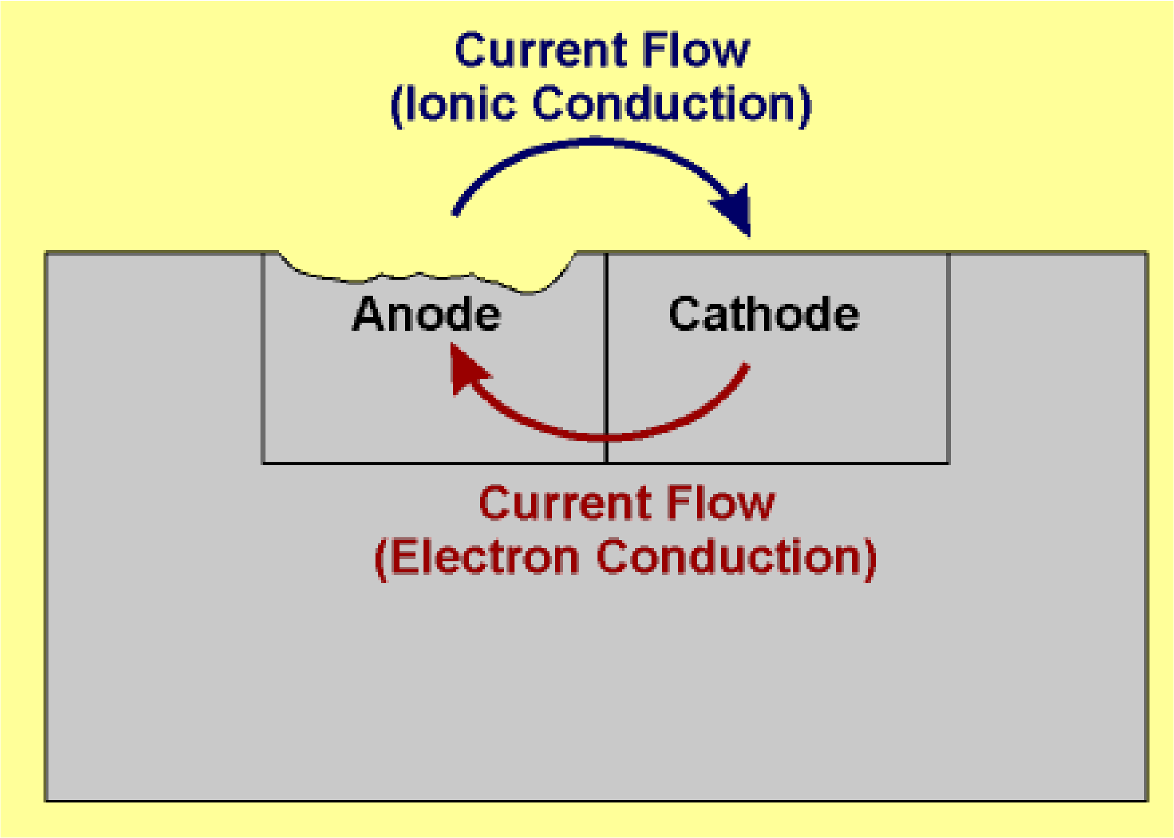
Chapter (2)

Corrosion Cells & Electrochemistry



Sept. 16th , 2017

2.1 Corrosion Cells & Electrochemistry

Most corrosion forms occur as aqueous electrochemical reactions. For corrosion to occur, a corrosion cell is formed. It is a galvanic cell consisting of:

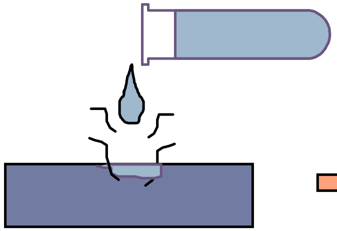
a) **Anode**: Oxidation reaction releasing positive ions as well as electrons as corrosion products, NEGATIVE (-) sign.

b) **Cathode**: Reduction reaction consuming electrons (depends on environment), POSITIVE (+) sign.

a) **Electrolyte**: Environment surrounding metal /conducts ions.

b) **Metallic path**: Transfers electrons from anode to cathode and current in opposite direction.

Oxidation (anodic /Corrosion) Reaction

$Fe(s)$  $\Rightarrow Fe^{2+} + 2\,e^-$

Corrosive environment

Reduction (Cathodic) Reactions

Depending on the surrounding medium (environment) :

1. acid environment :

$$2\,H^+ + 2\,e^- \Rightarrow H_2$$

2. alkaline or neutral environment :

