CORROSION CONTROL

Methods of combating corrosion (protection of metals against corrosion)

The following methods are used to protect metals against corrosion:

- I. Selection of the right material of construction
- II. Surface coating.
- III. Inhibitors
- IV. Proper equipment design
- V. Electrical protection

I. Selection of the right material of construction

The right material of construction should have the following properties:

(1) high mechanical strength   (2) high corrosion resistance   (3) low cost

The following table shows the corrosion resistance of costructional materials.

Corrosion resistance of constructional materials?

Code designation for corrosion resistance
A = acceptable, can be used successfully
C = caution, resistance varies widely depending on conditions; used when some corrosion is permissible
X = unsuitable
Blank = information lacking

Code designation for gasket materials
a = asbestos, white (compressed or woven)
b = asbestos, blue (compressed or woven)
c = asbestos (compressed and rubber-bonded)
d = asbestos (woven and rubber-frictioned)
e = CR-S or natural rubber
f = Teflon

Chemical	Iron and steel	cast ion (Ni-resist)	18-8	18-8 Mo	Nickel	Monel	Red brass	Alumi- num	Indus- trial glass	Carbon (Kar- bate)	Phe- nolic resins (Ha- veg)	Acrylic resins (Lucite)	Vinyl- idene chlo- ride [Saran]	Acceptable nonmetallic gasket materials
Acetic acid. crude	C	C	C	C	C	C	C	A	A	A	A	A	C	b, c, d, f
Acetic acid, pure	X	X	C	A	C	A	X	A	A	A	A	X	X	b, c, d, f
Acetic anhydride	C	C	A	A	A	A	x	A	A	A	A	x	C	b, c, d, f
Acetone	A	A	A	A	A	A	A	A	A	A	C	X	C	a, e, f
Aluminum chloride	X	C	X	X	C	C	A	A	A	A	A		A	a, c, e, f
Aluminum sulfate	X	C	C	A	C	C	X	A	A	A	A	A	A	a, c, d, e, f
Alums	X	C	C	A	C	A	X	A	A	A	A	A	A	a, c, d, e, f
Ammonia (gas)	A	A	C	A	A	A	x	C	A	.	A		C	a, f
Ammonium chloride	C	A	C	C	A	A	C	C	A	A	A	A	A	b, c, d, e, f
Ammonium hydroxide	A	A	A	A	C	C	X	C	A		A	A	C	a, c, d, f
Ammonium phosphate (monobasic)	X	C	A	A		C	X	X	A	A	A		...	b, c, d, e, f
Ammonium phosphate (dibasic)	C	A	A	A		A	c	C	A	A	A			a, c, d, e, f
Ammonium phosphate (tribasic)	A	A	A	A	A	A	X	C	A	A	A	.	.	a, c, d, e, f
Ammonium sulfate	C	A	C	C	A	A	C	A	A	A	A	A	A	b, c, d, e, f
Aniline	A	A	A	A	. .	A	X	...	A	A	C	.	C	a, f

Chemical	Iron and steel	Cast iron (Ni-resist)	18-8	18-8 Mo	Nickel	Monel	Red brass	Aluminum	Industrial glass	Carbon (Karbate)	Phenolic resins (Haveg)	Acrylic resins (Lucite)	Vinylidene chloride (Saran)	Acceptable nonmetallic gasket materials
Benzene. benzol	A	A	A	A	A	A	A	A	A	A	A	..	C	a, f
Boric acid	X	C	A	A	A	A	C	A	A	A	A		A	a, c, d, e, f
Bromine	X	C	C	C	C	C	C	.	A	C	X		X	b. f
Calcium chloride	C	A	C	C	A	A	C	C	A	A	A	A	A	b, c, d, e, f
Calcium hydroxide	A	A	A	A		A	A	C						a, c, d, e, f
Calcium hypochlorite	x	C	C	A	C	C	C	C	A	A	C	...	C	b, c, d, f
Carbon tetrachloride	C	C	C	A	A	A	C	C	A	A	A	A	C	a, f
Carbonic acid	C	C	A	A	A	A	C	A	A	A	A	A	A	a. e, f
Chloracetic acid	x		x	X	C	C	X	C	A	A	A		..	b, f
Chlorine, dry	A	A	C	A	A	A	A	A	A	A	A	.	X	b, e, f
Chlorine. wet	x	x	X	X	X	X	x	X	A	C	A		X	b, e, f
Chromic acid	C	C	C	C	C	C	X	C	A	X	X	X	A	b. f
Citric acid	x	C	C	A	C	A	C	A	A	A	A	A	A	b, c, d, e, f
Copper sulfate	X	C	A	A	C	C	x	x	A	A	A	X		b, c, d, e, f
Ethanol	A	A	A	A	A	A	A	A	A	A	A	.	A	a, c, e, f
Ethylene glycol	A	A	A	A	A	A	A	A	A	A	A	A	C	a, c, e, f
Fatty acids	C	C	A	A	A	A	C	A	A	A	A	.	A	a, e, f
Ferric chloride	x	x	x	C	X	x	X	x	A	C	A		A	b, e, f
Ferric sulfate	X	x	C	A	C	C	X	C	A	C	A		A	b, c, e, f
Ferrous sulfate	C	A	A	A	A	A	C	C	A	A	A		C	
Formaldehyde	C	C	A	A	A	A	C	A	A	A	A		A	a, c, e, f
Formic acid	X		C	C	C	C	X	X	A	A	A		A	b, c, e, f
Glycerol	A	A		A	A	A	A	4	A	A	C	A	C	a, c, e, f
Hydrocarbons (aliphatic)	A	A	A	A	A	A	A	A	A	A	A	A	C	a, c, d, f
Hydrochloric acid	X	X	X	x	C	C	X	X	A	A	A	A	C	b, c, d, f
Hydrofluoric acid	C	x	X	X	C	C	X	x	x	A	C		C	b, f
Hydrogen peroxide	C	.	C	C	C	C	C	A	A	A	A	A	C	a. e, f
Lactic acid	x	C	C	A	C	C	A	C	A	A	A			a, b, c, d, e, f
Magnesium chloride	C	C	C	C	A	A	C	C	A	A	A		A	b, c, e, f
Magnesium sulfate	A	A	A	A	A	A	A	A	A		A		A	b, c, e, f
Methanol	A	A	A	A	A	A	A	A	A	A	A		A	a, c, e, f
Nitric acid	X	C	C	C	X	x	X	C	A	C	c		c	b, f
Oleic acid	C	C	A	A	A	A	C	A	A	A	A		A	a, e, f
Oxalic acid	C	C	C	C	C	A	C	C	A	A	A			b, c, d, e, f
Phenol (carbolic acid)	C	4	C	A	A	A	C	A	A	A	C	A	C	a, f
Phosphoric acid	C	C	C	A	C	c	X	X	C	A	A		A	b, c, f
Potassium hydroxide	C	C	A	A	A	A	X	x					C	a, e, f
Sodium bisulfate	X	C	A	A	A	A	C	C	A	A	A		A	b, c, d, e, f

Corrosion resistance of constructional materials† (Continued)

Chemical	Metals								Nonmetals					
	Iron and steel	Cast iron (Ni-resist)	Stainless steel		Nickel	Monel	Red brass	Aluminum	Industrial glass	Carbon (Karbate)	Phenolic resins (Haveg)	Acrylic resins (Lucite)	Vinylidene chloride (Saran)	Acceptable nonmetallic gasket materials
			18-8	18-8 Mo										
Sodium carbonate	A	A	A	A	A	A	C	C	C	A	A	X	.	a, c, d, e, f
Sodium chloride	A	A	C	C	A	A	C	C	A	A	A		.	a, c, d, e, f
Sodium hydroxide	A	A	A	A	A	A	C	X	C	A	A	A	C	a, c, d, f
Sodium hypochlorite	X	C	C	A	C	C	C	X	A	C	X		A	b, c, d, f
Sodium nitrate	A	A	A	A	A	A	C	A	A	A	A		.	b, c, d, e, f
Sodium sulfate	A	A	A	C	A	A	A	A	A	A	A	...	A	a, c, d, e, f
Sodium sulfide	A	A	C	A	A	A	X	X	C	A	A		.	a, e, f
Sodium sulfite	A	A	A	A	A	A	C	C	A	A	A			
Sodium thiosulfate	C		A	A	A	A	C	C	A	A	A	...	A	a, c, d, e, f
Stearic acid	C	A	A	A	A	A	C	A	A	A	A			a, e, f
Sulfur	A	C	C	C	C	C	C	C	A	A	A		.	a, e, f
Sulfur dioxide	C	C	C	C	C	C	C	A	A	A	A		A	a, f
Sulfuric acid (98 % to fuming)	A	C	x	C	x	X	X	C	A	X	X	X	C	b, f
Sulfuric acid (75–95 %)	A	C	x	X	X	C	X	X	A	C	X	X	C	b, f
Sulfuric acid (10–75 %)	X	C	x	X	C	C	X	X	A	A	C	C	A	b, f
Sulfuric acid (<10 %)	X	C	X	C	C	C	C	C	A	A	C	A	A	a. b, c, e, f
Sulfurous acid	X	.	C	A	X	X	C	C	A	A	A	...	C	b, c, d, e, f
Trichloroethylene	C	A	C	A	A	A	C	C	A	A	A	...	C	a, f
Zinc chloride	C	C	C	X	A	A	X	C	.	...	A	A	..	b, c, d, e, f
Zinc sulfate	C	A	A	A	A	A	C	C	.	..	.	...	..	b, c, d, e, f

†From miscellaneous sources. For additional details, see "Chemical Engineers' Handbook," 6th ed., McGraw-Hill Book Company, New York, 1984.

Chemical resistance of plastics in various solvents?

	PVC rigid	PVC plasticized	Poly-ethylene	Poly-propylene	Meth-acrylates	Poly-esters	Epox-ies	Fluoro-carbon	Poly-sty-rene	ABS Polymers	Acetal poly-mers	Phenol-formal-dehyde	Poly-car-bonate	Cl-poly-ether	Furan	Saran
Acetone	U	U	S	S	U	U	F	S?	U	U	S_1	U	S	S	F	S
Alcohols, methyl	S	St	S_1	S_1	S	S_1	S	S_2	S	S_1	S_1	F	S_1	S_2	S	S_1
ethyl	S	S_1	S_1	S_1	S	S_1	S	S_2	S	S_1	S_1	F	S_1	S_2	S	S_1
butyl	S	S_1	S_1	S_1	S	S_1	S	S_2	S	S	S_1	F	S_1	S_2	S	S_1
Aniline	U	U	S	S			S	S_2	S	U		U		F	U	U
Benzene	U	U	U	U	U	S_1	S	S_2	U	U	S	S	U	S	S	F
Carbon tetrachloride	U	U	U	U	U	S_3	S	S_2	U	U	S_1	S	U	S_2	S	S
Cyclohexanone	U	U						S_2		U						U
Ethyl acetate	U	U	U	U	U	U	F	S_2	U	U		U	U	S	S	F
Ethylene dichloride	U	U	U	U	U	U	F	S_2	U	U	S	S	U	S_2		S
Ethyl ether	U	U	S	S	U		S	S_2	U	U	S_1	S	S_1	S_2	S	U
Hexane	S	U	F	F	S	S	S	S_2	U	F	S	S	S_1	S	S	S_1
Kerosene	S	S_1	S	S	S	S	S	S?	U	F	S	S	S_1	S	S	S_1
Lubricating oils	S_1	S	S	S	S	S	S_2	S_2	F	S	S	S	S_1	S_2	S	S_1
Naphthalene	U	U	S	S	U	S	S	S?	U	U	S	S	F	S_2	S	S_1
Triethanolamine	S_1	S	S	S				S_2						S_2		
Xylene	U	U	U	U	U	S_2	S	S_2	U	U	S_1	S	U	S	S	F

†From Biennial Materials of Construction Reports published by *Chemical Engineering*.

