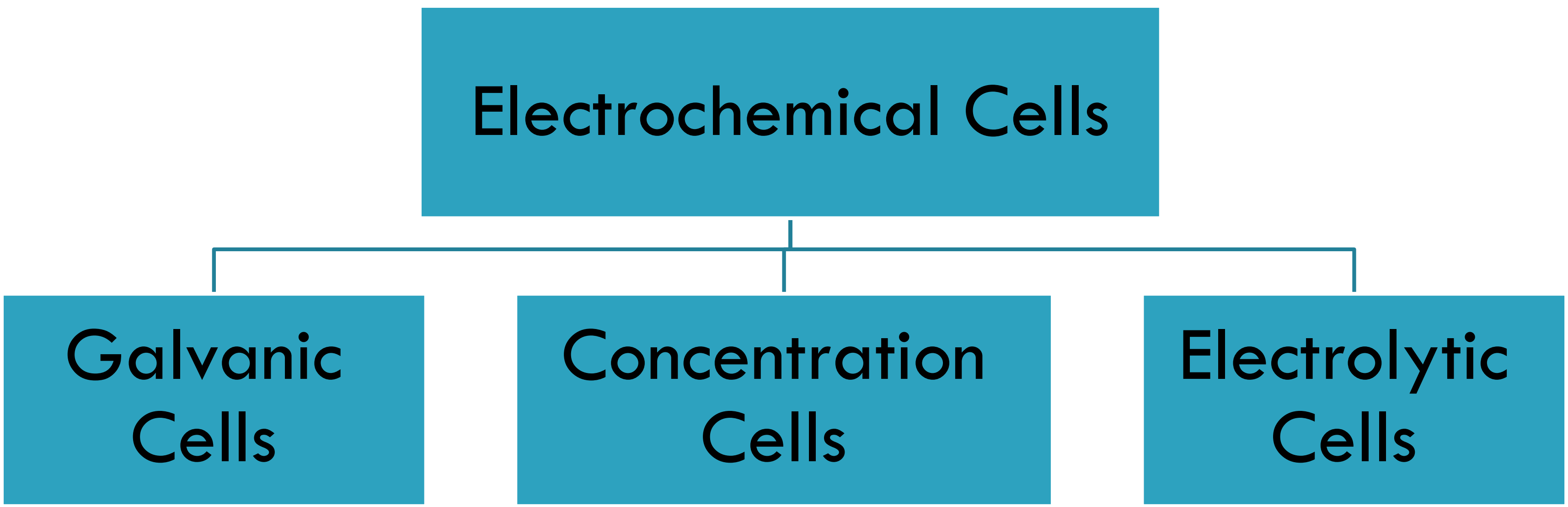
The Corrosion Cell (2/3)

The corrosion cell can be represented as follows



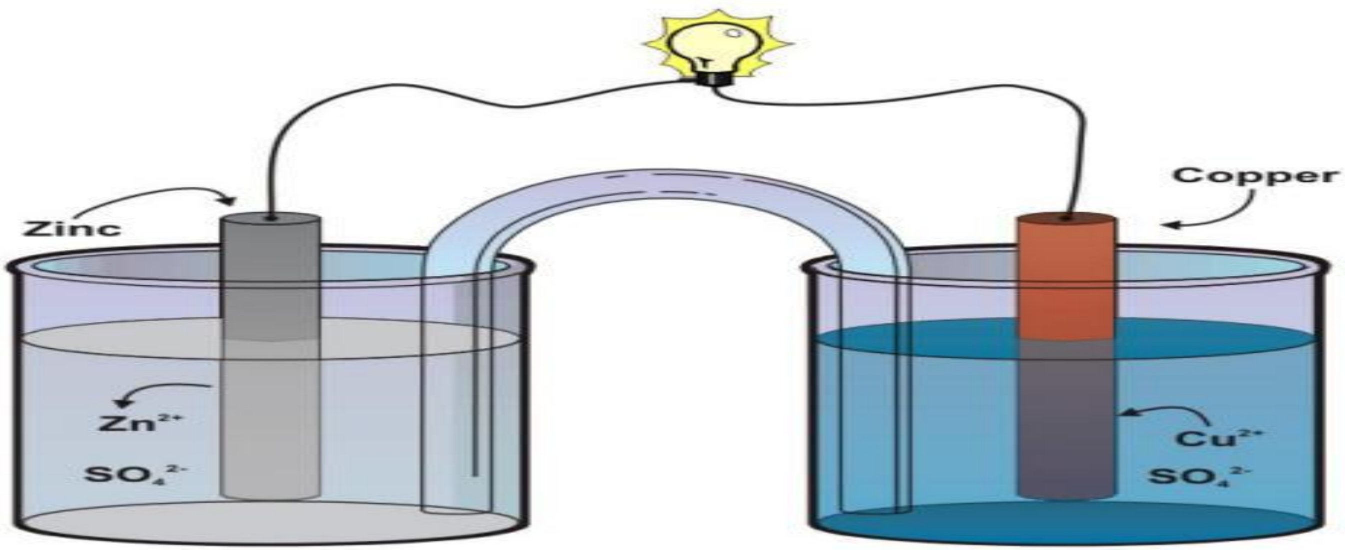
The Corrosion Cell (3/3)

Types of Electrochemical corrosion cells



Galvanic Cell

$$(-)Zn / Zn^{2+}, SO_4^{2-}{}_{(Conc_1)} // Cu^{2+}, SO_4^{2-}{}_{(Conc_2)} / Cu(+)$$



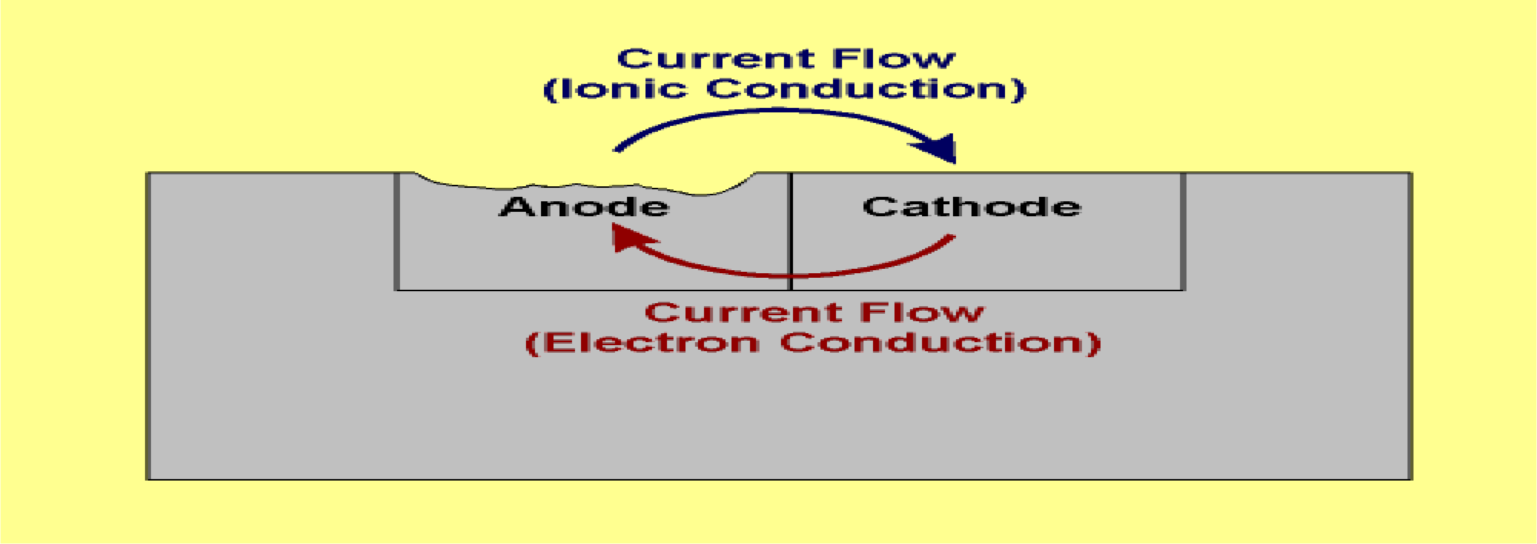
Zinc anode: $Zn_{(s)} \rightarrow Zn^{2+} + 2e^-$

Copper cathode: $Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$

Galvanic Cell

Anode	Cathode
Oxidation occurs	Reduction occurs
Electrons produced	Electrons are consumed
Anions migrate toward	Cations migrate toward
Has negative sign	Has positive sign

Galvanic Cell

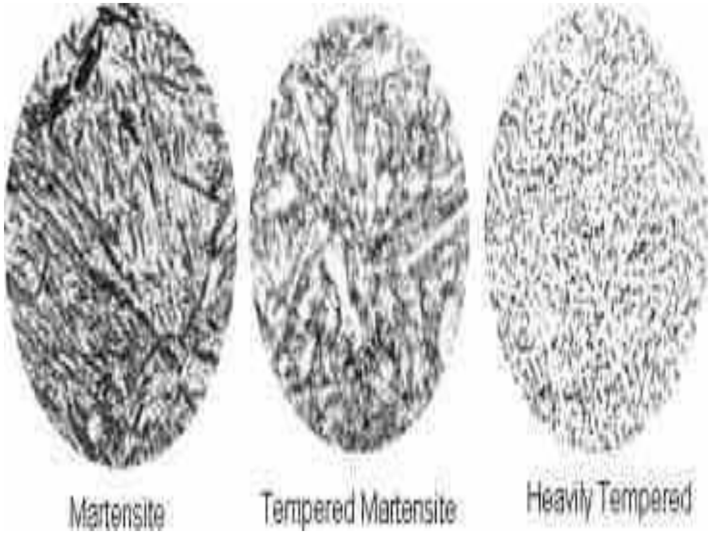


Two dissimilar metals in contact

- Two metals in contact may be entirely different in composition , e.g. iron pipe carrying water is anodic to copper pipe.
- Galvanic Corrosion with example of Couple between Steel and Brass.