$$O_2 + 2\,H_2O + 4\,e^- \Rightarrow 4\,OH^-$$

Examples of Anodic Reactions

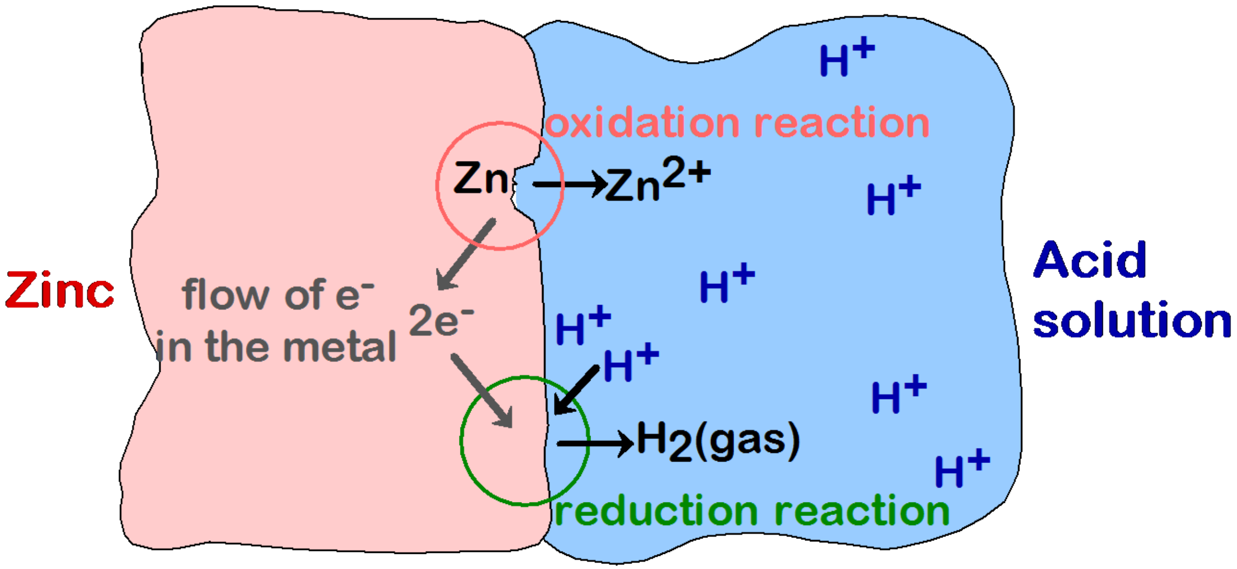
$Zn \rightarrow Zn^{2+} + 2e^-$	zinc corrosion
$Fe \rightarrow Fe^{2+} + 2e^-$	iron corrosion
$Fe^{2+} \rightarrow Fe^{3+} + e^-$	ferrous ion oxidation
$Al \rightarrow Al^{3+} + 3e^-$	aluminium corrosion
Oxidation reactions:	Produce electrons

Examples of Cathodic Reactions

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	oxygen absorption (reduction)
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	hydrogen evolution
$Cu^{2+} + 2e^- \rightarrow Cu$	copper reduction
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	ferric ion reduction
Reduction reactions:	Consume electrons

Example: CORROSION OF ZINC IN ACID

- **Two reactions are necessary:**
  -- oxidation reaction: $Zn \rightarrow Zn^{2+} + 2e^{-}$
  -- reduction reaction: $2H^{+} + 2e^{-} \rightarrow H_2(gas)$



- **Other reduction reactions (presence of oxygen):**
  -- in an acid solution
  $O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O$
  -- in a neutral or alkaline solution
  $O_2 + 2H_2O + 4e^{-} \rightarrow 4(OH)^{-}$

Types of Corrosion Cells

- Metal corrosion takes place upon the formation of one or more of the following cells:

1. **Galvanic cells**

    1.1 Dissimilar metals in equipment exposed to an electrolyte *(See Examples)*

    1.2 Dissimilar electrodes resulting in different potentials for <u>same metal.</u>

2. **Concentration cells:**

    2.1 Differential aeration *(different oxygen content of medium/ environment)*

    2.2 Differential stress (force/area): welding or threads on steel pipe

    2.3 Different moisture content of soil: wet soil vs. dry soil

    2.4 Different types of soil (different porosities) : clay vs. sand

3. **Differential temperature cells.**

Galvanic / Dissimilar-Metal Cells

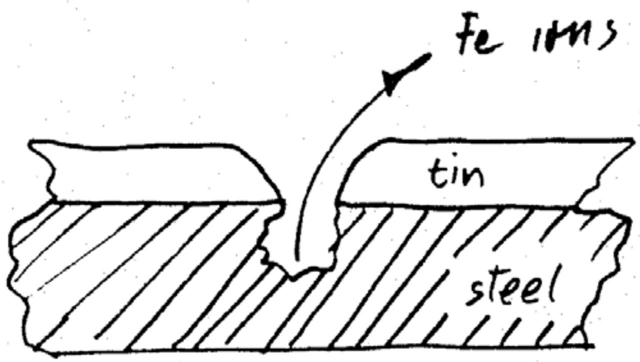
Examples

1. Stainless Steel (SS) screw combined with steel washer →
2. Scratch in iron sheet plated with tin (next)
3. Weld between carbon steel tank and SS bottom (SS more noble than Fe).
4. Steel tank connected to side tube made of copper.
5. Stirring system composed of iron shaft and copper impeller.
6. Heat exchanger (e.g. steel shell and copper tubes), next.
7. Storage of $CuSO_4$ in a steel tank. The following reaction will take place:

$$CuSO_4 + Fe \rightarrow Cu + FeSO_4$$

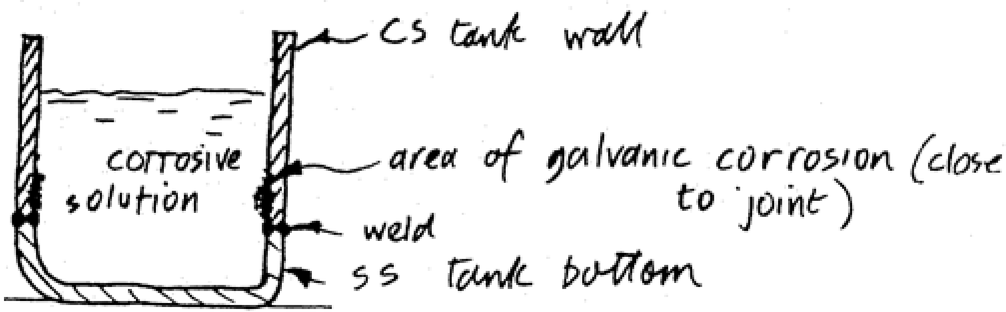
Galvanic / Dissimilar-Metal Cells

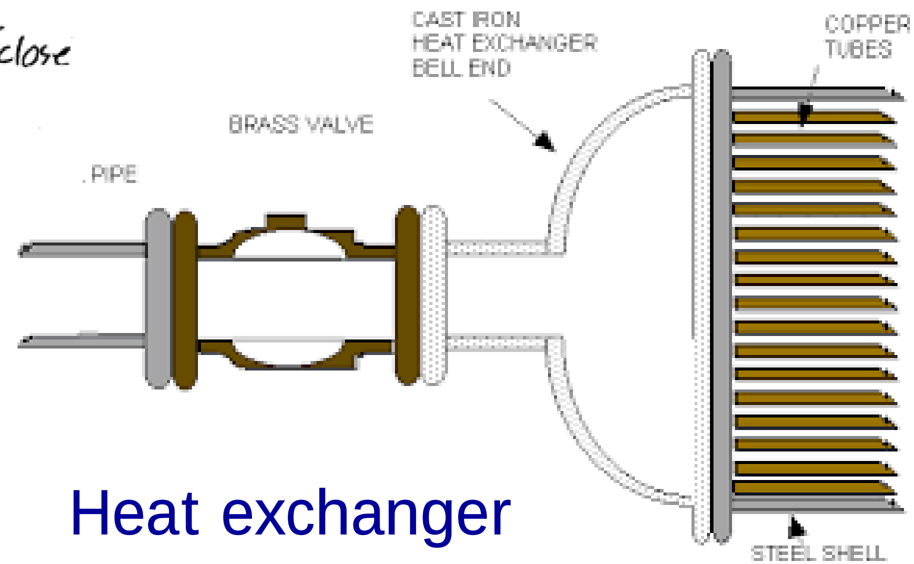
Scratch in metal (Fe) with a noble plate (Sn):



Anodic rxn: $Fe \rightarrow Fe^{2+} + 2\ e^-$

Cathodic rxn: $O_2 + H_2O + 4\ e^- \rightarrow 4\ OH^-$





Heat exchanger

Table 16.1 The Standard emf Series

	Electrode Reaction	*Standard Electrode Potential, V^0(V)*
↑	$Au^{3+} + 3e^- \longrightarrow Au$	+1.420
	$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.229
	$Pt^{2+} + 2e^- \longrightarrow Pt$	~+1.2
	$Ag^+ + e^- \longrightarrow Ag$	+0.800
Increasingly inert (cathodic)	$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.771
	$O_2 + 2H_2O + 4e^- \longrightarrow 4(OH^-)$	+0.401
	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.340
	$2H^+ + 2e^- \longrightarrow H_2$	0.000
	$Pb^{2+} + 2e^- \longrightarrow Pb$	−0.126
	$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.136
	$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.250
	$Co^{2+} + 2e^- \longrightarrow Co$	−0.277
	$Cd^{2+} + 2e^- \longrightarrow Cd$	−0.403
	$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.440
Increasingly active (anodic)	$Cr^{3+} + 3e^- \longrightarrow Cr$	−0.744
	$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.763
	$Al^{3+} + 3e^- \longrightarrow Al$	−1.662
	$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.363
	$Na^+ + e^- \longrightarrow Na$	−2.714
↓	$K^+ + e^- \longrightarrow K$	−2.924

Galvanic / Dissimilar-Metal Cells

- An example for dissimilar metal cells and their reactions is given below:

Zn / electrolyte / Cu

The anode reaction: $Zn \rightarrow Zn^{2+} + 2e^-$
The cathode reaction: $2H + 2e^- \rightarrow H_2$ (in acid medium)
or $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
(in neutral medium).

- Dissimilar metal corrosion takes place whenever there are two metals of different nobility in contact with each other in the presence of an electrolyte:

  – A corrosion cell is set up, with the less noble metal as the *negative* electrode (anode) and the more noble metal as the *positive* electrode (cathode).
  – The less noble metal dissolves, while at the surface of the more noble metal H2 evolution or O_2 absorption takes place depending on the pH of the medium.

Galvanic / Dissimilar Electrode Cells

- **Example**: Joining new pipe to old pipe (same metal) leads to corrosion of new one acting as anode. The old one is less active due to *film formation*:

New pipe (anode): $Fe \rightarrow Fe^{2+} + 2\,e^-$

Old pipe (Cathode): $O_2 + H_2O + 4\,e^- \rightarrow 4\,OH^-$

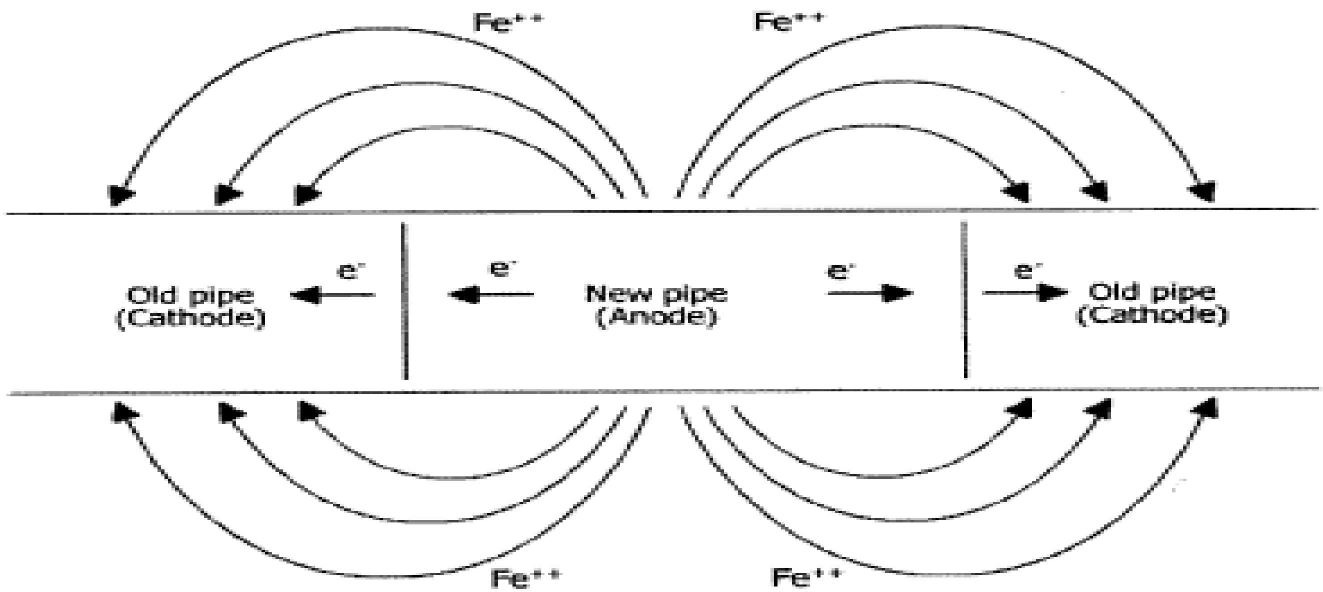
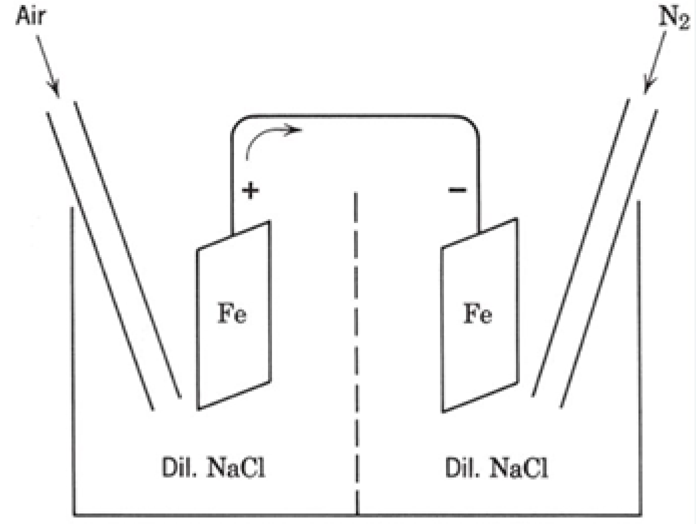


Figure 5.6 Dissimilar electrode cell formation by joining of an old pipe with a new pipe