Table 1, corrosion resistance of constructional materials

The material selection is carried out through the following steps

1. Preliminary selection

Based on experience, availability and safety aspects

2. Laboratory testing

Reevaluation of apparently suitable materials under process conditions

3. Interpretation of laboratory results and other data

Effect of possible impurities, excess temperature, excess pressure, agitation, and presence of air in equipment

4. Economic comparison of apparently suitable materials

Material and maintenance cost, probable life, cost of product degradation, and liability to special hazards

5. Final selection

II. Surface coating

There are two types of surface coating:
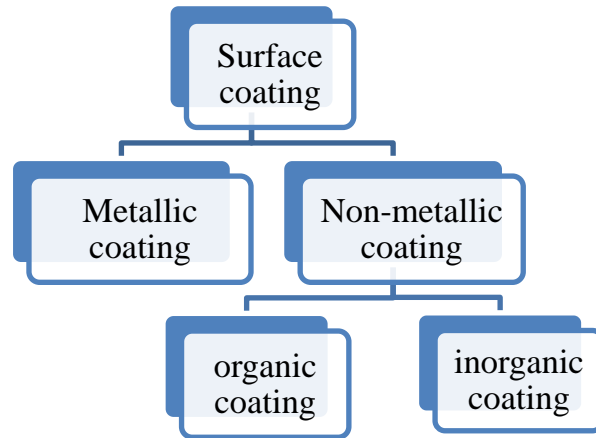
A. Metallic coating

The structure is coated with a layer of other metal which may be <u>more noble</u> than the structure or <u>less noble</u> than it e.g. steel structures can be coated with copper which is more noble than steel or zinc which is less noble. In case of coating the structure with a more noble metal care should be taken that the coat is free from pores or cracks to avoid the formation of dissimilar metal corrosion cells which would lead to corrosion of the structure.

Factors that must be considered in selection of a coating metal:

1. The coating should be able to resist direct attack of the environment.
2. The coating should be nonporous and continuous (no cracks) to a void acceleration of corrosion especially in case of a more noble metal (ex: coating of Fe by Cu).
3. The coating should be hard.

In case of coating the structure with a less noble metal the presence of pores and cracks in the coat is not dangerous because in this case the less noble metal will corrode by the formation of dissimilar metal cells while the structure will remain protected.

Question: give reasons

It is preferred to coat steel with Zn rather than with Cu.

In practice metallic coating is carried out by different methods such:

(1) Electroplating,

(2) Hot dipping of the work piece in molten metal covered with a flux,

(3) Spraying of the molten metal on the work piece.

(1) Electroplating

➤ Electroplating is the method of coating one metal with another. It is most commonly used for decorative purposes, appearance and protection.

➤ Electroplated items include chrome bumpers, jewelry, electronics, circuit boards and airplane parts.

Electroplating procedure

1. Preparation of the workpiece. Solutions such as alkaline cleaners, solvent degreasers or acidic pickling mixtures are used to remove dirt, greases, oxidation and contaminants from the piece.

2. The piece to be plated is connected to the negative pole (cathode) of the d. c. power supply while the plating (coating) metal anode is connected to the positive pole (anode). Multi-range ammeter (in series) and voltmeter (in parallel) are connected to the cell to measure the cell current and voltage.

3. The piece is then immersed in the plating solution until coated and rinsed and then buffed or polished, if necessary.

Note: The plating time depends on the required thickness and can be calculated from Faraday's law.

Factors affecting coating quality:

The quality of coating depends on:

1. Average thickness of coating
2. Porosity and continuity
3. Uniformity of thickness
4. Adherence
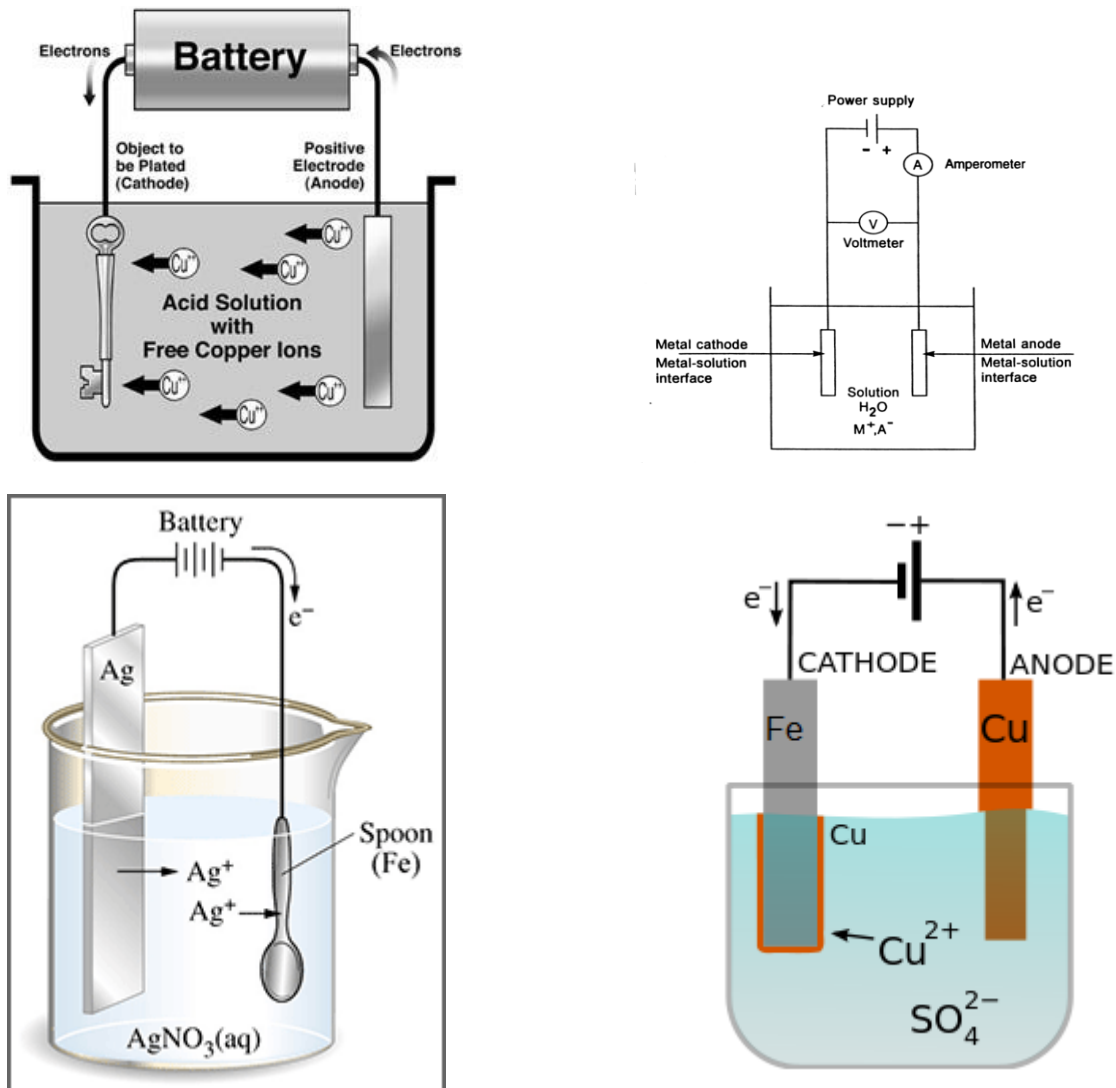
Fig. 1, Some examples for electroplating process

(2) Hot dipping of the work piece in molten metal covered with a flux

There are two common processes of hot dipping:

1. Hot dipping galvanizing

➤ It is a hot coating process whereby the cleaned steel is immersed in molten zinc usually at a temperature of between 445 °C and 450 °C.

➤ When the cleaned steel is immersed into the molten zinc, a chemical reaction results, which we refer to as following "metallurgical laws".

➤ As a result of this process the coating consists of a series of zinc iron alloy layers (inter-metallic layer) and usually a top pure zinc layer. The adhesion of the coating to the steel is therefore determined by means of a chemical bond, or a "metallurgical bond". Such bonding is considered to be far superior to that of a mechanical bond.

➤ A hot dipped galvanized coating will provide greater corrosion protection to steel when compared to that of an electroplated product.
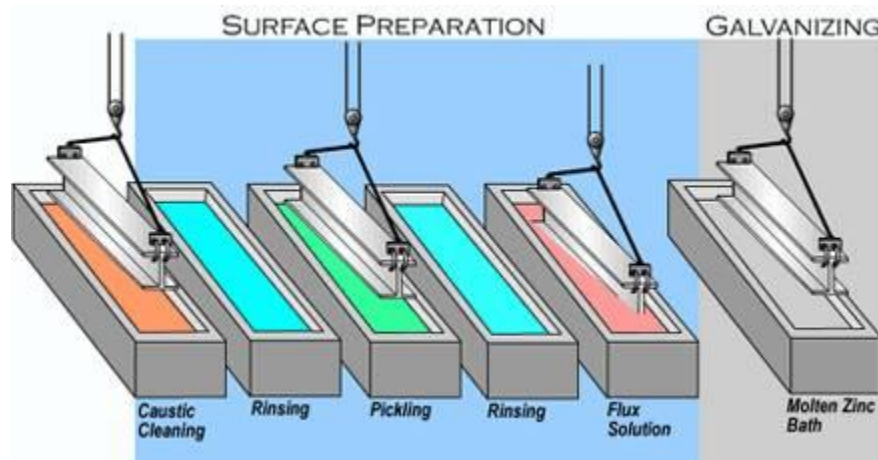
Fig. 2, Hot dipping galvanizing of steel
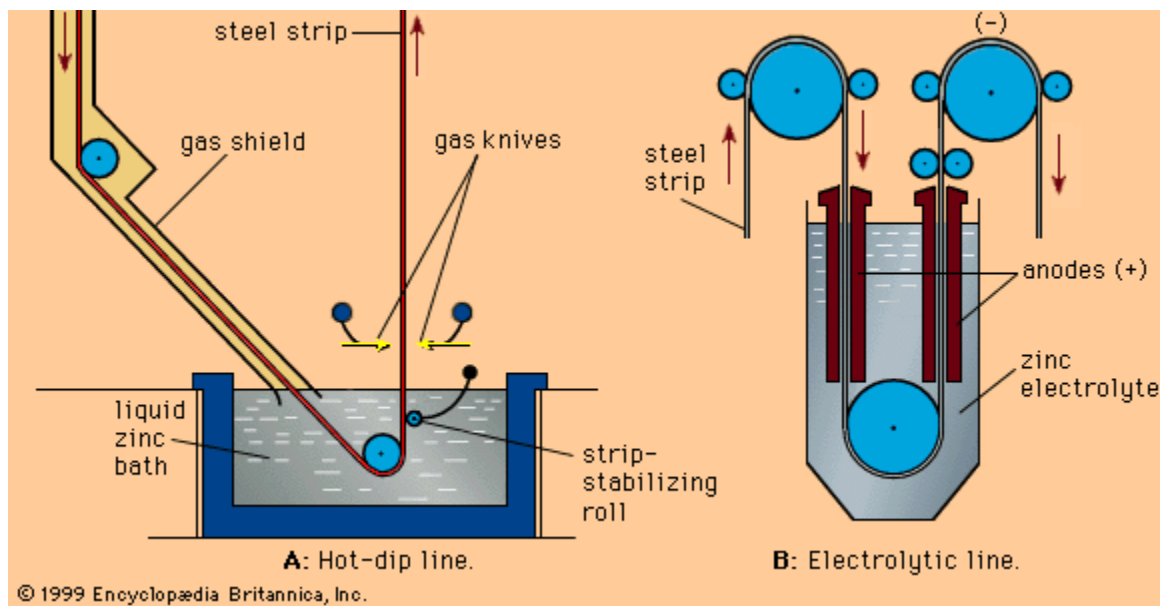
Fig. 3, Galvanization of steel by hot dipping and electroplating

Note: Coating of steel with Zn is called galvanization. It may be carried out by hot dipping or electroplating.