Different Heat Treatment

- **Behavior of the metal depends on the type of heat treatment given , e . g . <u>Tempered steel is anodic to annealed steel.</u>**
- **<u>Tempered : increase the hardness and strength of a metal by quenching or heat treatment.</u>**
- **<u>Annealed: heat of metal and then gradually cooling.</u>**



Scratches or Abrasion

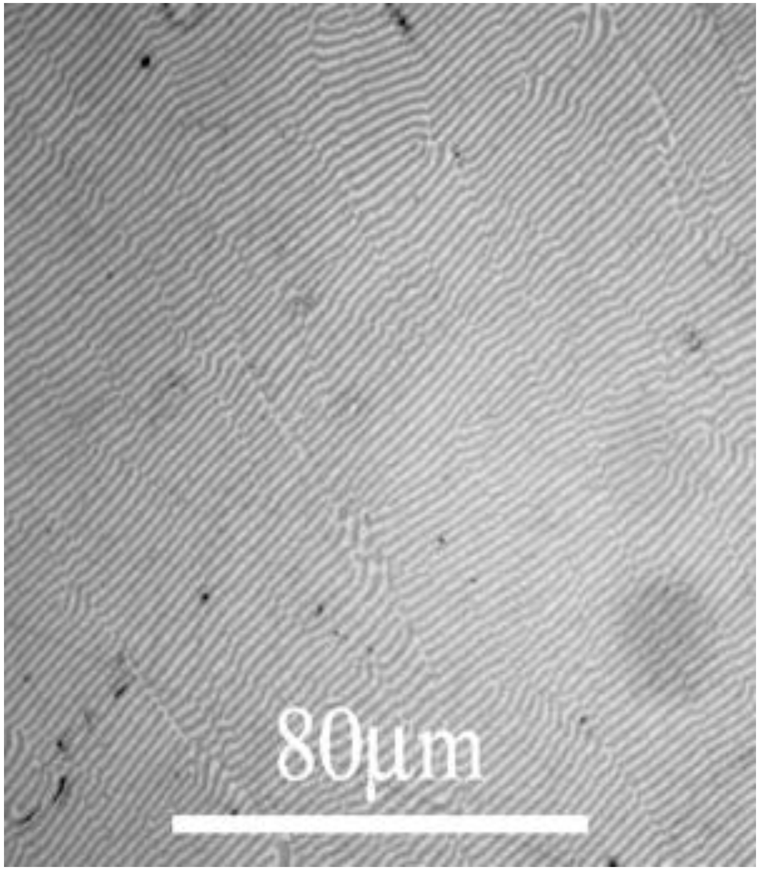
- If a piece of metal is scratched or abraded, the scratched or the abraded area will be anodic to remaining portion .

Differential strain

- A strained area is usually anodic to an unstrained area.

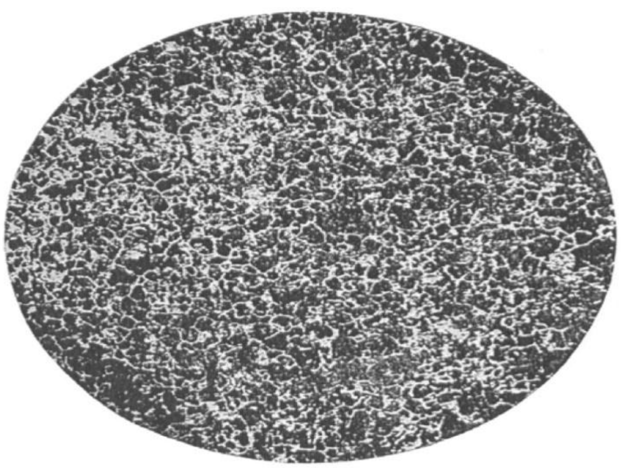
Differential Grain and Matrix Composition

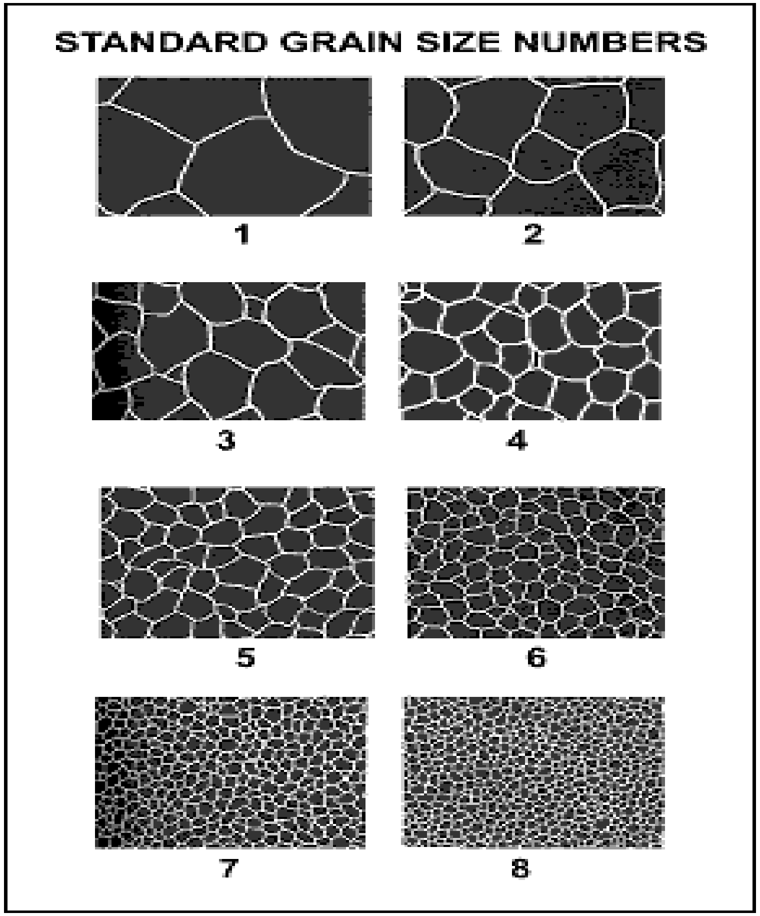
- Many alloys may consist of heterogeneous phases, which may have a potential difference. However, no general rule can be established . For example, in the case of Al-Cu alloy CuAl2 precipitate at the grain boundary is cathode to alpha matrix.



Different Grain Size

- Usually the smaller grains are anodic to large ones.



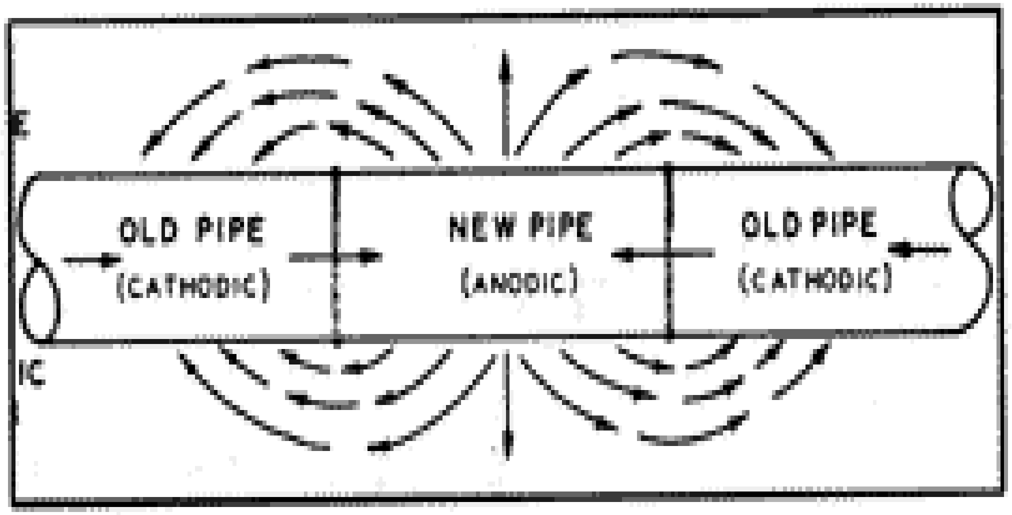


Picture 3

Surface condition

- Difference in surface condition may also create a potential difference. This explains why a new section of pipe when welded in old line becomes anodic and corrodes.