Differential Aeration Cells

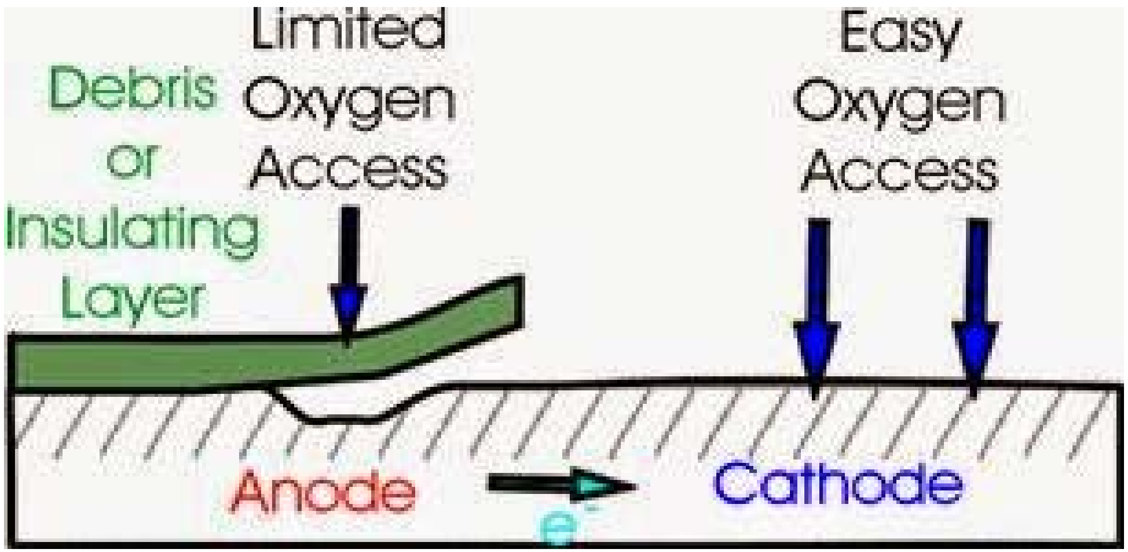


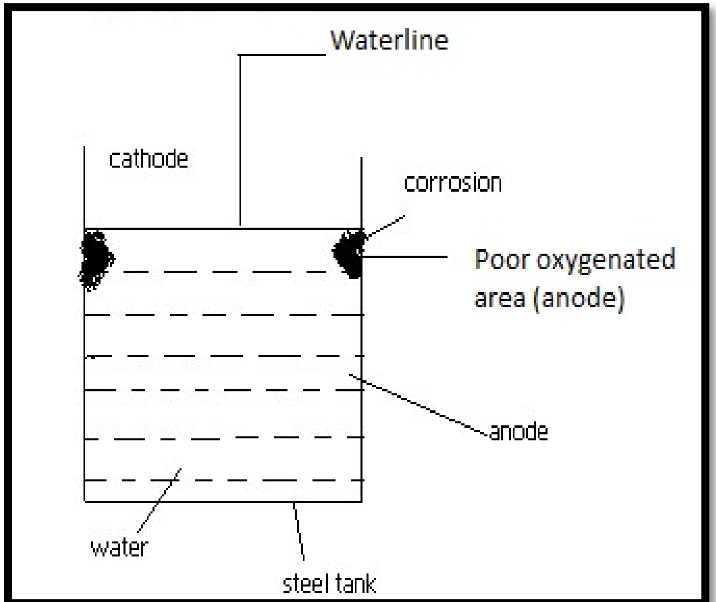
EXAMPLES:

1. Metal surface *partially covered* by droplets of electrolyte, dirt, slime debris or other impurities.
2. A partially-filled tank: oxygen-rich area over liquid level, oxygen-poor area below liquid level.
3. Ship body with little aeration at bottom, the rest exposed to more oxygen.
4. Part of pipeline buried in *uniform* soil with free oxygen supply, other part buried in soil receiving little oxygen.
5. Part of pipeline buried in sandy soil (high porosity- good aeration), other part buried in clay soil (low porosity- poor aeration).
6. One metal end exposed to soil, the other end to air.

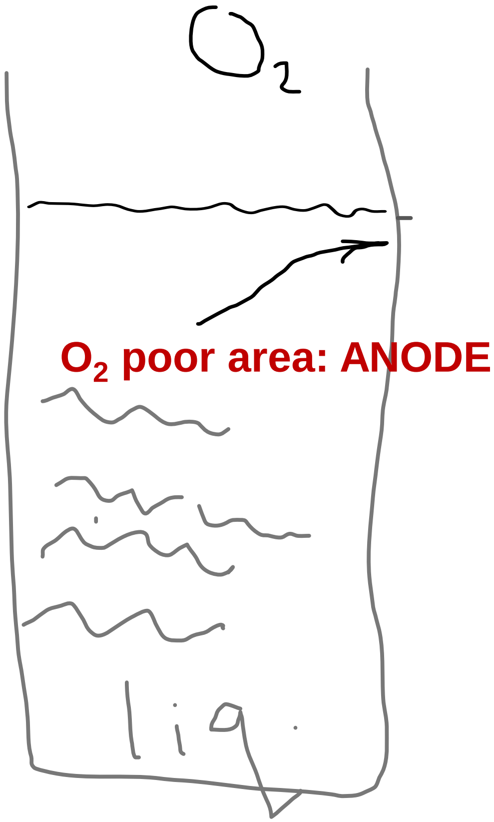
Differential Aeration Cells

- When water is stored in a steel tank, it is observed that the maximum amount of corrosion takes place along a line just beneath the level of the water meniscus.
- The area above the waterline (highly oxygenated) acts as cathodic and is not affected by corrosion.
- If the water is relatively free from acidity, little corrosion occurs.
- This type of corrosion is prevented to a great extent by painting the sides of the ships by antifouling paints.



