

Chapter (6-A)

Corrosion Control by

1. Addition of Inhibitors,
2. Coatings, and
3. Electrical Protection



INHIBITION



- The practice of corrosion prevention by adding substances which can significantly retard corrosion when added in small amounts to corrosive fluids.

INHIBITOR:

- Any reagent capable of converting an active corrosion process into a passive process.
 1. Inhibition is used internally with carbon steel pipes and vessels as an economic control alternative to:
 - stainless steels and alloys
 - coatings on non-metallic components.
 2. One unique **advantage** is that adding inhibitor can be implemented without disruption of a process.
 3. Corrosion inhibitors are selected on the basis of **solubility or dispersibility** in the fluids which are to be inhibited.

Applications of Corrosion Inhibitors

Corrosion inhibitors are used in:

1. Oil and gas exploration and production installation
2. Petroleum refineries
3. Chemicals and petrochemical industries
4. Water treatment
5. Cooling water systems
6. Boiler water systems.
7. Other industries.



The total consumption of inhibitors in the USA alone costs over one billion dollars annually.

Limitation of Inhibitors Use

Inhibitors are extremely useful in many environments. However, there are certain **exceptions** such as:

- Equipment and components subjected to high velocity (beyond 4 m/s) and turbulent flow.
- Systems operating above the stability limits of inhibitor.

However, adding inhibitors can raise the value of the critical flow rate above which erosion- corrosion starts.

CLASSIFICATION OF INHIBITORS (Figure 6.1):

I. Inorganic inhibitors:

❖ *Cathodic:*

- a- Precipitators: Zn salts, calcium carbonate
(react with corrosion products (OH^-) forming insoluble layer isolating cathode from environment)
- b- Adsorbing Poisons: As, Sb, Bi, Hg, sulphur (able to adsorb, high over-potential to suppress H_2 evolution, health & environmental hazards)

❖ *Anodic:*

- a- Precipitators: phosphates, silicates, carbonates (react with corrosion products, e.g. Fe^{2+} , forming insoluble layer isolating anode from environment)
- b- Passivators: chromates, nitrates, molybdates (react with anodic surface forming a passive film)

CLASSIFICATION OF INHIBITORS (Cont'd)

II. Organic inhibitors (Mixed cathodic & anodic):

monoamines, diamines, amine salts, amides, esters, ammonia derivatives

(compounds having polar groups (e.g. NH_2) able to adsorb on metal surface, both cathodic and anodic, forming protective films) Mechanism: Electrostatic