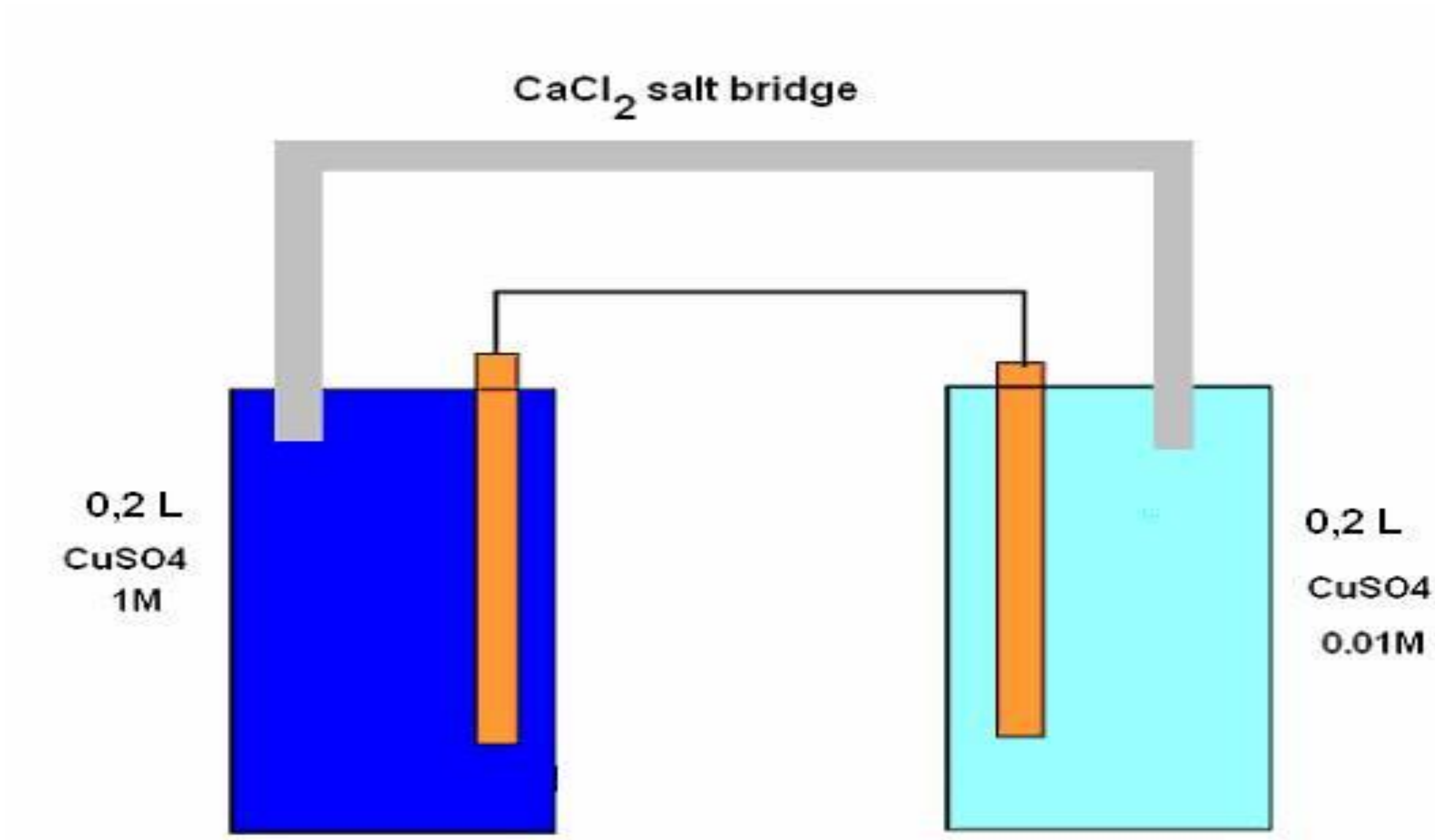
Failed pipe section shows the perforation clearly (Fig. 1).



Differential curvature

- If the metal has a curved surface, the more highly convex surface is anodic to the less convex surface.

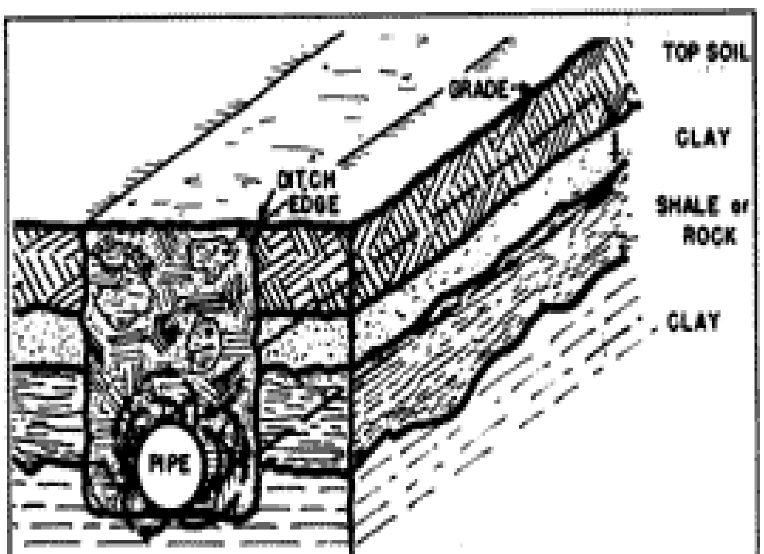
Concentration Cell

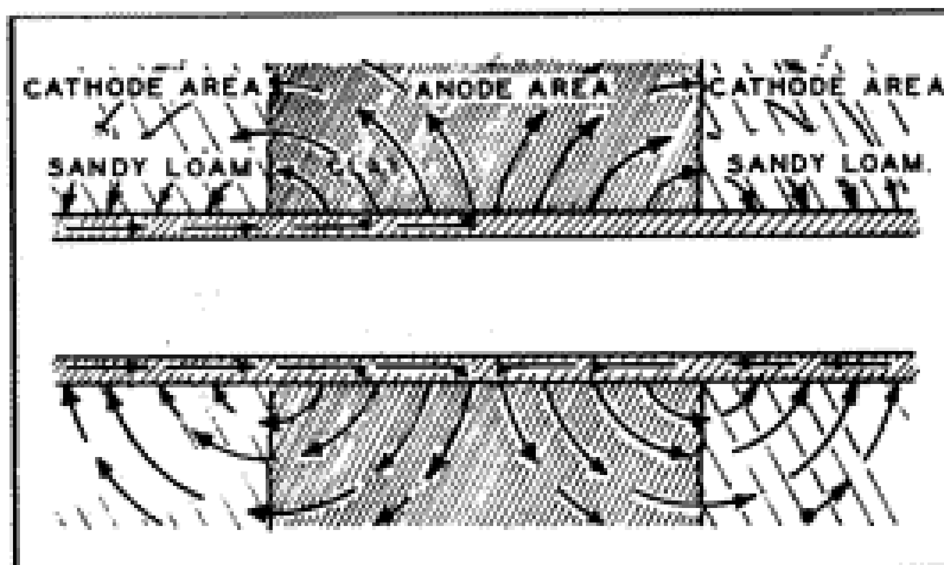


Differential Composition of the Electrolyte

Example of this type of corrosion is :

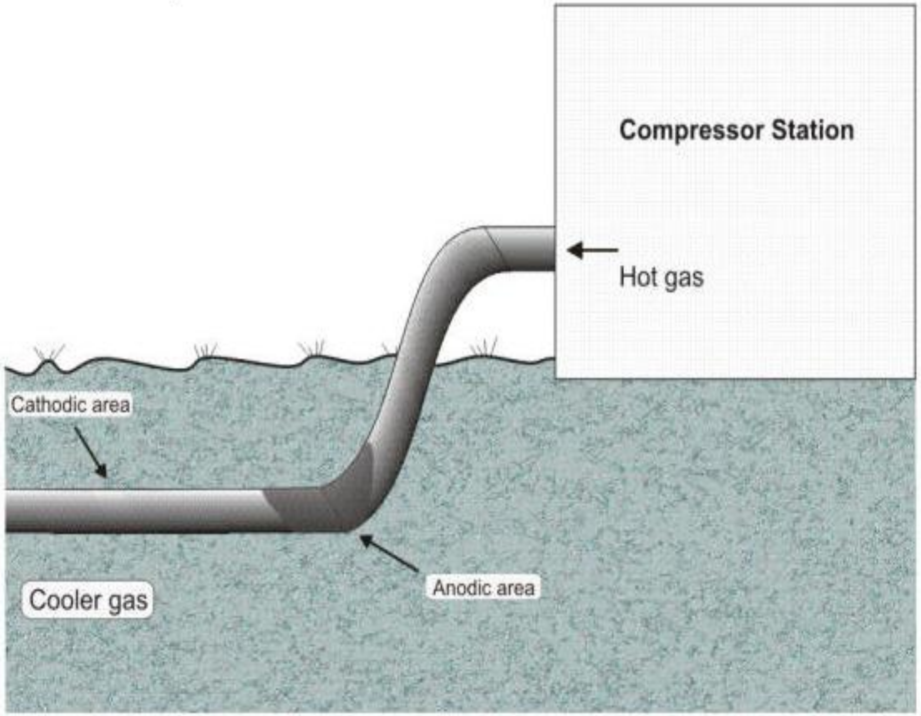
- A section of pipe buried in clay soil is anodic to pipe section buried in loam-soil.