2. Hot-dipped tin plating

Tinning is the process of thinly coating sheets of iron or steel with tin, and the resulting product is known as **tinplate**. It is most often used to prevent rust

Tinplate made via hot-dipped tin plating is made by cold rolling steel or iron, pickling or remove any scale, annealing to remove any strain hardening, and then coating it with a thin layer of tin. The attached figure shows the tinning process steps.
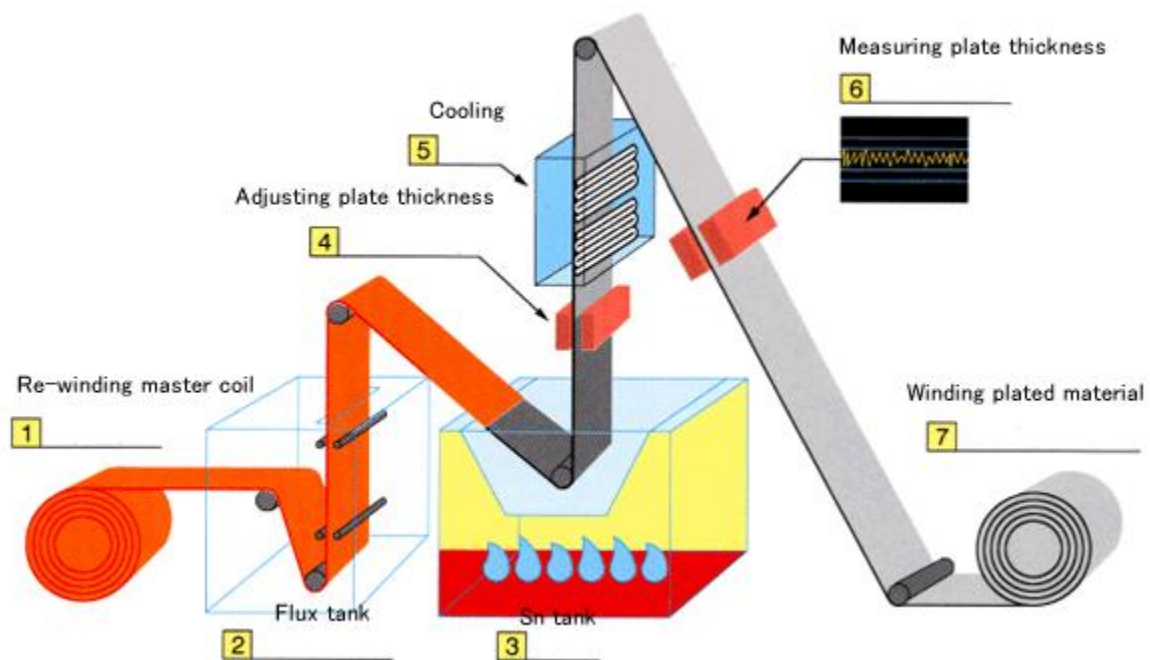
Fig. 4, Basic concept of hot dipped tin plating process

Advantage of hot dipping process
- ➢ No waste from production process.
- ➢ No hazardous substance (such as cyanogens, lead, etc.) is used at all in production process.
- ➢ The coating metal and the base metal are strongly bonded as inter-metallic layer formed.
- ➢ Provide greater corrosion protection to steel when compared to that of an electroplated product.

(3) Spraying of the molten metal on the work piece.

➢ Thermal spraying refers to a process by which a metal wire or powder is melted and sprayed onto a surface to form a coating.

➢ A thermal spray gun is used to apply the coatings.

➢ The thermal spray gun heats the metallic wire or powder to a molten state and compressed air or other gas propels it onto the surface to form a coating. The compressed gas also aids in division and atomization of the molten coating.

➢ The two metals most commonly applied by thermal spray are zinc and aluminum. These metals and their alloys provide excellent protection in a variety of marine and industrial corrosive environments.

Questions:

1. Sketch a simple cell for galvanization of steel one by electroplating and one by hot dipping
2. What are the advantages of hot dipping when compared with electroplating as a method for metallic coating?
3. What are the main factors that should be considered when selecting a coating metal and what are the main factors affecting the coating quality?
4. Explain the main steps involved in electroplating process with the help of simple sketch.
5. Why it is preferred to coat steel with zinc rather than with copper.

Non-metallic coating (the second method of surface coating)

There are two types of nonmetallic coating:

A. Inorganic coating

Methods of inorganic coating:

i. Oxidation (passivation)

Steel can be coated with an oxide film by a). Heating at high temperature, b). Chemical oxidation by treating steel with hot alkaline nitrate, or persulphate or perchlorate c). Anodic oxidation by making the steel structure an anode in electrolytic cell

ii. Phosphating

Steel is coated with a layer of iron phosphate by dipping in a solution containing phosphoric acid and zinc phosphate. The iron phosphate film is not highly protective because it is porous so it usually covered with paint. The phosphate film improves the bond between the metal and the paint.

i.e. Phosphating is a pre-painting step.

iii. Enamels

Enamels are glassy layer applied to the metal by dipping it in a suspension of powdered glass, and then the metal is heated in a stove (furnace) at high temperature where the glass powder melts and coat the metal.

iv. Cement coating

It is used to coat the inner side of steel pipelines carrying water or wastewater.

Fig. 5, Cement coating of the inner wall of water steel pipeline

B. <u>Organic coating</u> such as the following:

i. <u>Paints</u>:

Paint consists of;

1. a film forming substance such as linseed oil or a polymer (resin),
2. an organic solvent and
3. a pigment (usually an inorganic oxide or metal powder).

Before applying paint to a steel surface, the metal surface should be cleaned of oxides by sand blasting or acid pickling. After cleaning, the metal surface is coated with a thin layer of primer.

What is primer?

A primer is a paint containing a pigment such as lead oxide (Pb_3O_4 red lead) or zinc chromate which <u>oxidizes the steel surface and inhibits its corrosion</u>. Besides, <u>the primer film increases the strength of the bond between steel and final paint film</u>. When the primer film dries a thick film of the required paint is applied over the primer.

Polymers such as alkyd resins, PVC, polyethylene, polyesters, acrylics, polyurethanes, chlorinated rubber, epoxy resins, etc. are used in paint manufacture. For severe conditions such marine and industrial atmosphere, a paint containing epoxy resin (water resistant) is suitable.

ii. <u>Lacquers:</u>

A lacquer consists of a thermoplastic polymer dissolved in an organic solvent. Lacquers can be used to line steel tanks holding corrosive chemicals such as acids.

iii.<u>Coal tar</u>

Coal tar is a brown or black liquid of extremely high viscosity. Coal tar is among the by-products when coal is carbonized to make coke or gasified to make coal gas. Coal tars are complex and variable mixtures of phenols, polycyclic aromatic hydrocarbons (PAHs), and heterocyclic compounds, about 200 substances in all.

It is used to protect <u>underground structures</u>. A 50% coal tar + 50% epoxy is superior to coal tar.

Fig. 6, Coating of outside surface of pipeline with coal tar + epoxy

iv. <u>Temporary coating:</u>

It is used to protect metallic structures during shipping and storage by coating the structure with layer of lubricating oil which can be removed by an organic solvent when the structure is put to service.

III. <u>Corrosion Inhibitors</u>

Required: definition, mechanism and types

➢ <u>Definition of corrosion inhibitors:</u>

Corrosion inhibitors are substances that are added in small amount (e.g 0.1%) to the corrosive medium stop or slow down electrochemical corrosion reactions on a metal surface.

➢ <u>Mechanism:</u>

Corrosion inhibitors work by one or more of the following mechanisms.

• They adsorb on metal surfaces to form protective films.

• They combine with corrosion product films to protect metal surfaces.

• They form precipitates, which visibly coat and protect metal surfaces.

Types of inhibitors:

➢ Inhibitors can be divided into two main categories—inorganic and organic.

➢ Inorganic inhibitors are used mainly in boilers, cooling towers, and fractionation units.

➢ Organic inhibitors are used mainly in oil field systems.

As shown in the figure, inorganic inhibitors are further divided into anodic and cathodic classifications. These classifications describe the part of the electrochemical process that is interrupted by the inhibitor. Organic film-forming inhibitors interrupt both the anodic and cathodic processes.
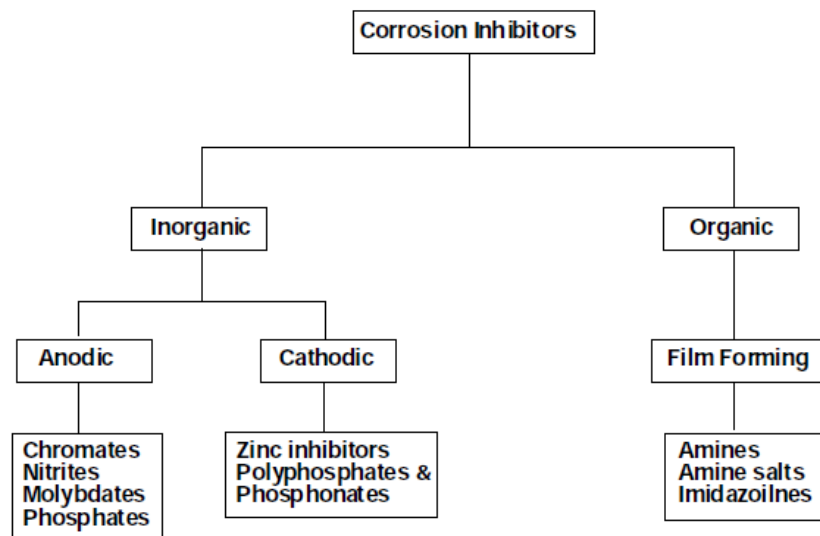
Classification of corrosion inhibitors

Inorganic inhibitors

1. **Cathodic inhibitors:**

Cathodic inhibitors are chemical compounds which inhibit the cathodic reaction of the corrosion cell.