III. Environmental Conditioners

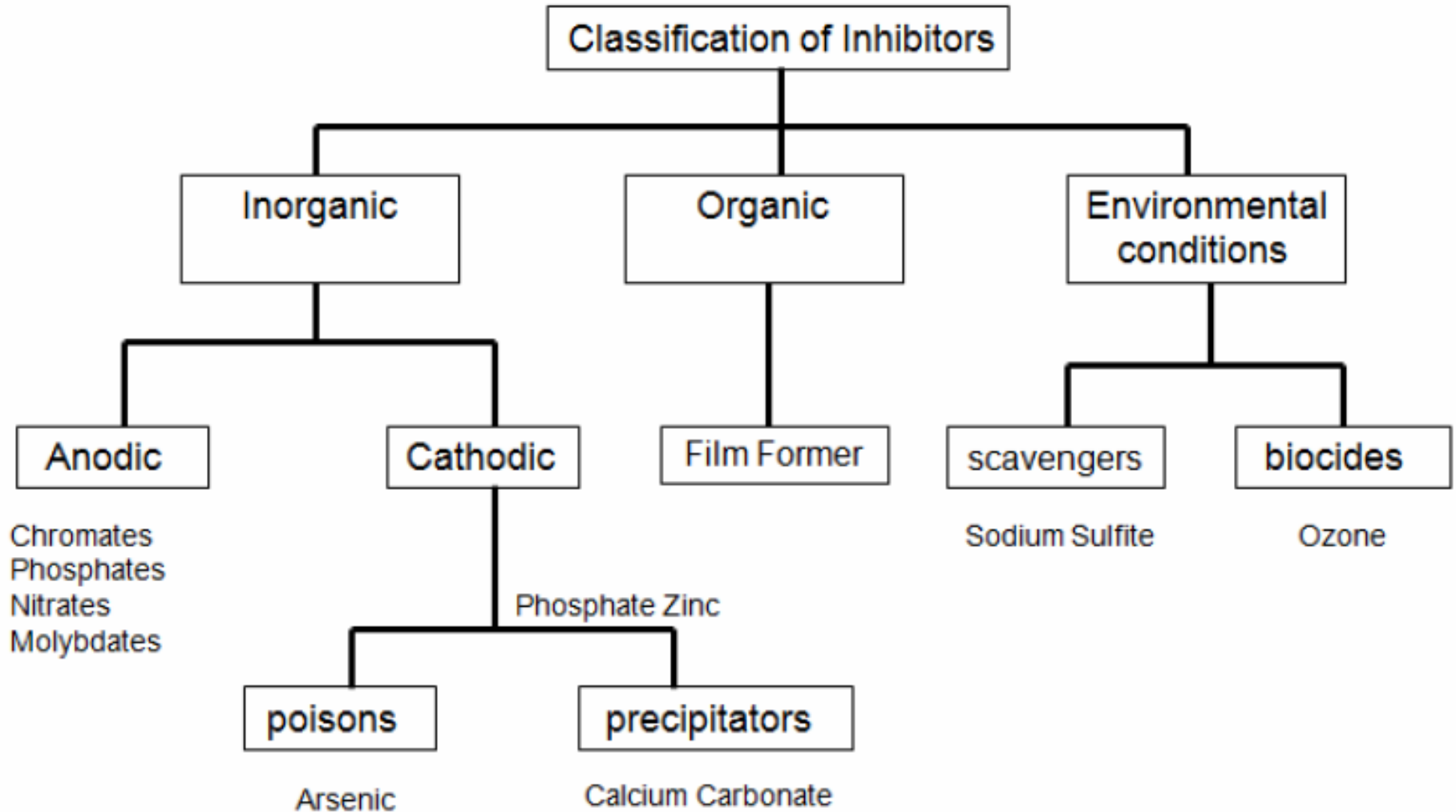
1. Oxygen Scavengers (cathodic) :

sodium sulfite, ammonium sulfite, hydrazine (N_2H_4)
(removes dissolved oxygen from corrosive medium)

2. Biocides:

Dialkyl-benzyl ammonium chloride, Chlorine dioxide, O_3
(kills bacteria and other microorganisms that deposit on materials causing them to corrode)