Temperature differential

- The two regions having a temperature difference may have different potential

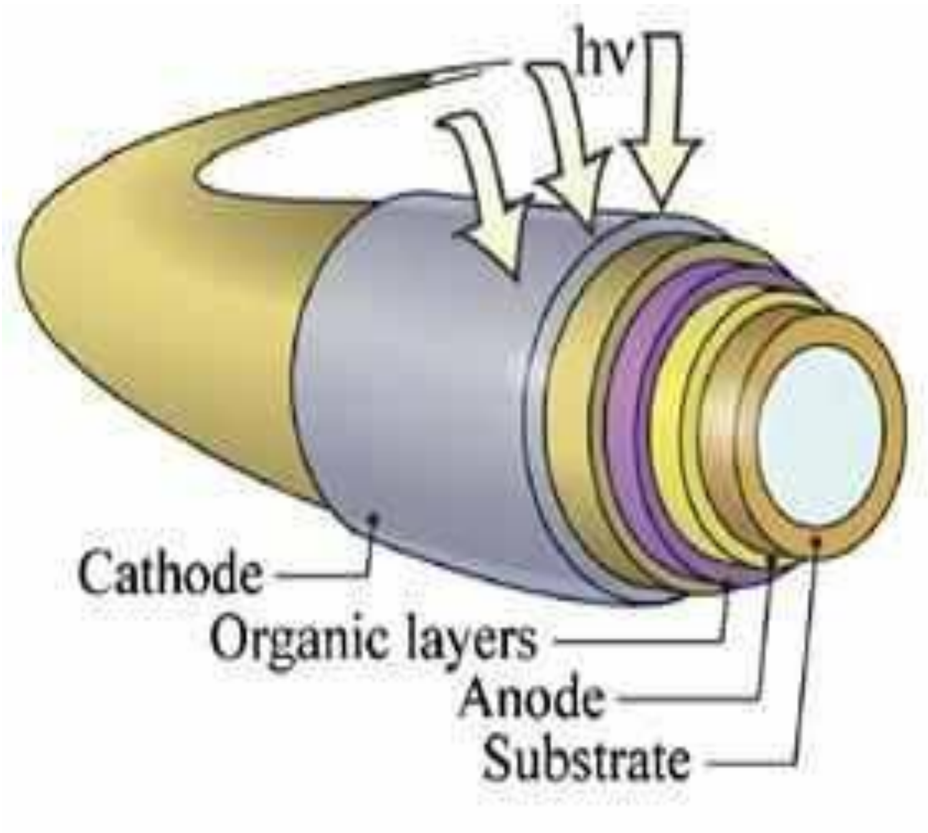


Differential Motion of the Electrolyte

- If a structure is subjected to varying velocities of the electrolyte , the area of higher velocity will be cathodic .

Differential illumination

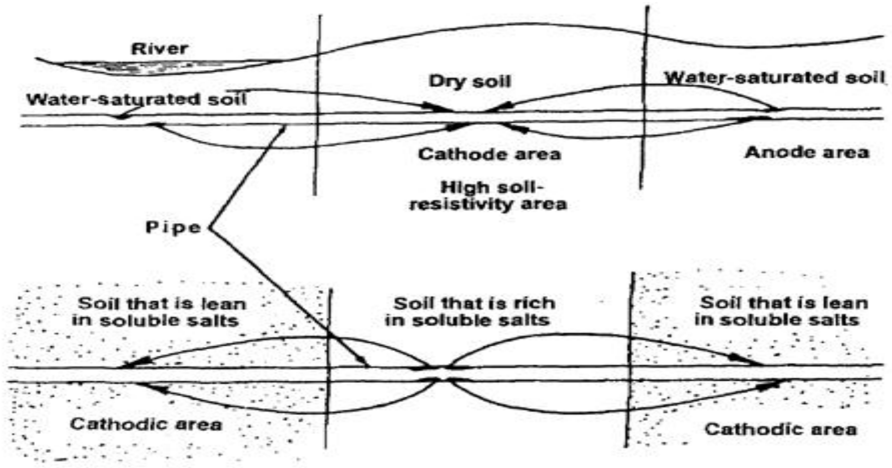
- The darker region well be anodic to the brighter ones.

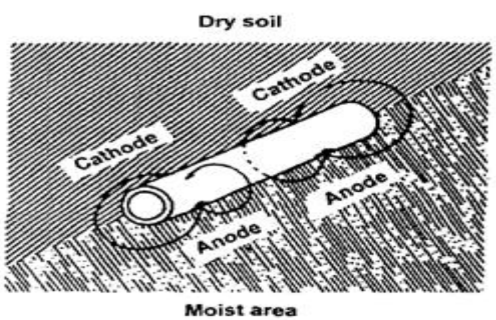


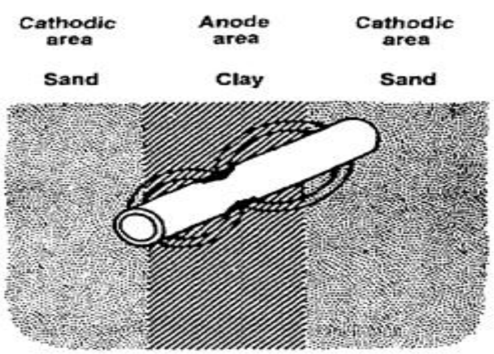
Differential concentration of the electrolyte

- These are also known as salt concentration cells and has two identical electrodes each in contact with a solution of different concentration of the same electrolyte.

<u>**The area of the metal in contact with the more dilute solution is usually anodic and corrodes.**</u>