Examples of cathodic inhibitors:-

a. Compounds such as ZnSO$_4$, MgSO$_4$ and Ca(HCO$_3$)$_2$, these compounds inhibit the cathodic reaction by forming insoluble Zn(OH)$_2$ film or Mg(OH)$_2$ film or CaCO$_3$ film with the cathodically formed OH^- ions (in neutral solutions) the insoluble film isolates the cathodic regions of the corrosion cells from the corrosive medium and stops corrosion.

b. Oxygen scavengers, these are compounds which react with dissolved oxygen and remove it from the neutral or alkaline corrosive environment such as sodium sulphite or hydrazine (used to inhibit boiler corrosion and are called high temperature oxygen scavengers)

$$Na_2SO_3 + \frac{1}{2} O_2 \xrightarrow{yields} Na_2SO_4$$

$$N_2H_4 + O_2 \xrightarrow{yields} N_2 + 2H_2O$$
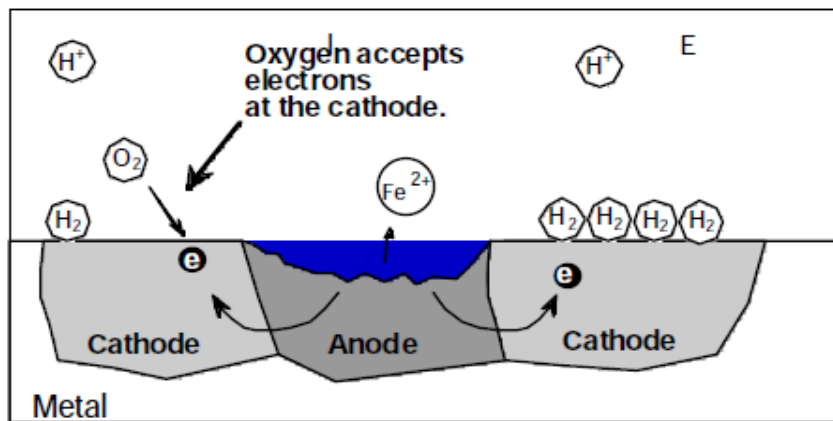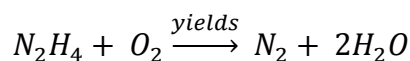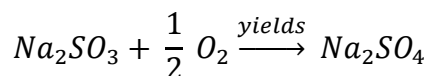
Fig. 7, Oxygen depolarize the cathode

c. Compounds such as arsenic (As), mercury (Hg), antimony (Sb) salts which are added to acidic corrosive environments to slowdown the cathodic H$_2$ evolution reaction.

➢ These compounds prevent the hydrogen atoms from forming hydrogen gas, and are called cathodic poisons.

➢ Cathodic poisons are used advantageously as corrosion inhibitors by stifling the cathodic reduction processes that must balance the anodic corrosion reaction. However cathodic poisons can also increase the susceptibility of a metal to hydrogen induced cracking since hydrogen can also be absorbed by metal during aqueous corrosion or cathodic charging.

When corrosion occurs in a low-pH solution, some of the reduced hydrogen does not form gaseous hydrogen, but instead, diffuses into the metal as atomic hydrogen and form metal hydride causing hydrogen embrittlement.

Note:

Also substances such as sulfur, selenium, tellurium, and cyanide ions do the same effect.

2. **Anodic inhibitors:** Are chemical compounds which inhibit the anodic reaction of the corrosive cells.

Examples

a. Compounds such as Na_2SiO_3, Na_2CO_3 and Na_3PO_4, these compounds form with the anodically formed Fe^{++} an insoluble film of iron silicate or iron carbonate or iron phosphate which isolates the anodic sites of the corrosion cells from the corrosive solution.

b. Passivators: these are oxidizing agents such as chromate inhibitors ($Na_2Cr_2O_7$) or nitrite inhibitors ($NaNO_2$) which react with the anodically formed Fe^{++} to form a passive oxide film on the anodic sites of the corrosion cells.

$$Na_2Cr_2O_7 + 2Fe^{++} + H_2O \xrightarrow{yields} Cr_2O_3 + Fe_2O_3 + 2NaOH$$

$$NaNO_2 + 2Fe^{++} + 2H_2O \xrightarrow{yields} NH_3 + Fe_2O_3 + NaOH$$
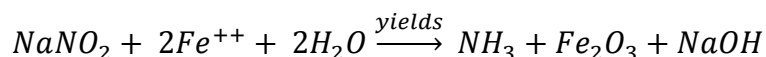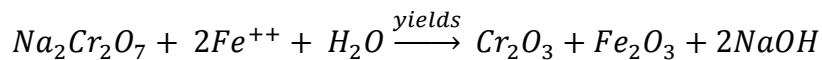
Chromate inhibitors are the most effective of the anodic inhibitors. They were used for many years in cooling towers and other recirculating cooling water systems; however, they are toxic to most organisms. Chromate inhibitors contain sodium chromate, Na_2CrO_4, or sodium dichromate, $Na_2Cr_2O_7$. Chromate, or dichromate, ions accept electrons that are lost in ferrous iron oxidation reactions. This reduction reaction forms chromium (III) oxide (Cr_2O_3). The chromium oxide combines with iron oxide to form a mixed oxide. This combination of iron oxide and chromium oxide makes chromium inhibitors effective. Normally, iron oxide deposits are loosely attached to metal surfaces. However, the combination of iron oxide and chromium oxide forms a deposit that tightly attaches to the metal surface.

$Na_2Cr_2O_7$ (0.2%, PH =8) was used widely in industry to protect the cooling system of the plant against corrosion. Recently chromate has been replaced by a mixture of Zn++, polyphosphate

and chromate which is less harmful to the environment because the mixture uses a lower doze of the toxic CrO_4^{--}. More recently zinc phosphate is being used without chromates.

Nitrite inhibitors may be used to replace the more toxic chromates. Sodium nitrite ($NaNO_2$) is used in closed, recirculating cooling water systems with a pH between 7 and 9. Nitrites perform similarly to chromates. They form a protective iron oxide film that passivates steel surfaces. Nitrites can reduce corrosion rates to less than 2 mpy. They are environmentally acceptable and easy to monitor.

Note:

Nitrites easily oxidize to nitrates. Nitrates are not effective corrosion inhibitors. That is why nitrites are used in closed systems.

3. **Adsorption Inhibitors: (organic inhibitors)**

These are organic compounds which contain a polar group such as NH_2 (amino group), these compounds (RNH_2) adsorb on the metallic surface and isolate it from the corrosive solution (usually acids).

Organic corrosion inhibitors are complex mixtures of many different molecular compounds. Organic inhibitors typically affect both anodic and cathodic areas of corrosion cells. They lay down an organic film on the entire metal surface. Their effectiveness depends upon the following conditions:

- the electrical potential of the metal
- the chemical structure of the inhibitor molecule
- the size and shape of the inhibitor molecule

An organic corrosion inhibitor molecule consists of a hydrocarbon chain that is attached to a strongly polar functional group. The hydrocarbon chain of the inhibitor molecule is oil soluble. This chain provides a barrier that keeps water away from the metal surface. The length of the

hydrocarbon chain varies (e.g., carbon numbers between 12 and 18). Polar functional groups are based on nitrogen, sulfur, or oxygen.

Most organic inhibitors used in the petroleum industry contain at least one nitrogen functional group. Frequently, these nitrogen-based inhibitors are reacted with organic acids, or they contain oxygen functional groups. The amine (NH2) portion of the molecule is water soluble and has a pair of unshared electrons. These electrons are available to bond with metal surfaces.
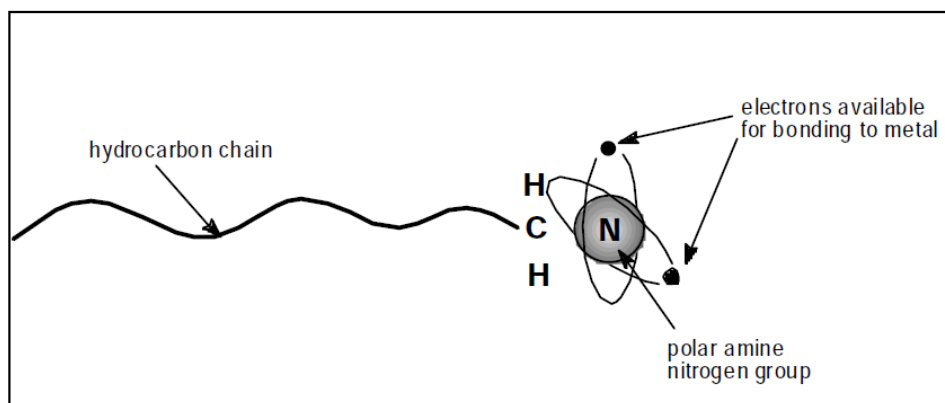

Fig. 8, Organic inhibitor molecule

Organic inhibitor molecules attach to metal surfaces by chemisorption and physical adsorption. When a metal is in contact with an aqueous solution, most of the metal surface is covered with adsorbed water molecules. If an organic inhibitor is introduced into the system, the unshared electrons in the polar amine group form a chemisorption bond with the metal surface. The chemisorption bond displaces water molecules and other corrosive agents from the metal surface. The long hydrocarbon chains also play an important part in the inhibition process. The hydrocarbon chains are oil soluble and attract crude oil molecules in the process stream. Together, the hydrocarbon chains and oil molecules form an oily layer several molecules thick. This oily layer acts as a barrier against corrosive fluids. The oily layer also increases the film life of the inhibitor. In addition to the chemisorption bond, organic inhibitors also physically adsorb to the metal surface. Physical adsorption is weaker than chemisorption. Physical adsorption does not involve a sharing of electrons with the metal surface. The figure below shows the molecular structures of some common oil field corrosion inhibitors.

Note:

Organic inhibitor molecules can be modified to increase their solubility or dispersibility in brine. These modifications include adding more polar groups to each inhibitor molecule. Sometimes,

the dispersibility of an oil soluble inhibitor is increased by blending it with a surfactant. This blending technique helps to disperse the oil soluble inhibitor into both the oil and water phases.

Name	Structure
Primary Amine	$R-NH_2$
Amide	$R-CONH_2$
Imidazoline	(Imidazoline ring structure with $R-C$, $N-CH_2$, $N-CH_2$, R^1)
Polyethoxylated Amines	$R-N$ with $(CH_2CH_2O)_y-H$ and $(CH_2CH_2O)_x-H$

Fig. 9, Molecular structure of some organic inhibitors

Questions:

Complete:

1. inorganic coating involves:

   a)……………… b)……………… c)……………… d)………………

2. organic coating involves:

   a)……………… b)……………… c)……………… d)………………

3. What is acid pickling and at what conditions it is used?

4. What is primer and what its function?

5. What are cathodic poisons? Give examples.

6. Why are nitrites not used in open systems as corrosion inhibitor?

7. Suggest a suitable method of corrosion protection for the following cases:

   ➢ Underground pipeline carrying wastewater

   ➢ Steel tank containing saline water

8. Give reasons:

   ➢ Chemicals such as Na_2SO_3 and Na_2CO_3 inhibit corrosion

   ➢ N_2H_4 is added to water feed boilers (WFB)

4. Electrical protection

A. Cathodic protection

Technique to reduce corrosion of a metal surface by making that surface the cathode of an electrochemical cell.

Cathodic protection is a method to reduce corrosion by minimizing the difference in potential between anode and cathode. This is achieved by applying a current to the structure to be protected (such as a pipeline) from some outside source. When enough current is applied, the whole structure will be at one potential; thus, anode and cathode sites will not exist. Cathodic protection is commonly used on many types of structures, such as pipelines, underground storage tanks and ship hulls.

Types of cathodic protection systems

There are two main types of cathodic protection systems:

  a) **Galvanic system (sacrificial anode method)**
  b) **Impressed current method**

The figures below show these two types. Note that both types have anodes (from which current flows into the electrolyte), a continuous electrolyte from the anode to the protected structure, and an external metallic connection (wire). These items are essential for all cathodic protection systems.