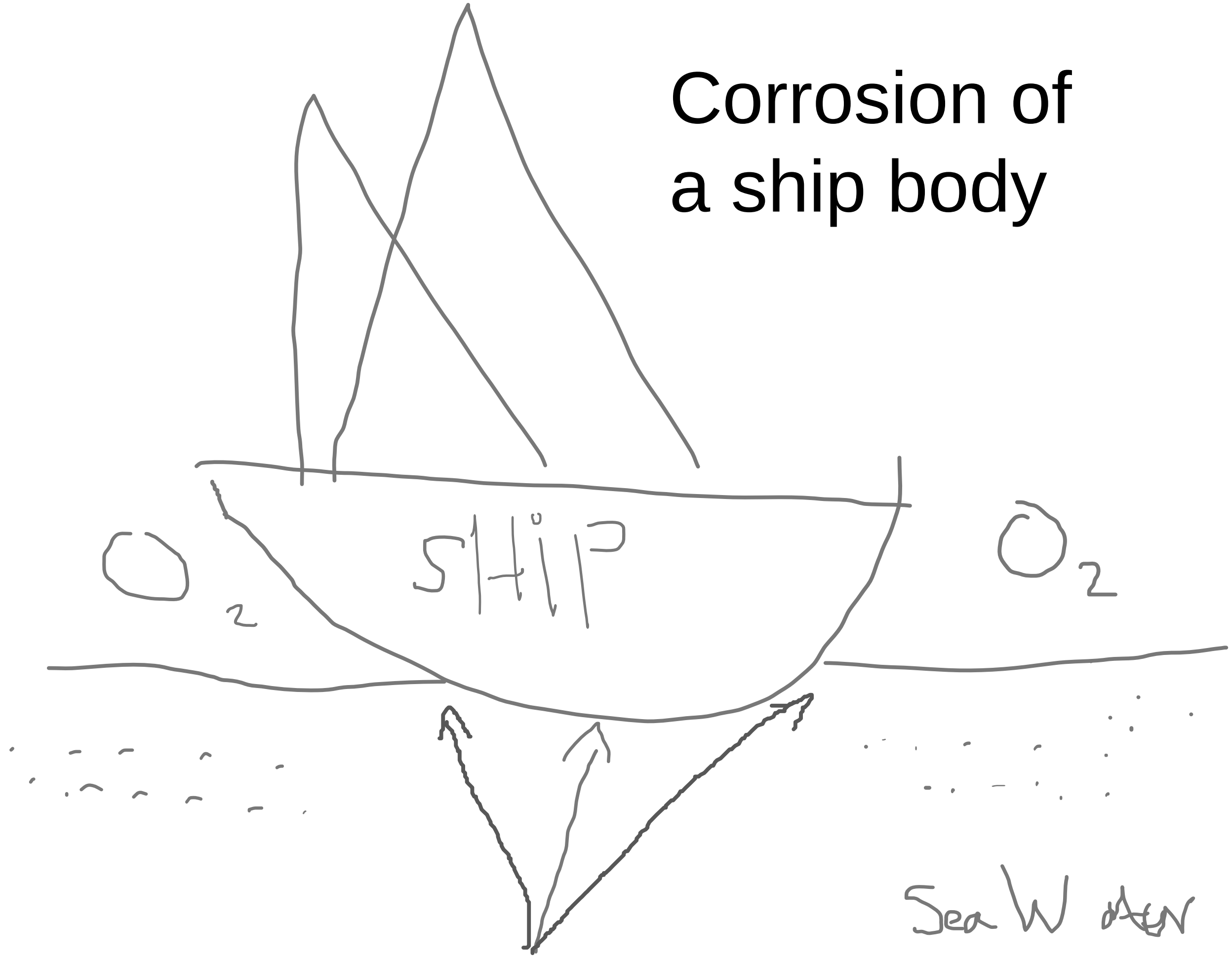


Differential Aeration Cells



Corrosion of a partially filled tank

Corrosion of a ship body



O_2 poor area: ANODE

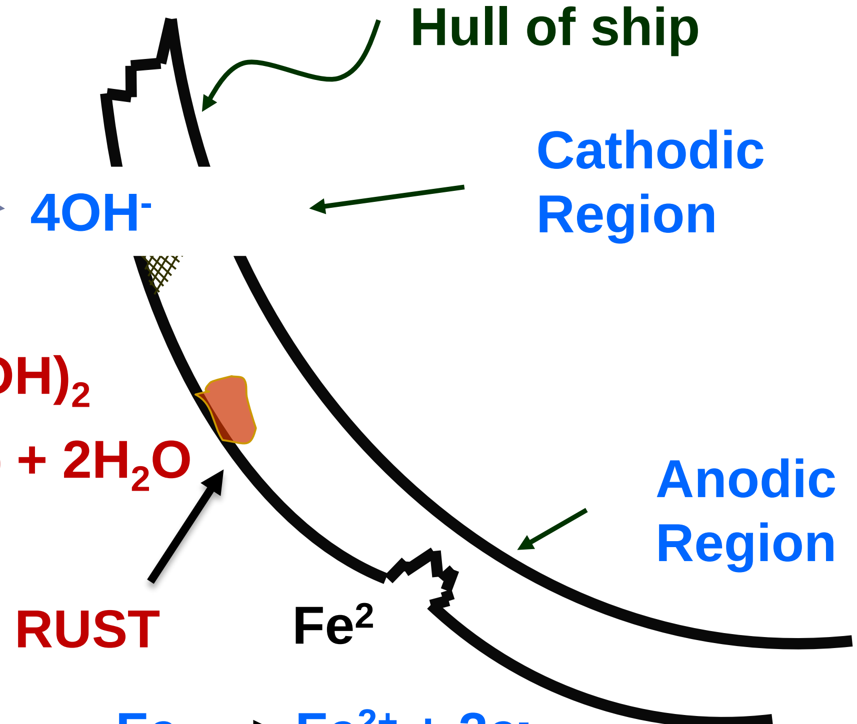
Corrosion of a Ship's Hull

Anodic and Cathodic Regions

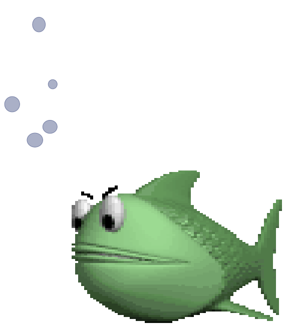
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

$4Fe(OH)_2 + O_2 \rightarrow 2(Fe_2O_3 \cdot H_2O) + 2H_2O$



$Fe \rightarrow Fe^{2+} + 2e^-$



Electrons Migrate from Anodic to Cathodic Region

Differential Aeration Cells
(Soil* Porosity Difference)