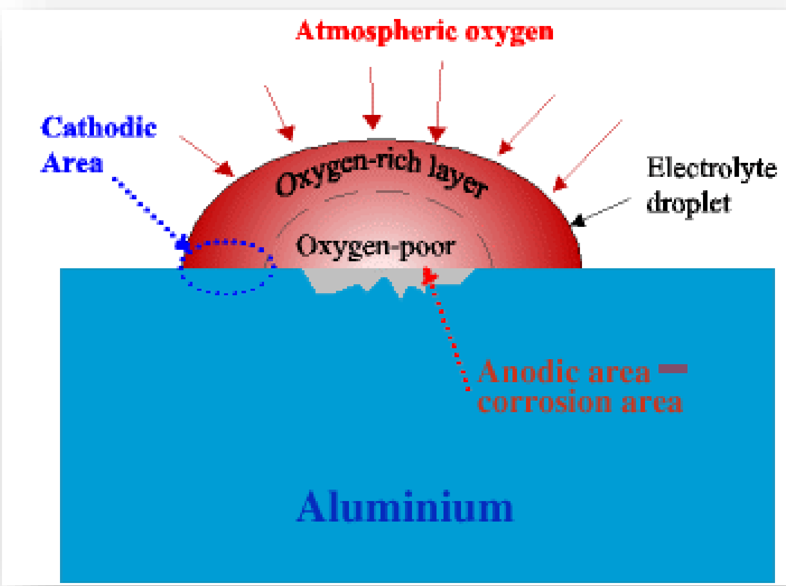


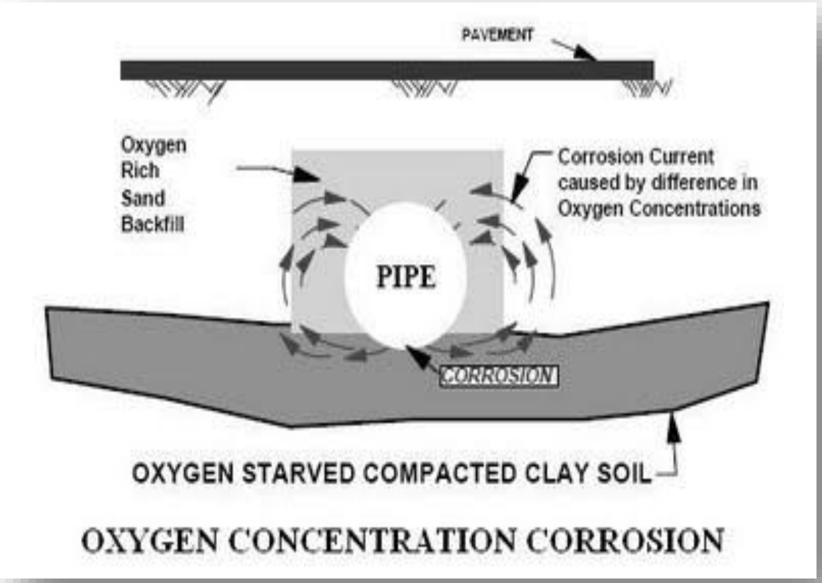




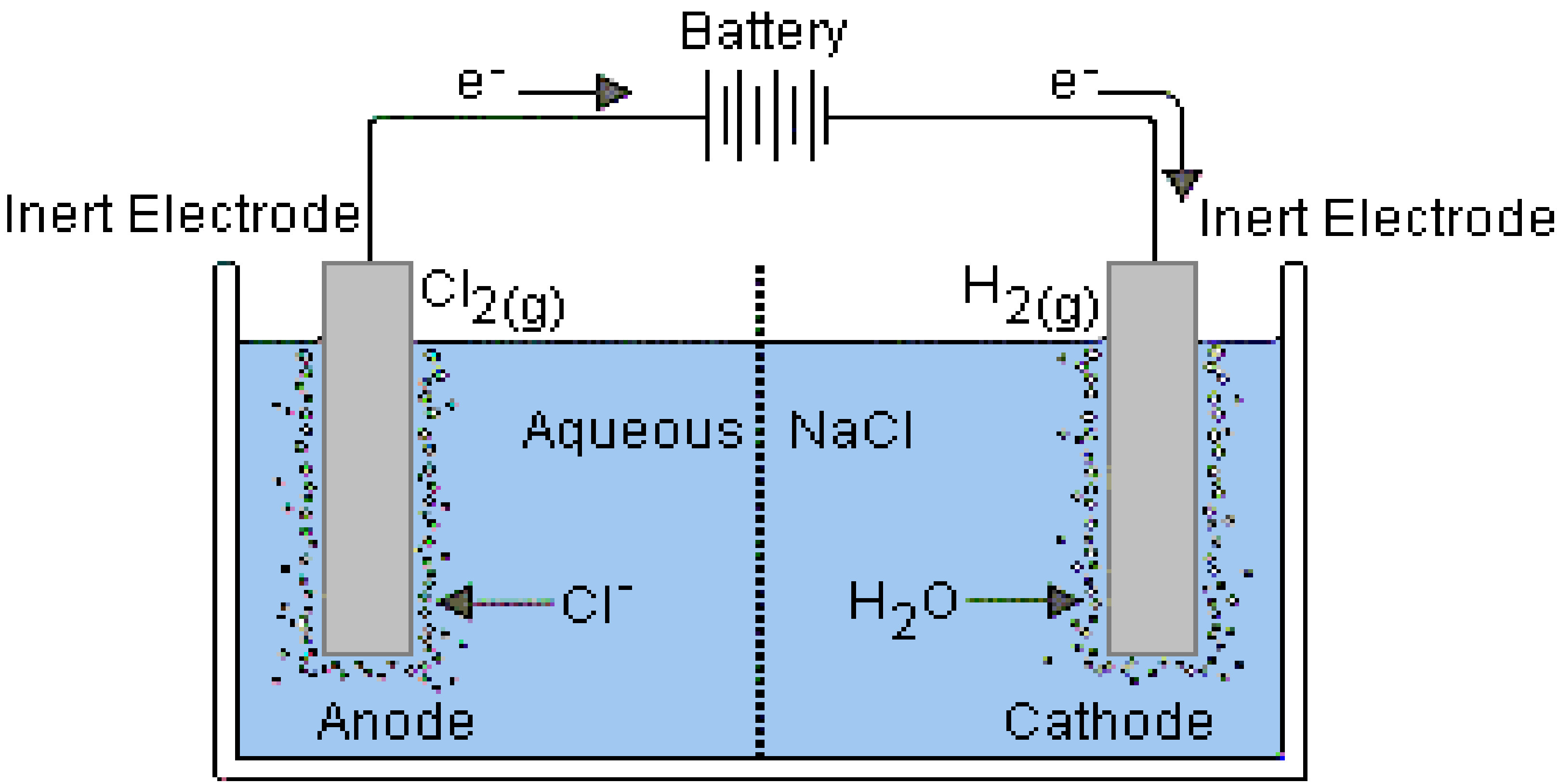
Differential Oxygen Concentration

- These are also known as differential aeration cells.
- The electrode in deaerated solution (solution with less oxygen) becomes anodic and corrodes.





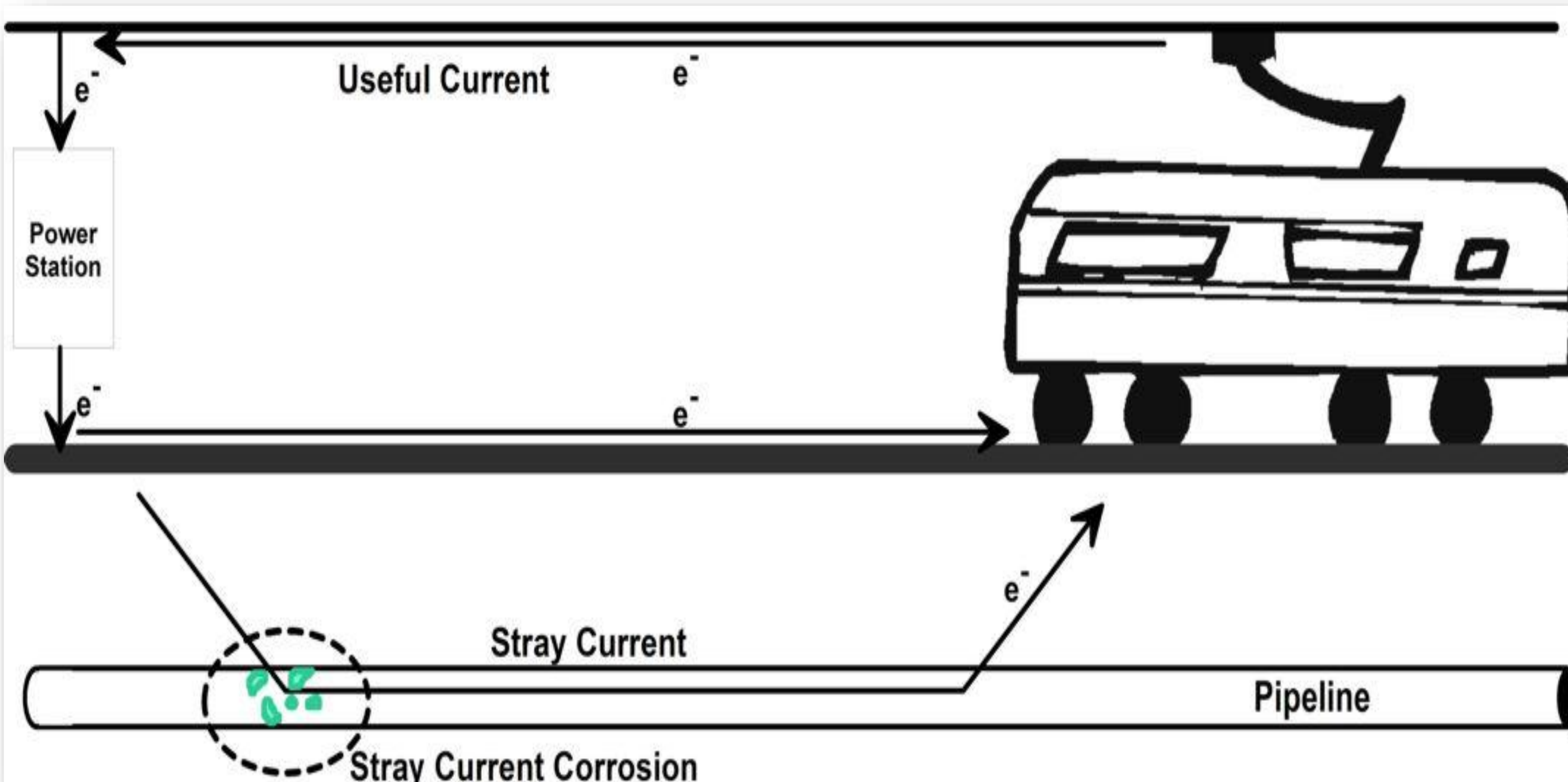
Electrolytic Cells



Electrochemical Vs Electrolytic

		Electrochemical	Electrolytic
Electrodes	Cathode	Site of reduction + charge	Site of reduction - charge
	Anode	Site of oxidation - charge	Site of oxidation + charge
Ions	Cations	Migrate to cathode	Migrate to cathode
	Anions	Migrate to anode	Migrate to anode
Electron flow		Anode to cathode	Anode to cathode
Voltage		+ voltage produces a voltage	- voltage requires a voltage source
Spontaneity		spontaneous	non spontaneous

Stray-current corrosion of buried pipeline.



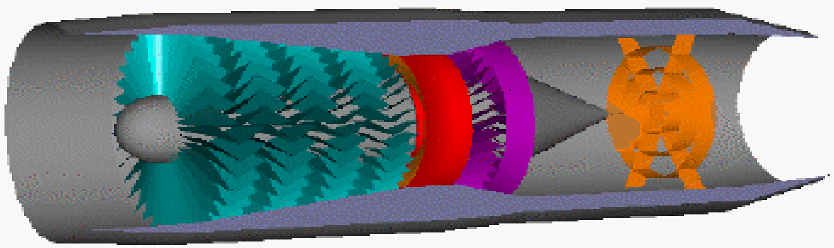
CORROSION PRINCIPLES

Thermodynamic Principles of corrosion

What is Thermodynamic

What is Thermodynamics?

Glenn
Research
Center



Thermodynamics is the study of the effects of work, heat, and energy on a system. Thermodynamics is only concerned with large scale observations.

Zeroth Law: Thermodynamic Equilibrium and Temperature

First Law: Work, Heat, and Energy

Second Law: Entropy

Thermodynamic Functions of State

Δ E, Δ H, ΔS, ΔG, ΔA and $\Delta\mu$

$$\Delta G \Delta = H - T\ \Delta S$$

Free energy

The total energy which can be utilized for work.

Enthalpy

The heat content

Entropy

The unavailable energy of a substance due to the internal motion of the molecules.