CLASSIFICATION OF INHIBITORS



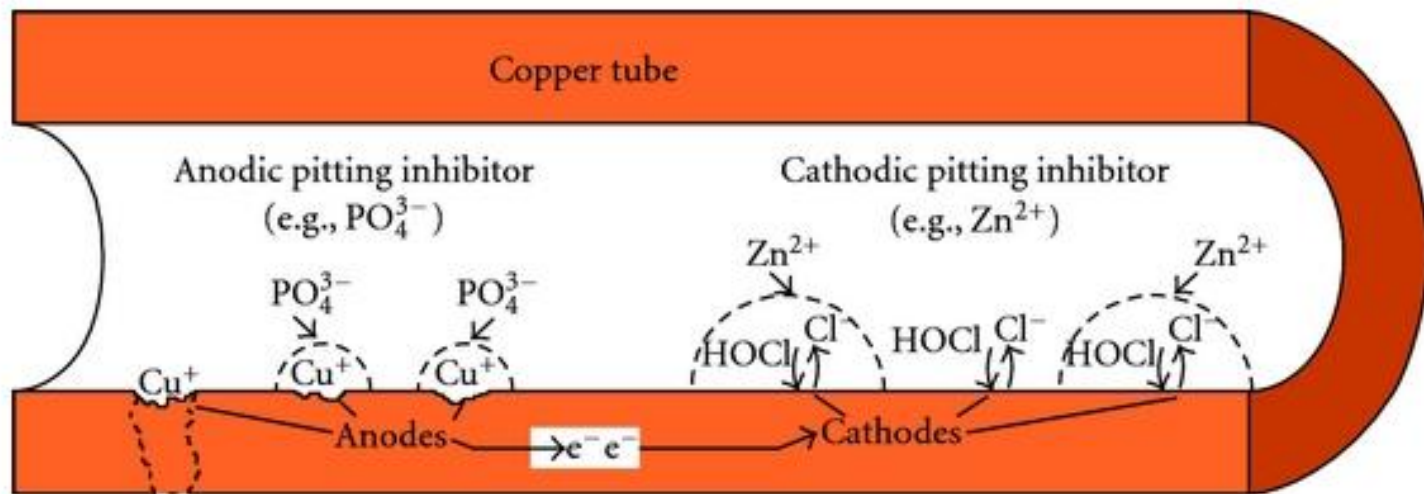
CONSIDERATIONS IN SELECTION OF INHIBITORS

- 1) The magnitude of suppression of uniform and localized corrosion.
- 2) Long range effectiveness.
- 3) Effect on bimetallic coupling to other metals joined to the main system.
- 4) Effect of temperature on the performance of inhibitors.
- 5) Effect of inhibitor on heat transfer characteristics.
- 6) Toxicity and pollution problems: *Green inhibitors are being sought.*
- 7) Economically and technically competitive with other considered inhibitors.

How Inhibitors Work

1- Cathodic Inhibitors:

- The polyphosphate molecule bonds with divalent calcium and other ions to form positively charged colloidal particles which are attracted to the cathode and form a *protective film*.
- Cathodic inhibitors also include zinc salts (e.g. ZnCl_2).



- Cathodic inhibitors are positively charged species (Zn^{2+}) that are drawn to the net negative charge (Cl^-) at cathode sites.

2- Anodic Inhibitors:

- Anodic inhibitors are negatively charged species (PO_4^{3-}) that would be drawn to the net positive charge (Cu^+).
- They are most effective inhibitors, but they are toxic and, hence, their application is restricted and is not advised. In industrial water, the threshold concentration is 120 mg/L.
- A high concentration is required if the systems to be inhibited contain bi-metal junctions or a high chloride concentration.
- They are oxidizers and raise the anodic current density above the limiting value needed for passivity.
- Chromate inhibitors contain either Na_2CrO_4 or $\text{Na}_2\text{Cr}_2\text{O}_7$. The protective passive film which is formed contains iron oxide and chromium oxide which makes the chromate inhibitors very effective.



- Other anodic inhibitors include phosphate salts (PO_4^{3-}) as shown in Figure (next).

3- Mixed Inhibitors

- It is rare that a single inhibitor is used in industrial practice.
- More often, a combination of inhibitors (anodic and cathodic) is used to obtain better corrosion protection properties.
- The blends which are produced by mixing of multi-inhibitors are called *synergistic blends*.

Following are the major applications of synergistic blends of inhibitors:

Chromate– polyphosphate	Metal surface cleaning	Polyphosphate– ferrocyanide	Protection of ferrous and non-ferrous constructional materials
Chromate– orthophosphate	More effective corrosion control in oilfield	Zinc–tannins	Protection of copper and many ferrous materials
Polyphosphate– silicates	Cooling water system	Amino–alcohol– sodium nitrite	Combines the precipitation effect of nitrite with the film forming properties of hydroxylamine

4- Oxygen Scavengers

- Oxygen may cause serious corrosion in:
 1. feed water lines,
 2. boiler metal and
 3. steam operated equipment.
- Chemicals which eliminate oxygen from the closed systems are called *scavengers*.
- Common & successful scavengers (cathodic inhibitors):
 - Sodium sulfite, Na_2SO_3 ,
 - ammonium sulfite, $(\text{NH}_4)_2\text{SO}_3$
 - hydrazine, N_2H_4