Fig. 10, Internal cathodic protection of pipeline by sacrificial anode method

Fig. 11, External cathodic protection of water pipeline by sacrificial anode method
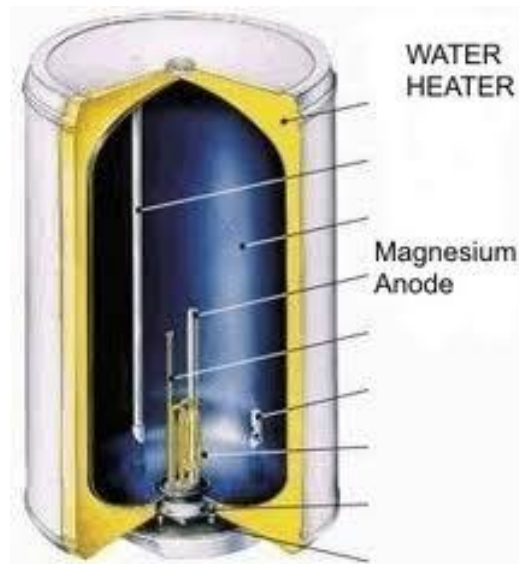
Fig. 12, Cathodic protection of water heater by sacrificial anode method
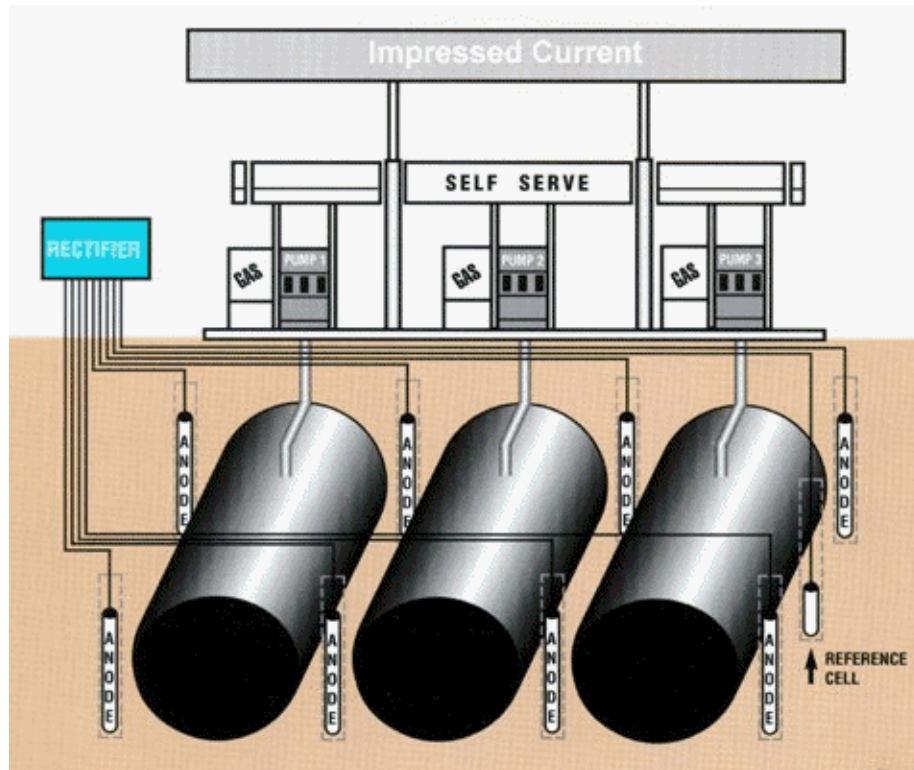
Fig. 13, Cathodic protection of underground storage tank by impressed current

a) <u>Galvanic system</u> (sacrificial anode cathodic protection)

A galvanic cathodic protection system makes use of the corrosive potentials for different metals. Without cathodic protection, one area of the structure exists at a more negative potential than another, and corrosion results. If, however, a much less inert object (that is, with much more negative potential, such as a magnesium anode) is placed adjacent to the structure to be protected, such as a pipeline, and a metallic connection (insulated wire) is installed between the object and the structure, the object will become the anode and the entire structure will become the cathode. That is, the new object corrodes sacrificially to protect the structure as shown in Figure 14 (a). Thus, the galvanic cathode protection system is called a *sacrificial anode* cathodic protection system because the anode corrodes sacrificially to protect the structure. Galvanic anodes are usually made of either <u>magnesium</u> or <u>zinc</u> because of these metals' higher potential compared to steel structures.
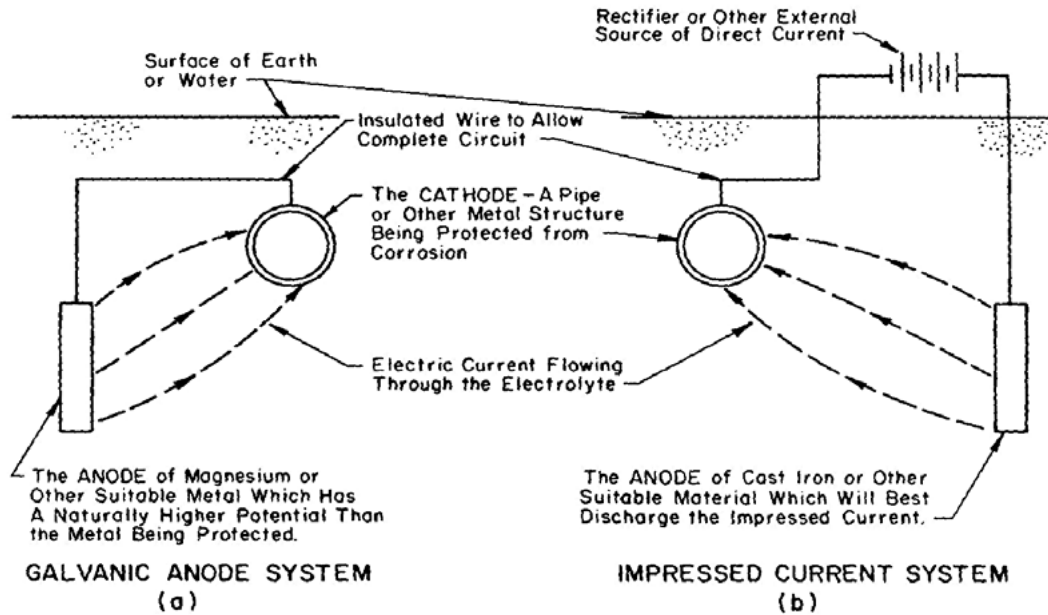
Fig. 14, Galvanic (a) and impressed (b) current systems for cathodic protection

b) **Impressed current systems**

Impressed current cathodic protection systems use the same elements as the galvanic protection system; only the structure is protected by applying a current to it from an anode. The anode and the structure are connected by an insulated wire, as for the galvanic system. Current flows from the anode through the electrolyte onto the structure, just as in the galvanic system. The main difference between galvanic and impressed current systems is that the galvanic system relies on the difference in potential between the anode and the structure, whereas the impressed current system uses an external power source to drive the current, as shown in Figure 1(b). The external power source is usually a rectifier that changes input AC power to the proper DC power level. The rectifier can be adjusted so that proper output can be maintained during the system's life. Impressed current cathodic protection system anodes typically are <u>high-silicone cast iron</u> or <u>graphite</u>.

CATHODIC PROTECTION DESIGN

Required information:

Before deciding which type, galvanic or impressed current, cathodic protection system will be used and before the system is designed, certain preliminary data must be gathered. The following is a list of these data.

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1. **Physical dimensions of structure to be protected**

One important element in designing a cathodic protection system is the structure's physical dimensions (for example, length, width, height, and diameter). These data are used to calculate the surface area to be protected (affect the required current).

2. **Drawing of structure to be protected**

The installation drawings must include sizes, shapes, material type, and locations of parts of the structure to be protected.

3. **Electrical isolation**

If a structure is to be protected by the cathodic system, it must be electrically connected to the anode, as Figure 14 shows. Sometimes parts of a structure or system are electrically isolated from each other by insulators. For example, in a gas pipeline distribution system, the inlet pipe to each building might contain an electric insulator to isolate in-house piping from the pipeline. Also, an electrical insulator might be used at a valve along the pipeline to electrically isolate one section of the system from another. Since each electrically isolated part of a structure would need its own cathodic protection, the locations of these insulators must be determined.

4. **Short circuits.** All short circuits must be eliminated from existing and new cathodic protection systems. A short circuit can occur when one pipe system contacts another, causing interference with the cathodic protection system. When updating existing systems, eliminating short circuits would be a necessary first step.

5. **Corrosion history of structures in the area**

Studying the corrosion history in the area can prove very helpful when designing a cathodic protection system. The study should reinforce predictions for corrosivity of a given structure and its environment; in addition, it may reveal abnormal conditions not otherwise suspected. Facilities personnel can be a good source of information for corrosion history.

6. **Electrolyte resistivity survey**

A structure's corrosion rate is proportional to the electrolyte resistivity. Without cathodic protection, as electrolyte resistivity decreases, more current is allowed to flow from the structure into the electrolyte; thus, the structure corrodes more rapidly. As electrolyte resistivity increases, the corrosion rate decreases (Table 2). Resistivity can be measured either in a laboratory or at the site with the proper instruments. The resistivity data will be used to calculate the sizes of anodes and rectifier required in designing the cathodic protection system.

Soil resistivity range (ohm-cm)	Corrosivity
0 to 2000	Severe
2000 to 10,000	Moderate to severe
10,000 to 30,000	Mild
Above 30,000	Not likely

Table (2) Corrosivity of soils on steel based on steel resistivity

7. Electrolyte pH survey

Corrosion is also proportional to electrolyte pH. In general, steel's corrosion rate increases as pH decreases when soil resistivity remains constant.

8. Structure versus electrolyte potential survey

For existing structures, the potential between the structure and the electrolyte will give a direct indication of the corrosivity. According to NACE Standard No. RP-01, the potential requirement for cathodic protection is a negative (cathodic) potential of at least 0.85 volt as measured between the structure and a saturated copper-copper sulfate reference electrode in contact with the electrolyte. A potential which is less negative than -0.85 volt would probably be corrosive, with corrosivity increasing as the negative value decreases (becomes more positive).

9. Current requirement

A critical part of design calculations for cathodic protection systems on existing structures is the amount of current required per square foot (called *current density*) to change the structure's potential to -0.85 volt. The current density required to shift the potential indicates the structure's surface condition. A well coated structure (for example, a pipeline well coated with coal-tar epoxy) will require a very low current density (about 0.05 milliampere per square foot); an uncoated structure would require high current density (about 10 milliamperes per square foot). The average current density required for cathodic protection is 2 milliamperes per square foot of *bare* area. The amount of current required for complete cathodic protection can be determined three ways:

> ➢ An actual test on existing structures using a temporary cathodic protection setup.
> ➢ A theoretical calculation based on coating efficiency.
> ➢ An estimate of current requirements using tables based on field experience.

The second and third methods above can be used on both existing and new structures.

Current requirements can be calculated based on coating efficiency and current density (current per square foot) desired. The efficiency of the coating as supplied will have a direct effect on the total current requirement, as Equation 1 shows:

$$I = i \times A \times (1 - CE) \tag{1}$$

where

I: is total protective current,

A: is total structure surface area in square feet,

i: is required current density,

and CE: is coating efficiency.

Equation 1 may be used when a current requirement test is not possible, as on new structures, or as a check of the current requirement test on existing structures. Coating efficiency is directly affected by the type of coating used and by quality control during coating application.

Note:

The importance of coating efficiency is evident in the fact that a bare structure may require 100,000 times as much current as would the same structure if it were well coated.

Current requirements also can be estimated from Table 2. The table gives an estimate of current, in milliamperes per square foot, required for complete cathodic protection. That value, multiplied by the surface area of the structure to be protected (in square feet) gives the total estimated current required. Caution should be used when estimating, however, as under- or overprotection may result.

Environment	Current density (mA/sq ft)	
	AFM 88-9[a]	Ger$rard_b$
Neutral soil	0.4 to 1.5	0.4 to 1.5
Well aerated neutral soil	2 to 3	2 to 3
Wetsoil	1 to 6	2.5 to 6
Highly acidic soil	3 to 15	5 to 15
Soil supporting active sulfate-reducing bacteria	6 to 42	Up to 42
Heated soil	3 to 25	5 to 25
Stationary freshwater	1 to 6	5
Moving freshwater containing dissolved oxygen	5 to 15	5 to 15
Seawater	3 to 10	5 to 25

Table 3, Typical current density requirements for cathodic protection of uncoated steel

10. Coating resistance

A coating's resistance decreases greatly with age and directly affects structure-to-electrolyte resistance for design calculations. The coating manufacturers supply coating resistance values.