The relationship between the change in Gibb's free energy and the emf of an electrochemical cell is given by:

- $\Delta G = -nFE$
- $\Delta G^{\circ} = -nFE^{\circ}$

The Nernst Equation

$$\underline{E}_{\underline{cell}} = E^0_{cell} - (RT/nF)\ln Q$$

FREE ENERGY

$Mg + H_2O(l) + 1/2\ O_2(g) = Mg\ (OH)_2\ (S)$; $\Delta G^o = -420{,}600$ cal

$Cu + H_2O(l) + 1/2\ O_2(g) = Cu(OH)_2(S)$; $\Delta G^o = -28{,}600$ cal

$Au + 3/2 H_2O + 3/4\ O_2(g) = Au\ (OH)\ 3(S$; $\Delta G\ ^o = +15.700$cal

Electromotive Series/Standard Electrode Potentials and Thermodynamic Corrosion Theory

The Electromotive Series or emf series is an orderly arrangement of the standard Electrode Potentials of all metals.

electrode potential

The electrical potential difference between an electrode and a reference electrode. We cannot measure the absolute potential of an electrode; therefore, the electrode potential must always be referred to an "arbitrary zero point", defined by the potential of the reference electrode. Consequently, it is very important always to note the type of reference electrode used in the measurement of the electrode potential. Not to be confused with electrochemical potential.

Standard Electromotive Force Potentials

- Cathodic Reactions
- $Au^{3+} + 3e^- \rightarrow Au$
- $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
- $Pt^{2+} + 2e^- \rightarrow Pt$
- $NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$
- $Ag^+ + e^- \rightarrow Ag$
- $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
- **$Cu^{2+} + 2e^- \rightarrow Cu$**
- **$2H^+ + 2e^- \rightarrow H_2$**
- $Pb^{2+} + 2e^- \rightarrow Pb$
- $Sn^{2+} + 2e^- \rightarrow Sn$
- $Ni^{2+} + 2e^- \rightarrow Ni$
- $Co^{2+} + 2e^- \rightarrow Co$
- $Cd^{2+} + 2e^- \rightarrow Cd$
- $Fe^{2+} + 2e^- \rightarrow Fe$
- $Cr^{3+} + 3e^- \rightarrow Cr$
- **$Zn^{2+} + 2e^- \rightarrow Zn$**
- $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
- $Al^{3+} + 3e^- \rightarrow Al$
- $Mg^{2+} + 2e^- \rightarrow Mg$
- $Na^+ + e^- \rightarrow Na$
- $K^+ + e^- \rightarrow K$

- Standard Potential, e° (volts vs. SHE)
- +1.498 **(Most Noble)**
- +1.229 (in acidic solution)
- +1.118
- +0.957
- +0.799
- +0.401 (in neutral or basic solution)
- **+0.337**
- **0.000**
- -0.126
- -0.138
- -0.250
- -0.277
- -0.403
- -0.447
- -0.744
- **-0.762**
- -0.828 (pH = 14)
- -1.662
- -2.372
- -2.71
- -2.931 **(Most Active)**

Applications of the Series

1. **Displacement of metal: One metal will displace another above it in the series.**
2. **Displacement of hydrogen.**
3. **Galvanic corrosion.**
4. **Electrolysis.**

Metal	Potential	
Barium	2.90	'Base or 'Anodic' End
Calcium	2.87	
Sodium	2.71	
Magnesium	2.40	
Aluminium	1.70	
Zinc	0.76	
Nickel	0.23	
Lead	0.12	
Iron	0.04	
Hydrogen	0.00	
Bismuth	-0.23	
Copper	-0.34	
Silver	-0.80	
Mercury	-0.80	
Lead	1.50	'Nobel' or 'Cathodic' End

Limitations of the Series

1. Only pure metal are listed in emf series, because it is not possible to establish a reversible potential for alloys containing two or more reactive components. But in most engineering applications the galvanic couple usually has one or more alloys.
2. The emf series has limited utility even in predict galvanic corrosion behavior of pure metals.
3. The emf series takes no account of the effect of surface films which may form on metals under a variety of conditions.
4. The emf series takes no account of the effect of pH .
5. Effect of temperature has not been considered in the emf series .

Galvanic series of metals and alloys

1) To overcome some of limitations of the emf series the so-called galvanic series can be used.
2) This series is an arrangement of metals and alloys in accordance with their actual measured potentials in a given environment.
3) The galvanic series of metals in contact with sea water is given .

Galvanic series (most noble at top)

The following is the galvanic series for stagnant (that is, low oxygen content) seawater. The order may change in different environments.

- Graphite
- Palladium
- Platinum
- Gold
- Silver
- Titanium
- Tantalum
- Chromium plating
- Nickel (passive)
- Copper
- Nickel (active)
- Cast iron
- Steel
- Lead
- Tin
- Indium
- Aluminum
- Uranium (pure)
- Cadmium
- Beryllium
- Zinc plating (see galvanization)
- Magnesium
- Stainless steel 316 (passive)
- Stainless Steel 304 (passive)
- Silicon bronze
- Stainless Steel 316 (active)
- Monel 400
- Phosphor bronze
- Admiralty brass
- Cupronickel
- Molybdenum
- Red brass
- Brass plating
- Yellow brass
- Naval brass 464
- Uranium 8% Mo
- Niobium 1% Zr
- Tungsten
- Stainless Steel 304 (active)

Galvanic series (most noble at top)

- Magnesium
- Mg alloy AZ-31B
- Mg alloy HK-31A
- Zinc (hot-dip, die cast, or plated)
- Beryllium (hot pressed)
- Al 7072 clad on 7075
- Al 2014-T3
- Al 1160-H14
- Al 7079-T6
- Cadmium (plated)
- Uranium
- Al 218 (die cast)
- Al 5052-0
- Al 5052-H12
- Al 5456-0, H353
- Al 5052-H32
- Al 1100-0
- Al 3003-H25
- Al 6061-T6
- Al A360 (die cast)
- Al 7075-T6
- Al 6061-0

Applications of Galvanic Series

1) Metals and alloys at the top of the series , i. e., at the noble end are corroded least , while metals and alloys at the bottom , i.e., at the active end are corroded to the maximum extent.

2) The further apart metal and alloys are in the series , the greater is the potential generated. Therefore , metals and alloys which are further apart in the series should not be connected together.

3) When metals and alloys within the same group are coupled together there is little danger of corrosion.