Common oxygen scavengers as shown below:

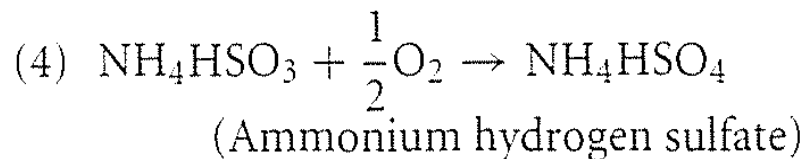
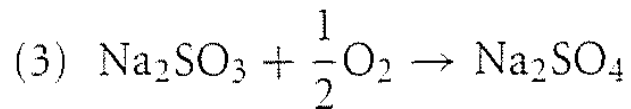
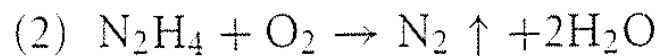
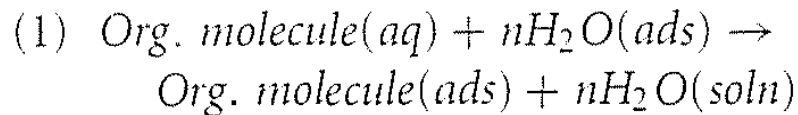
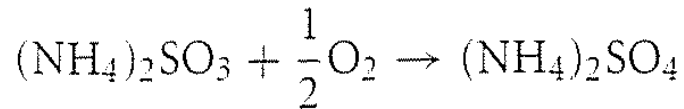


Table 6.1 Advantages and disadvantages of sodium sulfite and hydrazine

Chemical	Advantages	Disadvantages
Sodium sulfite	■ Rapid reaction	■ Does not reduce ferric oxide to magnetite
	■ Non-toxic	■ May decompose to form corrosive gases
	■ Contributes no solids	
Hydrazine	■ Reduces ferric oxide to magnetite	■ Reacts less rapidly compared to sodium sulfite
	■ Less dosage for scavenging compared to sodium sulfite required	■ More expensive than sodium sulfite
		■ Toxic and flammable

Green Approach towards Corrosion Inhibition

1. Plant products (extracts) are inexpensive, renewable and readily available. Extraction by water or organic solvents.
2. Tannins, organic amino acids, alkaloid, and organic dyes of plant origin have good corrosion-inhibiting abilities.
3. Plant extracts contain many organic compounds, having polar atoms such as O, P, S, and N.



Efficiency of Corrosion Inhibitor

$$\text{Efficiency of inhibitor} = \frac{(\text{Weight loss without inhibitor} - \text{Weight loss with inhibitor})}{\text{Weight loss without inhibitor}} \times 100$$

$$\text{Corrosion Rate} = \frac{534 \times \text{Weight loss (g)}}{\text{Density} \times \text{Area (cm)} \times \text{Time (hr)}}$$

$$\text{Surface Coverage } \theta = \frac{((\text{Weight loss without inhibitor}) - (\text{Weight loss with inhibitor}))}{\text{Weight loss without inhibitor}}$$



COATING



Introduction



- A **coating** is a high resistance barrier between the metallic structure and the surrounding electrolyte. Coatings are the first line of defense against corrosion.
- A quality dielectric coating material can reduce costs in additional corrosion control materials such as sacrificial anodes or impressed current type cathodic protection systems.
- By applying coatings of high resistivity, e.g. Epoxies, Vinyls and Chlorinated rubbers, the flow of electric current to the metal surface is impeded.
- The higher the **thickness** of the coating, the higher would be the electrical **resistance** of the coating.

Coatings characteristics for good corrosion resistance:

- a) A high degree of adhesion to the substrate
- b) Minimum discontinuity in coating (porosity)
- c) A high resistance to the flow of electrons (electrical insulator)
- d) A sufficient thickness to provide resistance
- e) A low diffusion rate for ions such as Cl^- and for H_2O molecules.