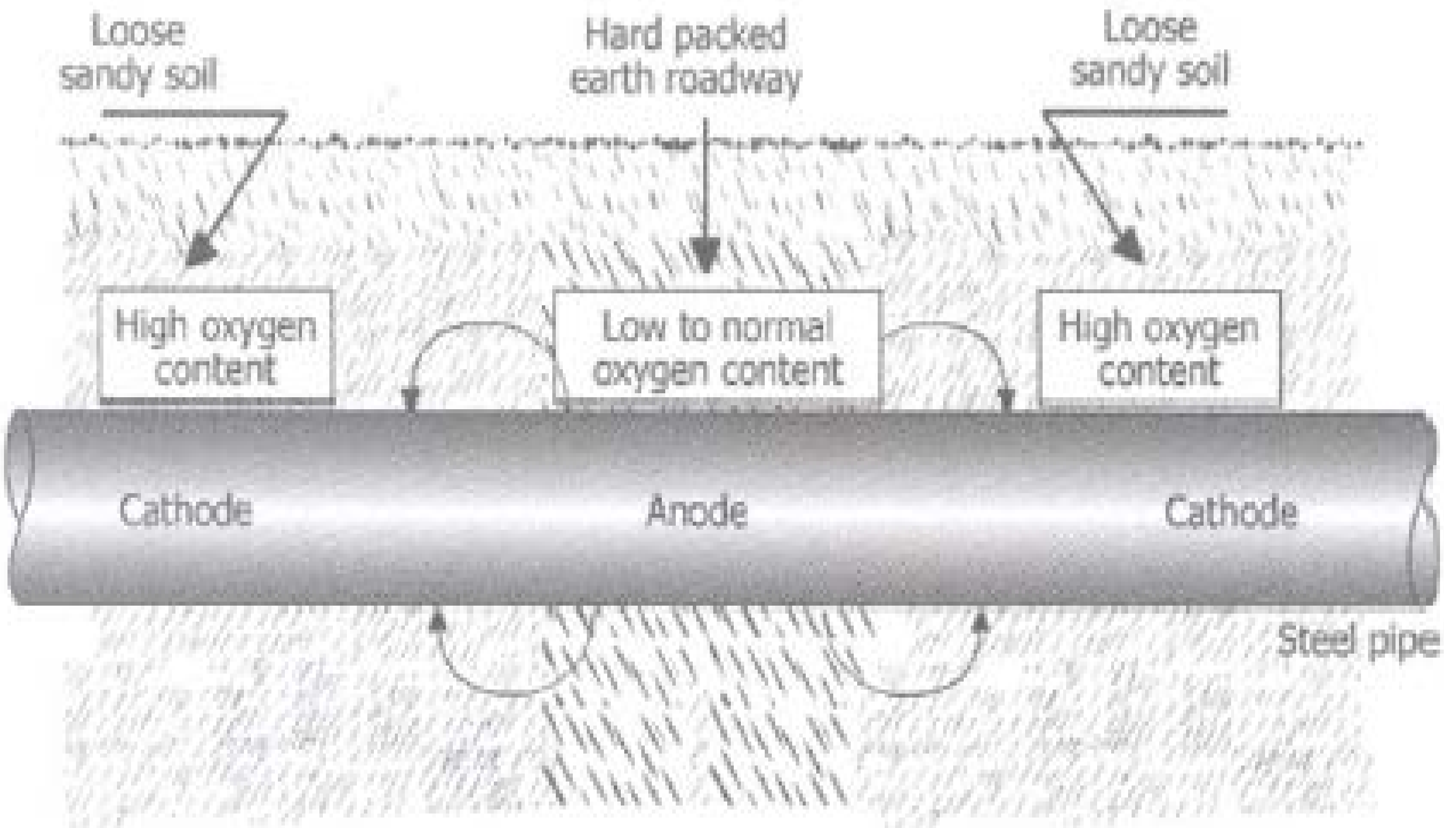


Figure 5.5 Formation of differential oxygen cells. (From CORRINTEC, USA, Presentation at KFUPM

*Same soil type

Differential Aeration Cells

- In the above examples:
  - oxygen- rich area forms the positive electrode of the cell, while
  - oxygen- poor area forms the negative electrode of the cell.

- The corrosion cell can be represented by:

Fe/ electrolyte/ O_2 / OH^-

- The reactions that occur in each case are similar to those mentioned earlier.

- Reactions that take place are:

  At anode (oxygen- poor area): $2\ Fe \rightarrow 2\ Fe^{2+} + 4\ e^-$
  At cathode (oxygen- rich area): $O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$

- In general, differential aeration corrosion takes place whenever there is O_2- rich and O_2- poor areas on the same metallic surface.

Differential Stress / Strain Cells

- This type of cells can be represented as follows:
  strained metal / electrolyte / unstrained metal
- <u>The cell reactions are:</u>
  Anode (strained): $Fe \rightarrow Fe^{2+} + 2\ e^-$
  Cathode (unstrained): $2\ H^+ + 2\ e- \rightarrow H_2$ (in acid medium)

or $O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$ (in neutral medium)

- Stresses may be internal (e.g. due to fabrication) or external (e.g. due to stretching or bending).