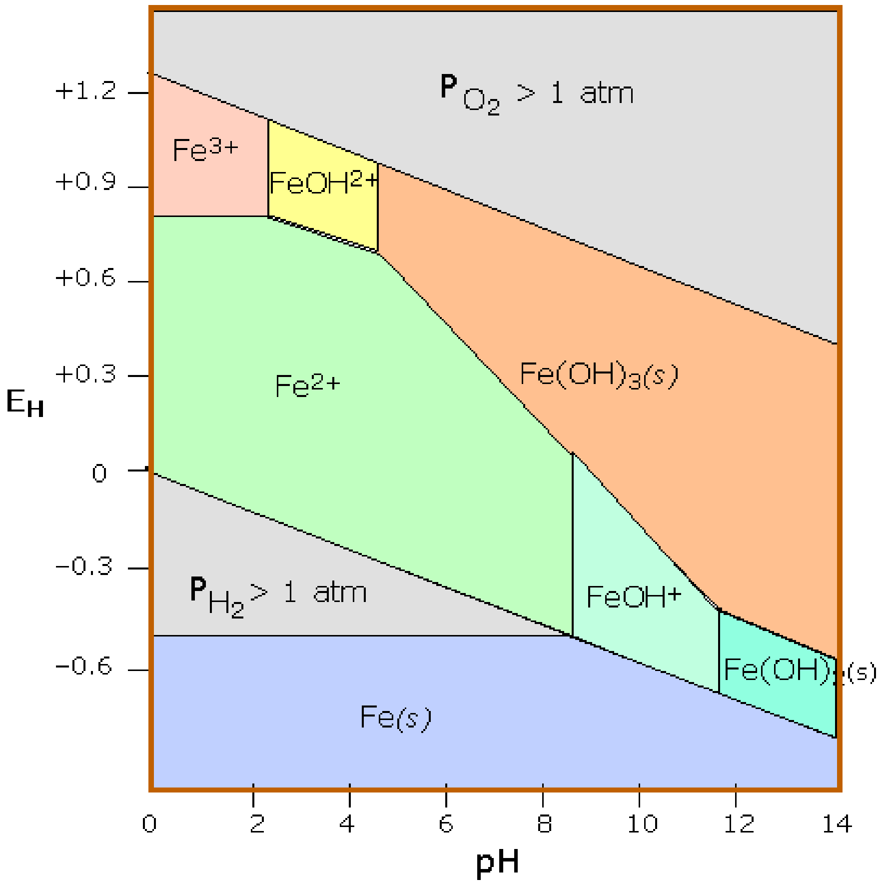
Limitations of Galvanic Series

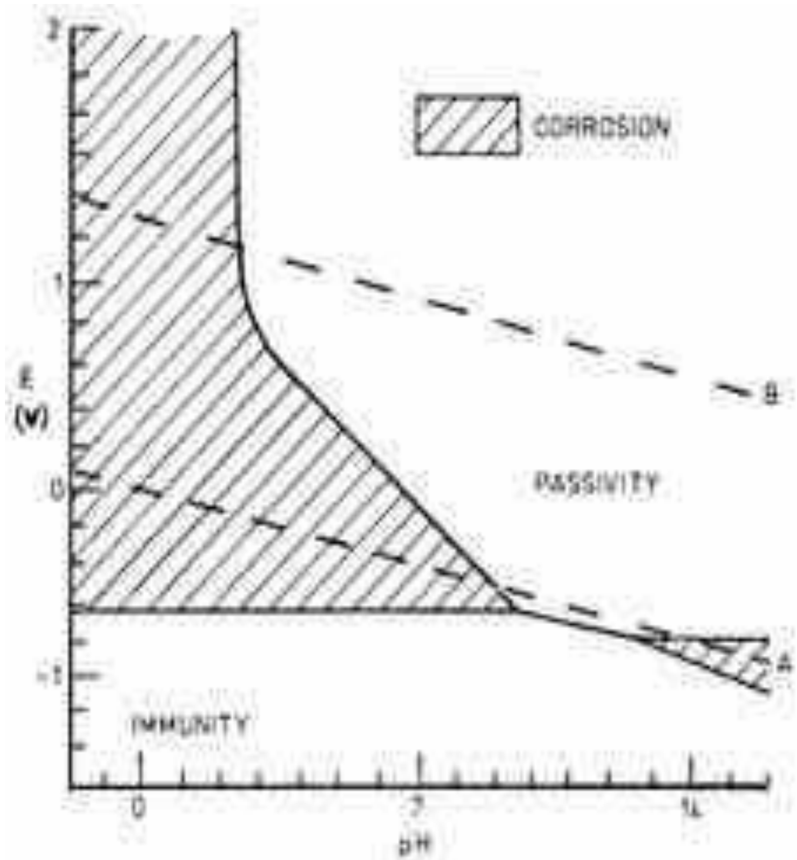
1) In case of EMF series only one series exists but there can be several galvanic series because of differing tendencies of various environments to form surface films.

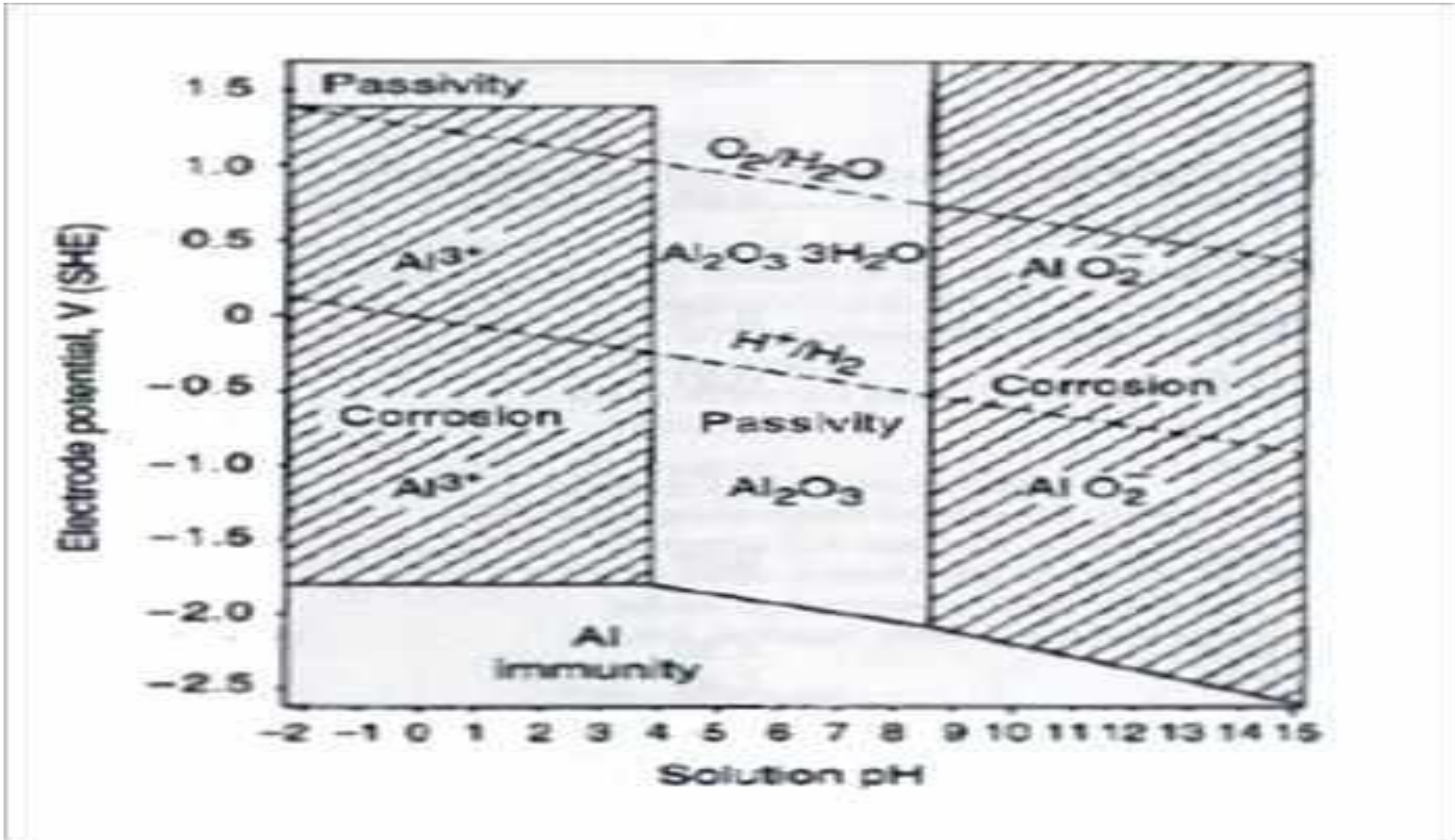
2) Galvanic Series like EMF series cannot be used to predict the effect of a change in solution pH on corrosion tendency

- To overcome some of limitations of the emf and galvanic series a system of showing the effect of both potential and pH has been evolved by Pourbaix in the form of **E/pH digrams or Potential/pH diagrams.**

Extended Thermodynamics – E/pH Diagrams



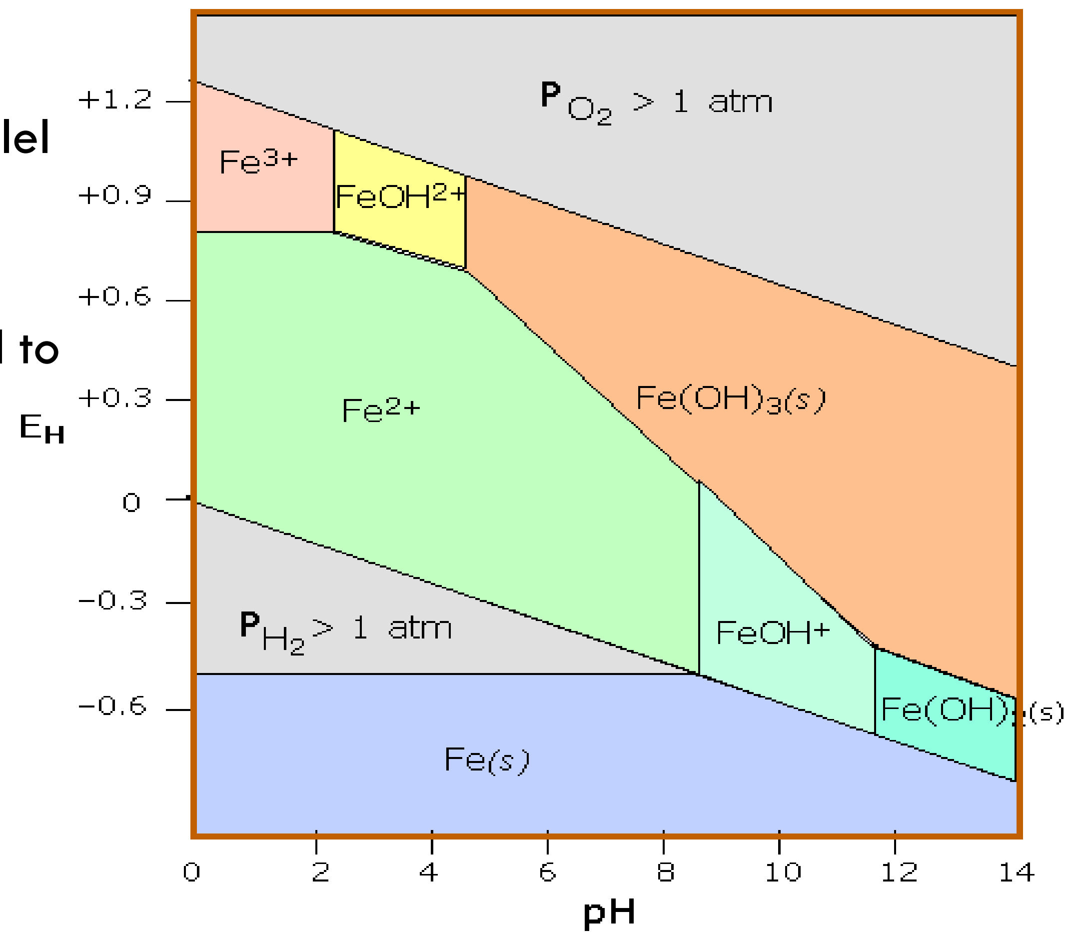




Passivity
O_2/H_2O
Al^{3+}
$Al_2O_3\ 3H_2O$
$Al\ O_2^-$
H^+/H_2
Corrosion
Passivity
Corrosion
Al^{3+}
Al_2O_3
$Al\ O_2^-$
Al
immunity
Electrode potential, V (SHE)
1.5
1.0
0.5
0
−0.5
−1.0
−1.5
−2.0
−2.5
−2 −1 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Solution pH

The diagram consists of three types of straight lines each represent an equilibrium state.