Good Practice:

Coating and paint technology is adapting to the environmental requirements, i.e. takes into consideration pollution prevention and environmental protection.

SCOPE OF COATING APPLICATIONS

1. Power plants: turbines, ...
2. Oil and mining industry: pumps, valves, drilling rigs, ...
3. Desalination plants: brine heaters, heat exchangers, circulation pumps, valves, ...
4. Automotive industry: gears, valves, pistons, panels, etc.
5. Aerospace industry: aircrafts, ...
6. Solar energy: photovoltaic cells, solar cells.
7. Biomedical technology: artificial hearts, valves and joints.
8. Utilities: all household appliances, washing machines, kitchenware and all electrical appliances.
9. Pipelines: oil, gas and utilities pipelines.
10. Transportation: decks, bridges and railcars.
11. Information storage: discs (magnetic coatings), TV displays.



Coatings Examples

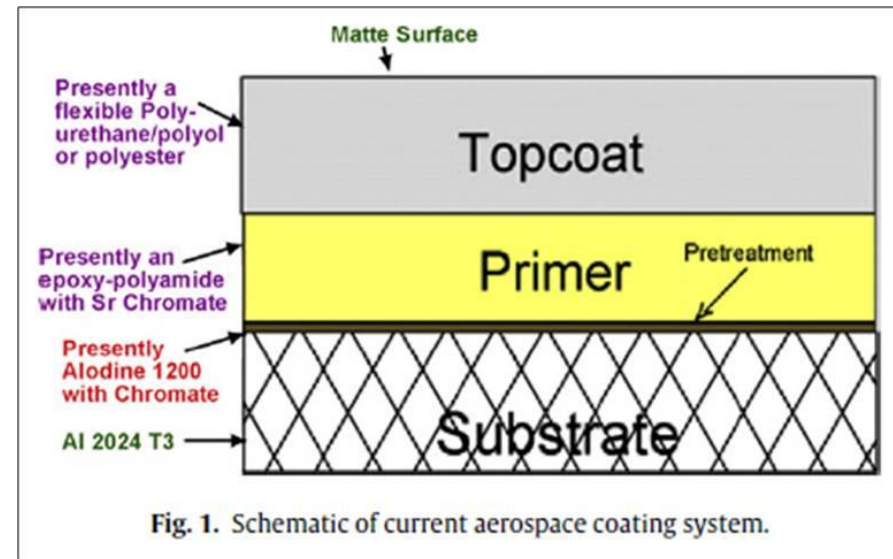
Zinc Phosphate/ Chromate Primer



Structural steel primer: paint



gas pipeline coating butyl rubber tape anti-corrosion pipe wrap tape high performance



CLASSIFICATION OF COATINGS

Coatings can be classified according to *material type* into:

- A. Metallic Coatings (anodic & cathodic; or less noble & more noble than substrate metal)
- B. Non-metallic Coatings (paint, glass, cement, chemical passivation, lubricant, etc.).

They can *also* be classified into the following categories according to *function* in corrosion resistance:

- I) Barrier coatings
- II) Conversion coatings
- III) Anodic coatings: less noble than substrate metal
- VI) Cathodic coatings: more noble than substrate metal

(I) BARRIER COATINGS (4 Types)

1) Anodic Oxides

- A layer of metal oxide , e.g. Al_2O_3 is produced on aluminium surface by *electrolysis*. As the oxides are porous, they are sealed by a solution of potassium dichromate .

2) Inorganic Coatings

- Ceramics and glass coatings: virtually impervious to water. Cement coatings are impervious as long as they are not mechanically damaged.

3) Inhibitive Coatings

- Inhibitors are added to corrosive solution form surface layers which serve as barriers to the environment OR Inhibitors are added to paint coatings to prevent steel corrosion in neutral or alkaline media.