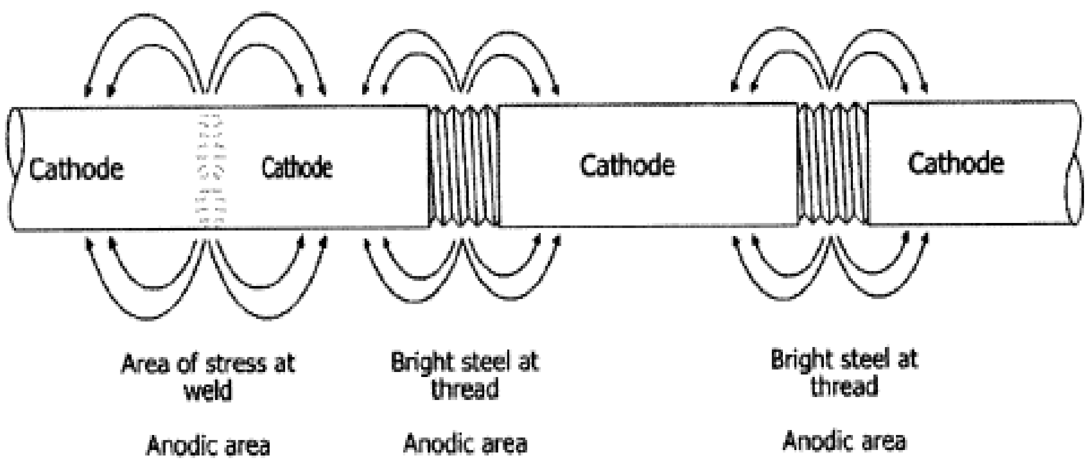


Figure 5.7 Stress cell. Corrosion caused by areas of stress and areas of bright steel on an underground pipeline

Different Moisture Content of Soil

- Part of metal *in contact with wet soil will* corrode (anode)
- Part in contact with dry soil will not corrode. Wet soil acts as electrolyte.

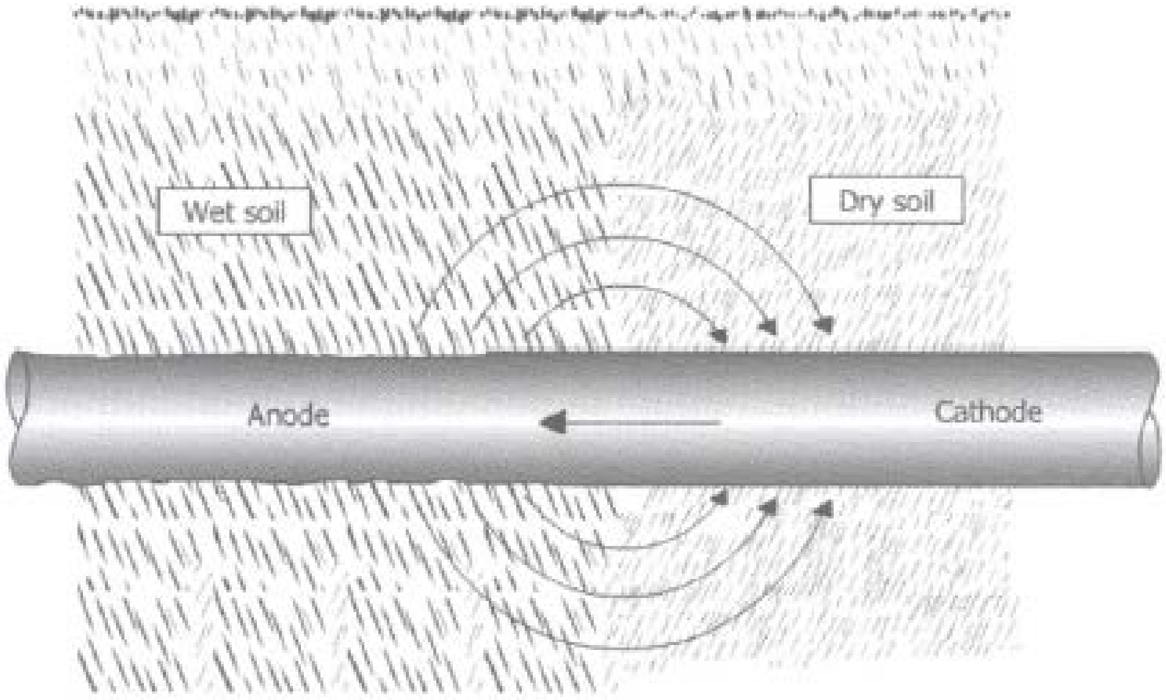


Figure 5.9 Differential concentration cell

More: Different types of soil gives similar effect

Exercise: Corrosion of a Soldered Brass Fitting

A brass fitting used in a marine application is joined by soldering with lead-tin solder. Will the brass or the solder corrode?

SOLUTION

From the galvanic series, we find that all of the copper-based alloys are more cathodic than a 50% Pb-50% Sn solder. Thus, *the solder is the anode and corrodes.*

In a similar manner, the corrosion of solder can contaminate water in freshwater plumbing systems with lead.

Types of Forms of Corrosion

Though the basic corrosion mechanism is the same, i.e. the oxidation of a metal due to transfer of electrons, conditions under which the process occurs can be vastly different, and has lead to the classification of corrosion into the following types:

1. Uniform
2. Galvanic
3. Crevice
4. Pitting
5. Inter-granular
6. Selective leaching
7. Erosion/cavitation
8. Stress corrosion
9. Fretting
10. High temperature.

These will be discussed in detail later.