11. Protective current required

By knowing the physical dimensions of the structure to be protected, the surface area can be calculated. The product of the surface area multiplied by current density obtained previously gives the total current required.

12. The need for cathodic protection

For existing structures, the current requirement survey *(*above*)* will verify the need for a cathodic protection system. For new systems, standard practice is to assume a current density of at least 2 milliamperes per square foot of bare area will be needed to protect the structure. (However, local corrosion history may demand a different current density.) In addition, cathodic protection is *mandatory* for underground gas distribution lines and for water storage tanks with a 250,000-gallon capacity or greater. Cathodic protection also is required for underground piping systems located within 10 feet of steel reinforced concrete because galvanic corrosion will occur between the steel rebar and the pipeline.

Determining type and design of cathodic protection system

When all preliminary data have been gathered and the protective current has been estimated, the design sequence can begin. The first question to ask is: **which type (galvanic or impressed current) cathodic protection system is needed?**

The criterion used most widely is based on <u>current density required and soil resistivity</u>.

A galvanic system can be used at the following conditions:

1. If the soil resistivity is low (less than 5000 ohm-centimeters) and

2. The current density requirement is low (less than 1 milliampere per square foot).

However, if the soil resistivity and/or current density requirement exceed the above values, an impressed current system should be used.

a. Sacrificial anode (galvanic) cathodic protection system design

The following steps are required when designing galvanic cathodic protection systems:

1. Review soil resistivity.

The site of lowest resistivity will likely be used for anode location to minimize anode-to-electrolyte resistivity. In addition, if resistivity variations are not significant, the average resistivity will be used for design calculations.

2. Select anode
Galvanic anodes are usually <u>magnesium</u>, <u>Aluminum</u> or <u>zinc</u>.

Anode specification will include:

- anode weight
- anode dimensions
- and package dimensions(anode plus backfill)

Table 4 shows for magnesium-alloy anodes.

Weight (lb)	Size (in.)	Packaged wt (lb)	Packaged size (in.)
3	3.75 x 3.75 x 5	12	6 x 10
5	3.75 x 3.75 x 7.5	17	6 x 12
9	2.75 x 2.75 x 26	35	6 x 31
9	3.75 x 3.75 x 13.25	27	6 x 17
12	3.75 x 3.75 x 18	36	6 x 23
14	2.75 x 2.75 x 41	50	6 x 46
14	3.75 x 3.75 x 21	42	6.5 x 26
17	2.75 x 2.75 x 50	60	6 x 55
17	3.75 x 3.75 x 26	45	6.5 x 29
20	2.5 x 2.5 x 59.25	70	5 x 66
24	4.5 x 4.5 x 23	60	7 x 30
32	5.5 x 5.5 x 21	74	8 x 28
40	3.75 x 3.75 x 59.25	105	6.5 x 66
48	5.5 x 5.5 x 30	100	8 x 38
48	8 x 16	100	12 x 25
60	4.5 x 4.5 x 60	—	—

Table 4, specifications for Mg alloys anodes

Notes:

> ➢ Zinc anodes are used in extremely corrosive soil (resistivity below 2000 ohm-centimeters).

> ➢ The choice of anode from those available is <u>arbitrary</u>; design calculations will be made for several available anodes, and the most economical one will be chosen.

<u>**Notes about backfill**</u>

<u>**Backfill material:**</u>

It is a material used to reduce the groundbed resistance

The type of backfill used in a groundbed depends on whether the cathodic protection system is sacrificial or impressed.

- **Chemical backfills:**

The chemical backfill used with galvanic anodes provides an environment which is conducive for anode dissolution. A typical mixture is 75% powdered gypsum (calcium sulfate), 20% granular bentonite and **5%** sodium sulfate. This mixture has a resistivity of 50 ($\Omega \cdot$ cm) and is suitable for use in high resistivity soils. The function of the bentonite is to absorb water and expand, thus ensuring good contact between anode and soil by lowering groundbed resistance. A 75% bentonite 25 % gypsum mixture (**250** $\Omega \cdot$ cm) is recommended for low moisture soils.

- **Carbonaceous backfills:**

Impressed current anodes are usually surrounded by a carbonaceous backfill. Types of materials use include <u>coke breeze</u>, <u>calcined petroleum coke</u> and <u>natural graphite</u>.

The backfill serves three basic functions: (a) it decreases the anode-to-earth resistance by increasing the anode's effective size, (b) it extends the system's operational life by providing additional anode material, and (c) it provides a uniform environment around the anode, minimizing deleterious localized attack.

To ensure good electrical contact, the backfill must be tamped around the anode. Resistivity of carbonaceous backfills is in the order of **50 Ω cm**.

3. **Calculate net driving potential for anodes**

The anode is coupled with a reference electrode (copper-copper sulfate) to measure its potential. The potential of iron (**The structure to protected**) in contact with soil or water

usually ranges around -0.55 to -1 volt relative to copper-copper sulfate. For practical approach consider iron polarized to -0.85 volt.

Accordingly the net driving potential for the anode will be:

$$\Delta E = anode\ potential - iron\ potential$$

4. Calculate the total resistance of the galvanic cell

The total resistance is calculated from the equation:

$$R_T = R_A + R_W + R_C$$

where:

- R_T: **is the total resistance**
- R_W: **is the wire resistance**
- R_A: **is the anode to electrolyte resistance**
- R_C: **is the cathode to electrolyte resistance**

$$R_T = \frac{\Delta E}{I}$$

ΔE: **is the net driving potential for anode**

I: is the protection current

$$R_C = R \times A$$

R: is the average coating resistance per unit area at the end of the proposed lifetime (R is specified by the supplier)

A: is the structure's surface area

R_W: **is negligible**

$$\therefore R_A = R_T - R_C$$

5. Calculate the number of anodes needed

The number of anodes should fulfill the following:

a. **Should meet groundbed resistance**

   The number of anodes needed to meet the groundbed resistance is calculated from the equation:

$$N = \frac{0.0052 \times \rho}{R_A \times L} \left[ln\frac{8L}{d} - 1 \right]$$

where:

ρ: **is the soil resistivity in ohm.centimeter**

L: is the length of the backfill column, ft

d: diameter of backfill column, ft (L and d are specified by the supplier)

b. **Should meet system's life expectancy**

Each cathodic protection system will be designed to protect a structure for a given number of years. The number of anodes that should be used to protect the structure for a period n is given by the equation:

$$N = \frac{n \times i}{49.3 \times W}$$

where:

n: is the number of years the structure will be protected

I: is the current density required to protect the structure milliampere/square feet

W: is the weight of one anode in pounds

There are two values for N now. How to select N?

The greater value of the above two equations will be used as the number of anodes needed for the system.

6. **Select groundbed layout**

When the required number of anodes has been calculated, the area to be protected by each anode is calculated by the equation:

$$A = \frac{A_T}{N}$$

7. **Calculate the life cycle cost for proposed design**

The design process should be done for several different anode choices to find the one with minimal life cycle cost.

b. **Impressed current cathodic protection system design**

When designing impressed current cathodic protection systems the following steps are required.

1. **Review soil resistivity**

As with galvanic systems, this information will contribute to both design calculations and location of anode groundbed.

2. **Review current requirement test**

The required current will be used throughout the design calculations. The calculated current required to protect 1 square foot of bare pipe shall agree with the values in Table 3.

3. Select anode

As with the galvanic system, the choice of anode is arbitrary at this time; economy will determine which anode is best. Table 5 gives common anode sizes and specifications. The anodes used most often are made of high-silicon chromium-bearing cast-iron (HSCBCI). When impressed current-type cathodic protection systems are used to mitigate corrosion on an underground steel structure, the auxiliary anodes often are surrounded by a carbonaceous backfill. Backfill materials commonly used include coal coke breeze, calcined petroleum coke breeze, and natural graphite particles.

Anode weight (lb)	Anode dimensions (in.)	Anode surface size (in.)	Package area (sq ft)
12	1 x 60	1.4	10 x 84
44	2 x 60	2.6	10 x 84
60	2 x 60	2.8	10 x 84
110	3 x 60	4.0	10 x 84

Table 5, weights and dimensions of selected circular high silicon chromium bearing cast iron anodes

4. Calculate number of anodes needed

a. The number of anodes needed to satisfy manufacturer's current density limitations
Impressed current anodes are supplied with a recommended maximum current density. Higher current densities will reduce anode life. To determine the number of anodes needed to meet the current density limitations, use the equation:

$$N = \frac{I}{A \times i}$$

where:

I: is the total protection current

A: is the anode surface area in square feet per anode

i: is the recommended maximum current density output in milliamperes/square feet

b. The number of anodes needed to meet design life requirement
The following equation is used to find the number of anodes needed to meet design life requirement:

$$N = \frac{n \times i}{1000 \times W}$$

where:

n: **is the number of years the structure will be protected**

I: **is the current density required to protect the structure milliampere/square feet**

W: **is the weight of one anode in pounds**

c. The number of anodes needed to meet the maximum anode groundbed resistance requirements

The number of anodes is calculated from the equation:

$$R_A = \frac{\rho K}{NL} = \frac{\rho P}{S}$$

where:

R_A: is the anodes' resistance in Ohm

ρ: is soil resistivity in Ohm. Centimeter

K: is the anode shape factor (from table 6)

N: is the number of anodes

L: is the length of the anode backfill column in feet

P: is the paralleling factor (from table 7)

S: is the center to center spacing between anode backfill column in feet

L/d	K	L/d	K
5	0.0140	20	0.0213
6	0.0150	25	0.0224
7	0.0158	30	0.0234
8	0.0165	35	0.0242
9	0.0171	40	0.0249
10	0.0177	45	0.0255
12	0.0186	.50	0.0261
14	0.0194	55	0.0266
16	0.0201	60	0.0270
28	0.0207		

Table 6, shape factor as a function of L/d

N	P	N	P
2	0.00261	14	0.00168
3	0.00289	16	0.00155
4	0.00283	18	0.00145
5	0.00268	20	0.00135
6	0.00252	22	0.00128
7	0.00237	24	0.00121
8	0.00224	26	0.00114
9	0.00212	28	0.00109
10	0.00201	30	0.00104
12	0.00182		

Table 7, Paralleling factor as a function of N

Now we have three equations to get N. The highest number calculated by the above three equations will be the number of anodes used.