(I) BARRIER COATINGS

Cont'd



4) Paint (Organic) Coatings

- Epoxy, polyurethane, chlorinated rubber and polyvinyl chloride coatings are extensively used in industry. They serve as barriers to water, oxygen, etc. They prevent occurrence of a cathodic reaction beneath the coating. Barrier properties are further enhanced by addition of an inhibitor, e.g. chromate.
- Main Paint system components:
 - Vehicle (liquid in which pigment is dispersed, composed of binder & solvent).
 - Binder (Resin): Binds pigments in coating in a homogeneous film and also binds total coating to substrate metal.
 - Pigment (Color). Provides pleasing color as well as protects.
 - Solvent. Organic compound of low molecular weight, it dissolves the binder in the paint. After application, solvent is no longer required and should be evaporated from the paint film.

Organic Pigments for Paint Coatings

Organic pigments are generally categorized into six types :

1. Acid and base dye Pigments:
2. Diazo Pigments
3. Monoazo Pigments
4. Phthalocyanine Pigments
5. Other polycyclic Pigments
6. Quinacridone Pigments.



Key features and characteristics of Organic Pigments

Cost effectiveness, Consistency and unique shades, Completely non-toxic, Organic pigments shows good color strength, Very bright, pure, rich colors, Very good stability to solvents, light, heat, and weathering.

(II) CONVERSION COATINGS

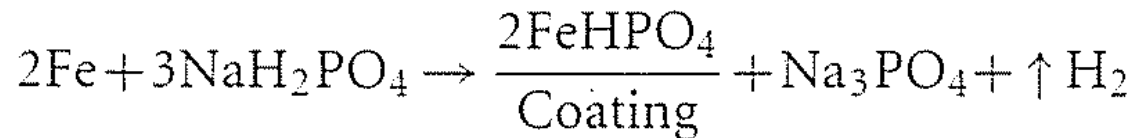
- Conversion coatings refer to the types of coating which on application convert the substrate into a compound with desirable properties. Metal surface is converted into a compound having the desired porosity to act as a good base for a paint.

Examples: Phosphate and chromate coatings.

- The surface so prepared, provides a high degree of adhesion and corrosion resistance.

An important conversion coating is PHOSPHATING, presented below..

- Reaction that takes place (e.g. for iron phosphate):



- Phosphate conversion coatings are well-known and widely used for applications on steel, zinc and aluminum.

Common Types of Phosphate coatings

Zn phosphate, Fe phosphate, other (Mg, Cr) phosphate.

PROCESS OF PHOSPHATING

- Phosphate coatings are generally applied by *immersion or spraying*.
- The bath contains generally zinc phosphate in phosphoric acid and an oxidizing agent, e.g. nitrate.
- Metallic workpiece passes through the following stages:
 - 1) Alkaline cleaning with an alkali (3-8 g/L) at 82°C.
 - 2) Hot rinsing with water at 77°C.
 - 3) Cold rinsing with water at 25°C.
 - 4) Acid pickling by H_2SO_4 (15 wt%) at 60°C.
 - 5) **Zinc phosphate bath at 25°C.**
 - 6) Neutralization by NaNO_2 .
 - 7) Lubrication with soap at 66°C.

Car body immersed in ZnPHOS bath before painting



ADVANTAGES of Phosphating

1. Phosphate coatings have a good resistance to corrosion.
2. They are porous and so make an attractive **base (primer)** for application of paints and organic coatings.
3. The rate of corrosion is substantially decreased when paints are applied on phosphate coatings.
4. Used as protection against corrosion in combination with sealing film of oil or grease instead of paint.
5. Phosphate coatings find application in: military equipment, cars, refrigerators, washing machines, etc...

Metal (Hot) Spraying

- The coating metal is filled in spraying gun/piston and sprayed on metal.
- The gun is equipped with oxyacetylene flame & supply of compressed air.
- Melting of metal wire and spraying occurs simultaneously and a uniform coating is developed.
- Widely used for applying coating of Cu,Pb,Ni,Sn, Al,Zn,etc.