1. lines Horizontal or Lines Parallel to pH Axis.
2. Vertical Lines or Lines Parallel to Potential Axis.
3. The Sloping Lines.

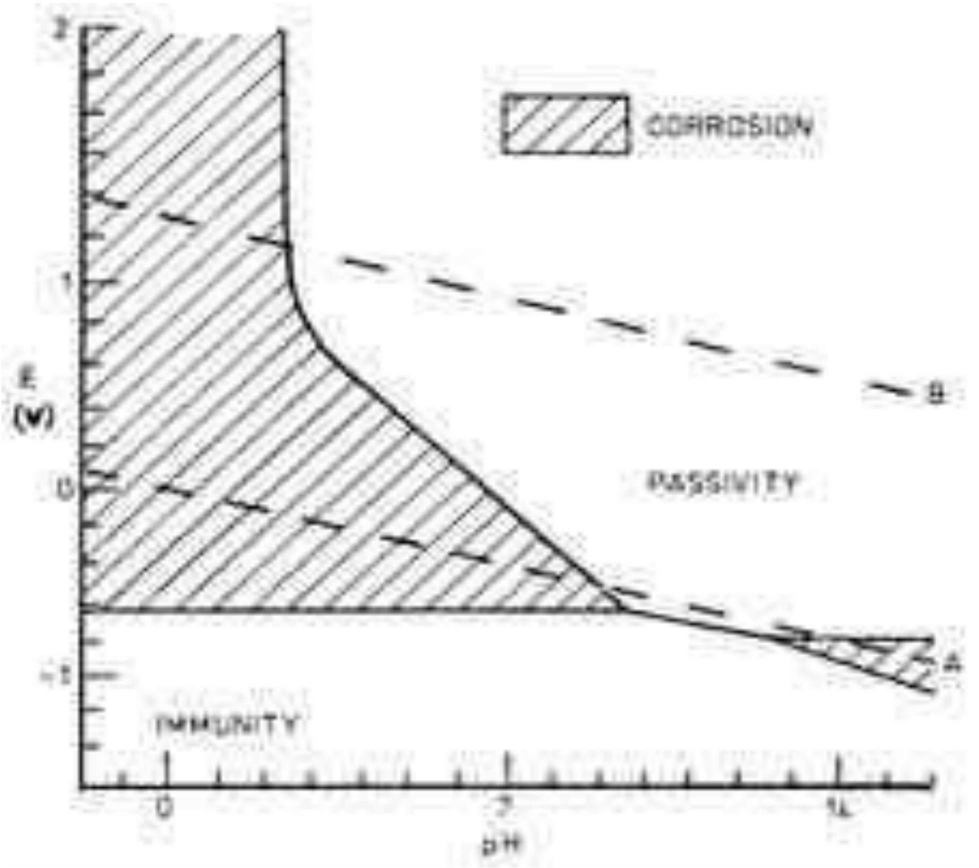


The horizontal, vertical and sloping lines in the diagram form the following three types of regions or domains.

I. **Immunity domain.**

II. **Passive domain.**

III. **Corrosion domain.**

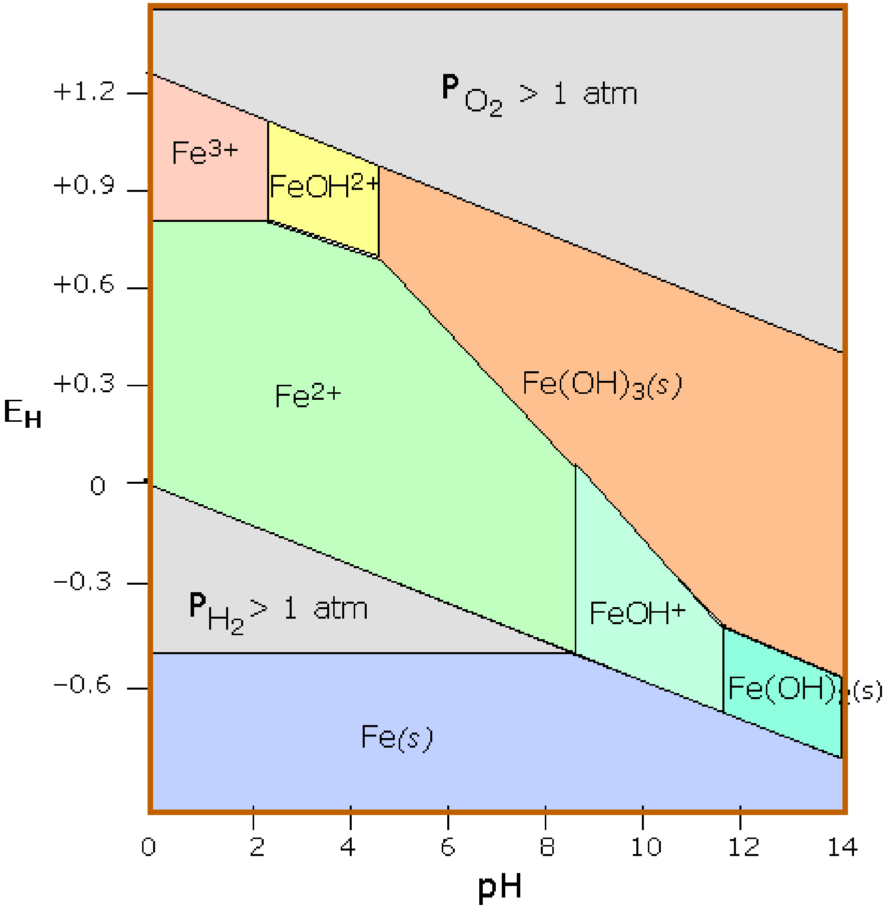


These diagrams are used for predicting :-

1) **Spontaneous direction of reaction.**

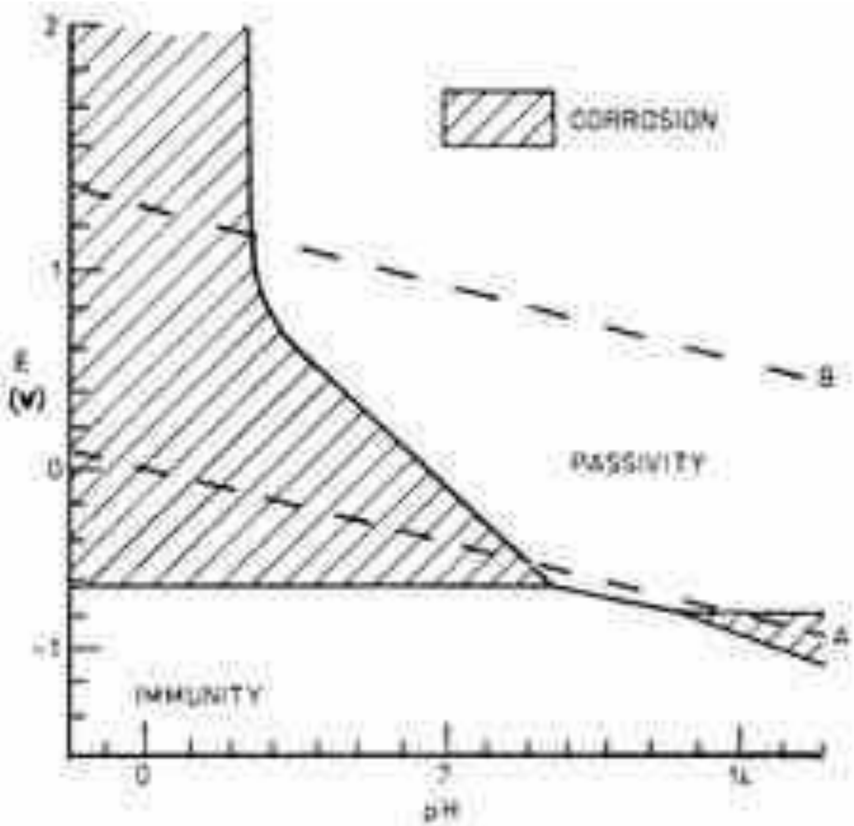
2) **Stability and composition of corrosion products.**

3) **Environmental changes which will prevent or reduce corrosive attack.**



According to E/pH diagram , following methods can be used to reduce corrosion:

1) By lowering the electrode potential down into the region of immunity, e.g., by cathodic protection.
2) By raising the electrode potential up into region of passivity ,e .g ., by anodic protection.
3) By raising the pH or alkalinity of solution so that a passive film is formed



Limitation of E/pH Diagrams:

1) These diagrams give no information on the corrosion rate, since they are based on thermodynamic and not on kinetic data.
2) The effect of impurities in solution is difficult to consider.
3) The effect of alloy element has not been considered
4) Generally the diagrams are drawn for room temperature conditions.

Thank You