5. **Calculate the total circuit resistance (as mentioned before)**

$$R_T = R_A + R_W + R_C$$

6. **Calculate the rectifier voltage and select the rectifier that satisfy the required I and V**

$$V_{rec} = I \times R_T \times 1.5$$

Note: 1.5 is a safety factor to allow for aging the rectifier stack

7. **Calculate the system cost and repeat steps for different anodes to choose the system of the minimum cost**

B. <u>**Anodic Protection:**</u>

It is based on the phenomenon of passivity. To understand how the anodic protection is carried out the phenomenon of passivity should be explained first.
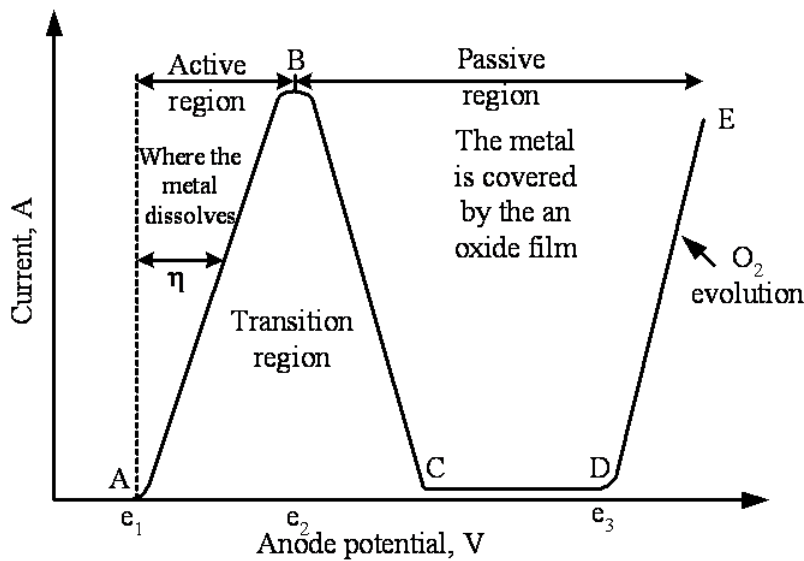
Consider a metal M acting as an anode in electrolytic cell. If the anode potential is increased gradually the metal M starts to dissolve at a potential e_1 given by:

$$M \rightarrow M^{++} + 2e$$

$$e_1 = e_o - RT/ZF \ln[M^{++}]$$

At the point A current starts to flow in the cell as a result of metal dissolution, with increasing the anode potential the current increases till the point B is reached, after this point any further increase in the anode potential result in a decrease of the current from B to C owing to the

formation of an oxide film on the metal surface which prevents its dissolution. Oxide film formation takes place at the potential e_2 which is given by the equation:

$$M + H_2O \rightarrow MO + 2H^+ + 2e$$

$$e_2 = e_o - RT/ZF \ln[H^+]^2$$

With further increasing the anode potential no current flows through the cell until the potential e_3 is reached at point D where oxygen evolution starts to evolve according to the reaction

$$4OH^- \rightarrow O^2 + H_2O + 4e$$
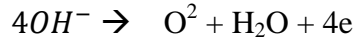
$$e_3 = e_o - RT/ZF \ln[OH^-]^4$$

At point D the current increases again with increasing anode potential as represented by the part DE.

Anodic protection is carried out by connecting the structure to be protected to the positive pole of an external d.c power supply, an auxiliary cathode made of corrosion resistant material is used to complete the circuit. The anode potential of the structure is adjusted to be in the passive region i.e the region represented by the area BCDE on the passivity curve. Under this condition the structure will be coated with a layer of oxide which protects it against corrosion.

Limitation of anodic protection:

1. Anodic protection can be used only with metals which exhibit the phenomenon of passivity such as steel, stainless steel, nickel and its alloys, chromium and its alloys, Al and Ti and their alloys, anodic protection cannot be used with metals such as Cu and Zn and their alloys.

2. Anodic protection cannot be used when the electrolyte contains chloride ions because chloride ions attack the oxide film and destroy it.

5- Minimizing corrosion by proper design

The following are examples of how proper equipment design can reduce corrosion

1. Avoid dissimilar metal contact in the presence of an electrolyte especially when the cathode/anode ratio is high such as the following example:
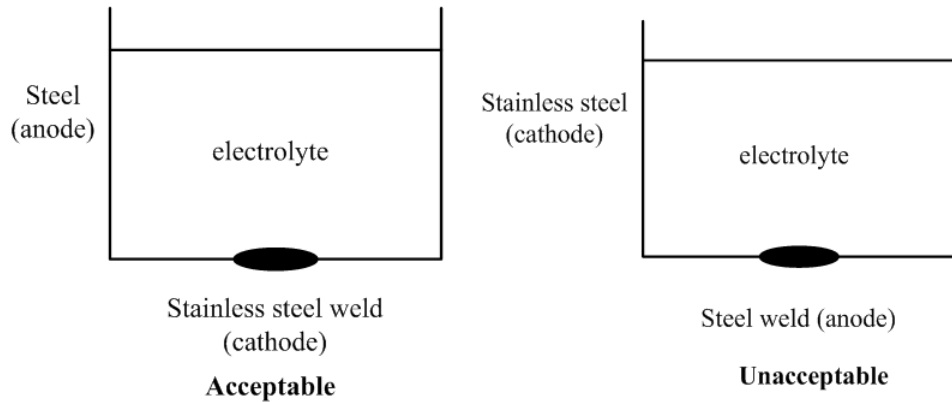
If the use of dissimilar metals is unavoidable in building the structure they should be separated by an insulator such as plastic or rubber as shown by the following example:
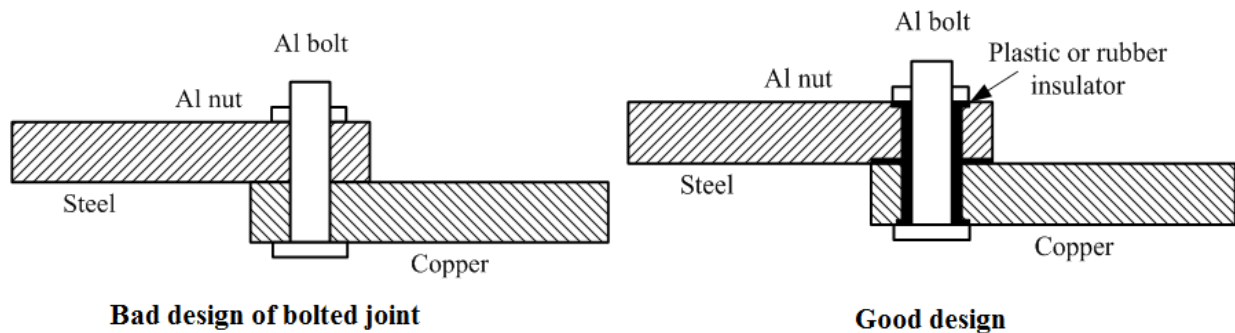
Dissimilar metals are sometimes used intelligently to design structures which are corrosion resistant and less expensive as shown by the following examples:
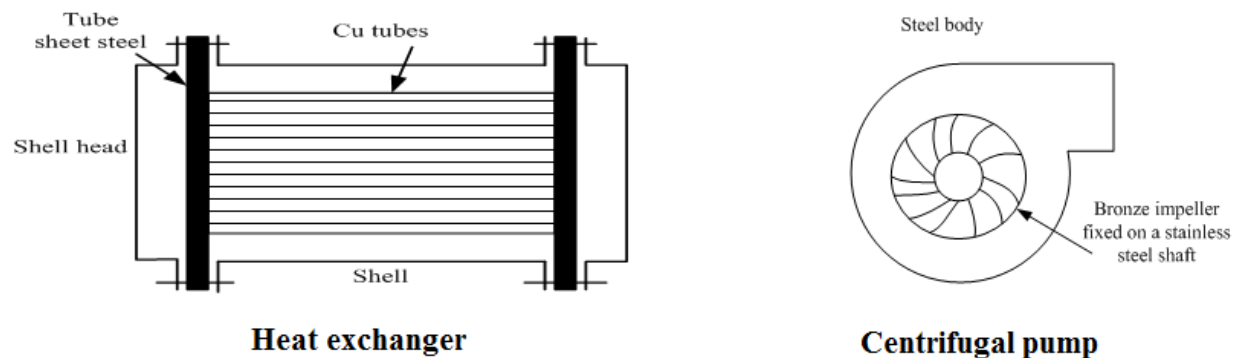
Cooper tubes are used in building heat exchangers because copper has the highest thermal conductivity among all metals. Other parts of the heat exchanger such as the shell, tube sheet and head are made of steel not copper to <u>lower the capital costs</u> of the heat exchanger. The use of steel offers also the advantage of protecting copper tube against corrosion by <u>cathodic protection</u> through the cell: Fe/electrolyte/Cu.

Example 2 shows a centrifugal pump made of three different materials chosen to produce inexpensive corrosion resistant efficient pump where the steel body protects the other parts of the pump against corrosion by cathodic protection.

2. It is better from the corrosion point of view to join different sections by welding rather than riveting to avoid crevice corrosion. After welding the heat affected zone (H.A.Z) should be post weld heat treated (P.W.H.T) to eliminate residual stresses which may lead to corrosion.

[Crevice = clearance or gap between two surface in contact]


Revit
Poor design

Weld
Good design
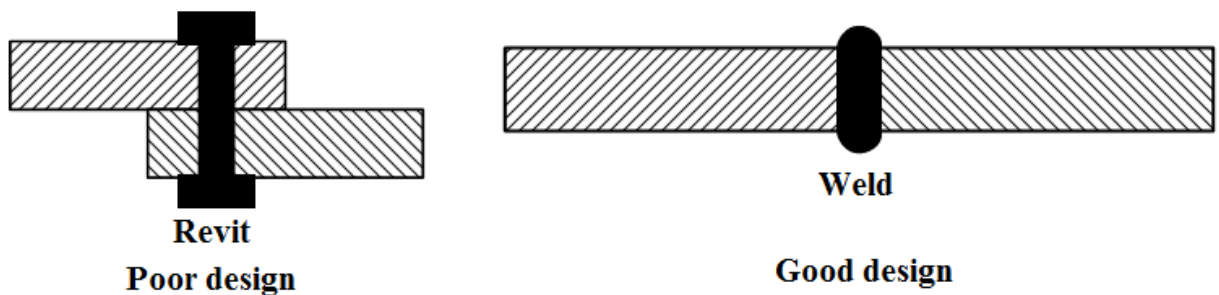
3. Avoid erosion-corrosion (impingement corrosion) by doubling the thickness of the parts subjected to high degree of turbulence (high shear stress) or subjected to flowing solutions which contain suspended solids such as tube inlets, elbows, bends, impellers of agitated vessels, etc.


Tube inlet

Elbow

Bend
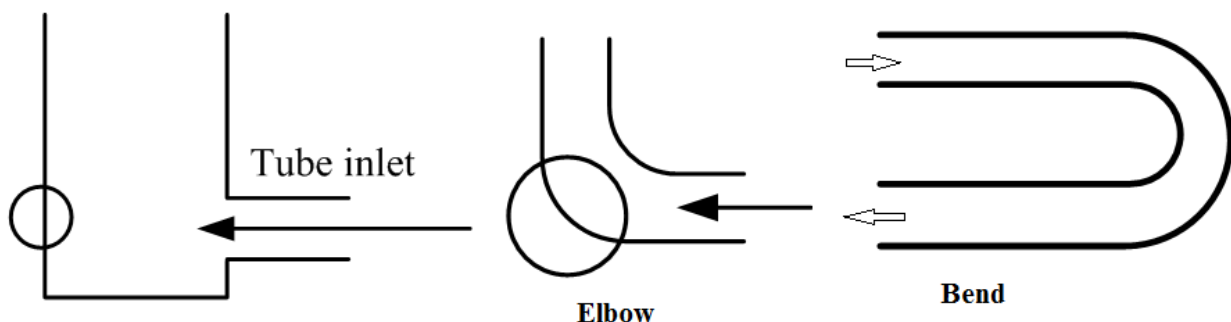
High turbulence may damage the protective oxide film on the metal and increase the rate of bare metal corrosion by increasing the rate O_2 transfer from the solution bulk to the metal surface.

4. Avoid vibration of equipment as far as possible. Vibration increases the rate of O_2 transfer from the solution bulk to the corroding surface with a consequent increase in the rate of steel corrosion.

Vibration leads also to corrosion fatigue. Metallic objects subjects to cyclic stresses (e.g. vibrations) undergoes failure at a stress below the ultimate tensile stress of the metal especially in the presence of corrosive solutions, the stress at which failure takes place decreases with increasing the number of cycles per second as shown in the following figure.
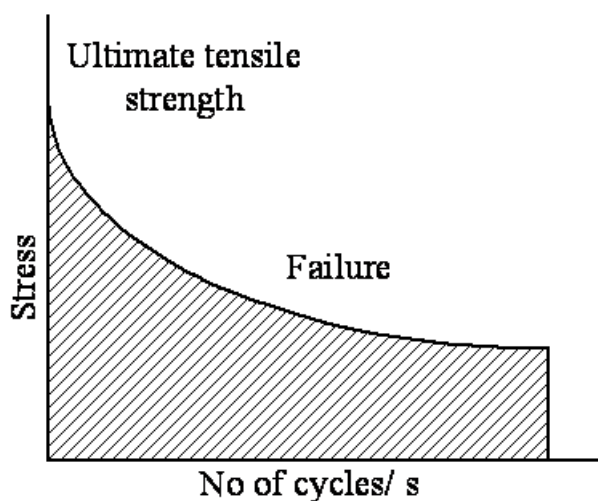
5. Dry your equipment (e.g packed columns pipelines, etc) after testing or cleaning by passing dry N_2. Leaving this equipment wet for a long time before operation leads to serious corrosion.

6. Design tanks for easy drainage as shown below.
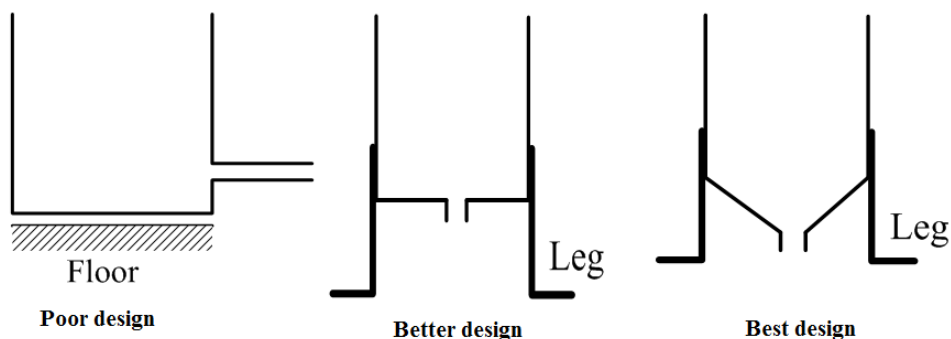
Resting the tank on the floor leads to crevice corrosion of the bottom (through a differential aeration cell). Residual solution in the tank resulting from poor drainage leads to serious corrosion of the lower part of the tank because of the high rate of O_2 diffusion through the thin residual liquid layer left at the tank bottom.

7. Avoid stresses in the structure

As mentioned before residual stresses left in the structure during fabrication leads to stress corrosion cracking of the metal if used in contact with certain electrolyte. Stress corrosion cracking can be avoided by either removing of residual strains from the metal by annealing or avoiding contact between the metal and electrolytes to which it is sensitive.

Stresses may be also induced in heat exchanger tube if the thermal gradient across the tube wall is high (dT/dx) where dT is the difference in temperature across the tube wall and dx is the thickness of the wall.

**Factors affecting the rate of corrosion**

In view of the importance of steel as a material of construction its corrosion will be used to illustrate the factors affecting the rate of corrosion.

1. Effect of temperature

➢ In the pH range 4-10 where O_2 reduction is the cathodic reaction of the corrosion cell, the rate of corrosion increases with increasing solution temperature up to 80 $^{\circ}$C and then the rate of corrosion decreases with further increase in temperature.

➢ The decrease in the rate of corrosion beyond 80 $^{\circ}$C is attributed to the decrease in O_2 solubility in water.

➢ In acid medium where the cathodic reaction of the corrosion cell is H_2 evolution, the rate of corrosion increases with increasing temperature according to Arrhenius equation:
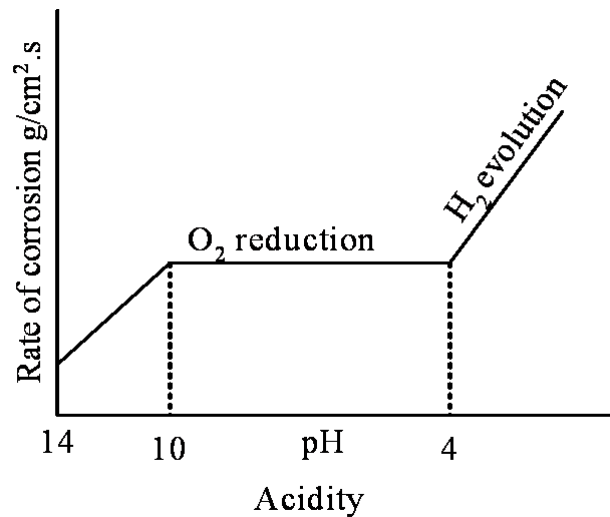
$$Rate\ of\ corrosion: r = A\,e^{-E/RT}$$

r = rate of corrosion; A = constant; E = activation energy; R = gas constant; T = temperature
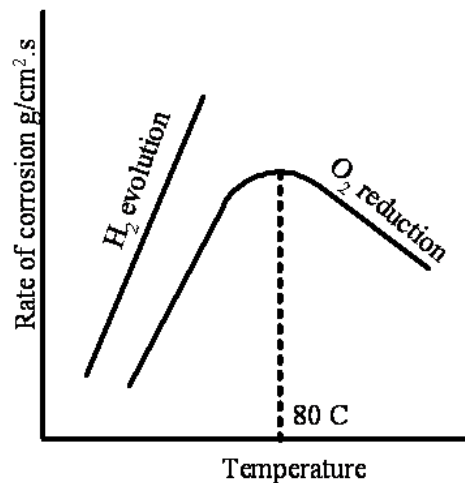
Effect of temperature on the rate of corrosion

2. Effect of pH

In the pH range 4 – 10 the cathodic reaction of the corrosion cell is O_2 reduction i.e. in this range of pH the rate of corrosion depends on the rate of O_2 diffusion to the cathodic sites of the corrosion cells and not the pH.

Below pH = 4 the rate of corrosion increases with decreasing the pH (increasing acidity) as the cathodic reaction becomes H_2 evolution instead of O_2 reduction. At pH higher than 10 the rate of corrosion decreases with increasing pH and steel becomes coated with a protective oxide film.

3. Effect of solution stirring

- ➤ If the cathodic reaction of the corrosion cell is oxygen reduction (pH 4-10) the rate of corrosion increases in general with increasing the degree of stirring owing to the increase in the rate of transfer of dissolved O_2 from the solution bulk to the steel surface.

- ➤ If the cathodic reaction is H_2 evolution (pH < 4) stirring has no effect on the rate of corrosion because the reaction is chemically controlled (i.e not diffusion controlled as in the case of O_2 reduction)

4. Effect of metallurgical factors

- ➤ As mentioned before in the pH range 4-10 the cathodic reaction of corrosion cells is O_2 reduction, the rate of this reaction depends on the rate of transfer of dissolved O_2 from the solution bulk to the surface of the corroding metal. Accordingly in the pH range 4-10 the rate of corrosion does not depend on the composition of the steel or its heat treatment.

➢ In acid solution (pH < 4), the cathodic reaction of the corrosion cell is H_2 evolution, this reaction is chemically controlled i.e <u>its rate depends on nature of the metallic surface and its composition.</u>

➢ Pure iron dissolves slowly in acids while impure iron containing impurities such as P, N, S and C dissolves rapidly because these impurities form nobler phase with iron on which H_2 evolution is fast.

➢ On the other hand addition of Ni and Cr to iron decreases its rate of dissolution in acids.

5. Effect of dissolved salts
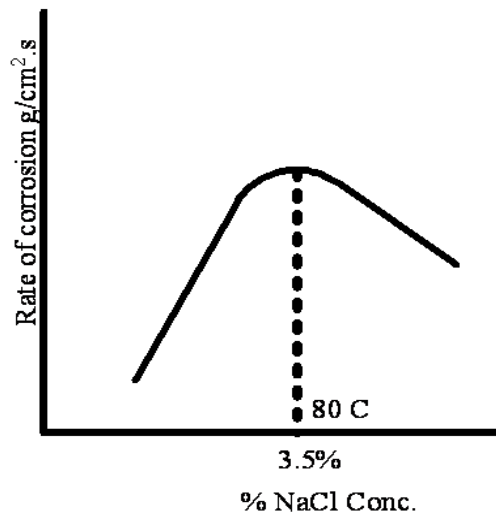
a. NaCl: the rate of corrosion of steel increases with increasing NaCl concentration up to a certain point and then decreases with further increase in salt concentration

➢ The initial increase in the rate of steel corrosion is attributed to the increase in solution conductivity with increasing NaCl concentration.

➢ The decrease in the rate of corrosion at high NaCl concentration is attributed to the decrease in the amount of dissolved oxygen [NaCl salt out O_2, the phenomena is known as salting out].

b. Acidic salts such as $NiSO_4$, $AlCl_3$, NH_4Cl, $FeCl_2$, $MnCl_2$, etc these salts produce acidic solutions because of hydrolysis. Steel dissolves in these solutions with H_2 evolution especially in concentrated solutions.

c. Alkaline salts such as Na_2SiO_3, Na_3PO_4, Na_2CO_3 and $Na_2B_4O_7$ (Borax), these salts produce alkaline solutions because of hydrolysis. Under this condition these salts form an insoluble

iron salt on steel surface which acts as a diffusion barrier and inhibit corrosion. Alkalinity also favors the formation of a protective oxide film on steel.

d. Oxidizing salts such as $FeCl_3$, $CuCl_2$, $HgCl_2$ and NaOCl and oxidizing salts such as $Na_2Cr_2O_7$, $NaNO_2$ and $KMnO_4$.

The first group of salts is highly corrosive (contain chloride ions) while the second groups oxidizes the steel surface and inhibit its corrosion.

e. Water

Water can be divided into <u>soft</u> and <u>hard</u> water.

Hard water which contains cations such as Mg^{++}, Ca^{++} is less corrosive than soft water because Mg^{++}, Ca^{++} combine with the cathodically formed OH^- to form an insoluble film of $Ca(OH)_2$ or $Mg(OH)_2$ which blocks the cathodic sites of corrosion cells and inhibit corrosion.

Polarization

- Definition
- Types of polarizations
- Comparison
- Effect of polarization on rate of corrosion.

Polarization ≡ rdation ≡ Slowness

Any electrochemical (reaction) process takes place through two main steps, namely;

1. Diffusion step [Physical]
2. Chemical reaction [Chemical]

The speed of the reaction is controlled by the slowest step and the reaction is said to be retarded or polarized.

Definition of polarization:

Retardation of an electrochemical reaction due to the slowness of diffusion or charge transfer step (electron transfer).

Types of polarization:

1. Concentration polarization

This type appears when the diffusion step is the controlling step and is defined as the retardation of an electrochemical process due to the slowness of diffusion step.

2. Activation polarization

This type appears when the chemical reaction step is the controlling step and is defined as the retardation of an electrochemical process due to the slowness of the charge transfer step.

Comparison between concentration and activation polarization:

Concentration polarization is sensitive to stirring or agitation while activation polarization is insensitive to stirring or agitation increase stirring and decrease concentration polarization.

Relation between polarization and rate of corrosion:

As the magnitude of polarization increase the rate of corrosion decrease.

Passivity

Definition:

Loss of chemical activity under particular specific conditions (oxidizing solution). It is displayed by some metals as Cr, Fe, Ni, Ti

Reasons of passivity

The passive behaviour of these metals is resulted from the formation of <u>highly adherent</u> and very thin oxide film on the metal surface. This film acts as a <u>protective barrier</u> to further corrosion. This is why stainless steel resists corrosion.

N.B. The passivity appears in a specific environment at specific condition.

Factors affecting passivity:

1. Type of metal or alloy
2. Type of environment