ADVANTAGES:

- High speed
- Capable to cover larger area in short time
- Uniform coating can be obtained

Metal (Hot) Spraying

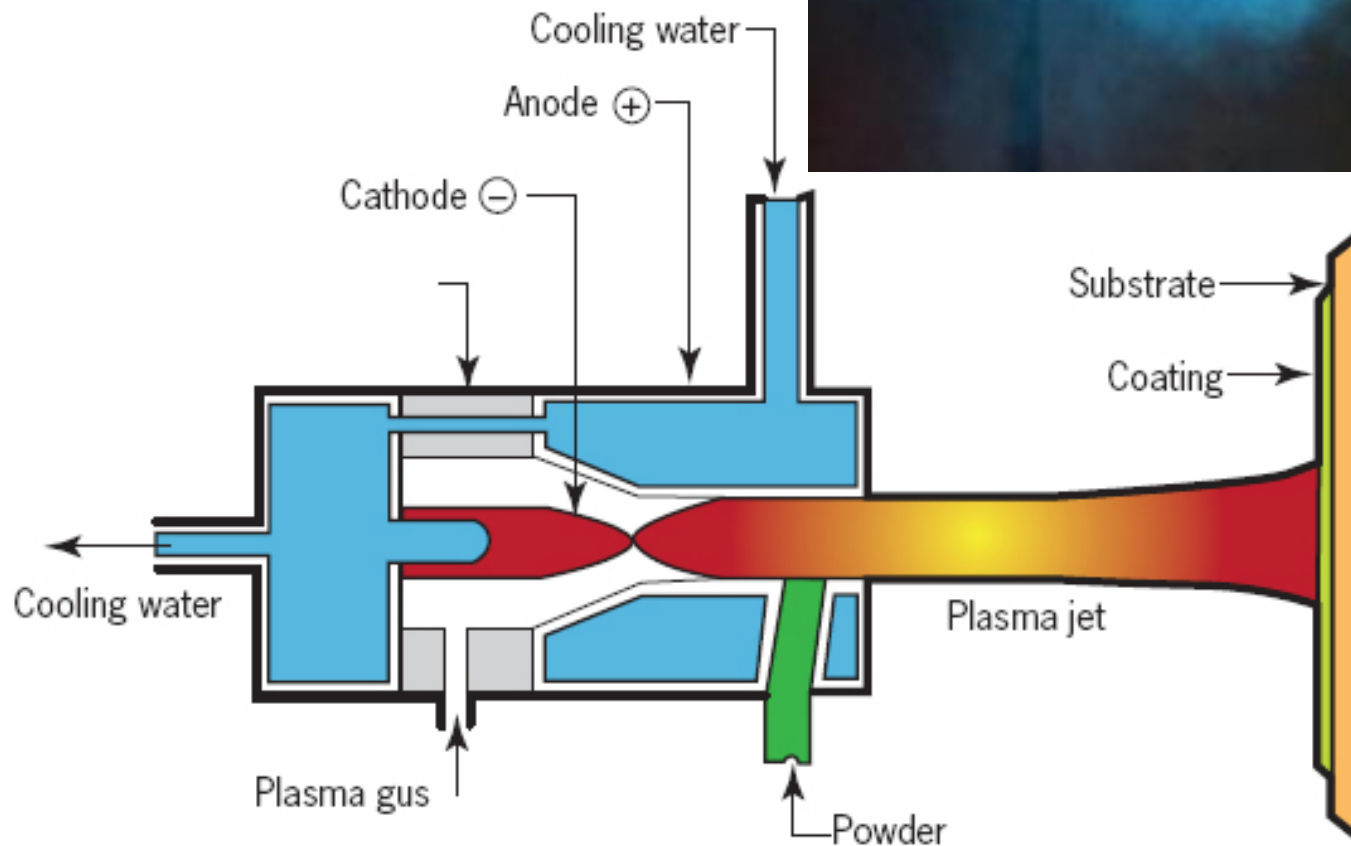


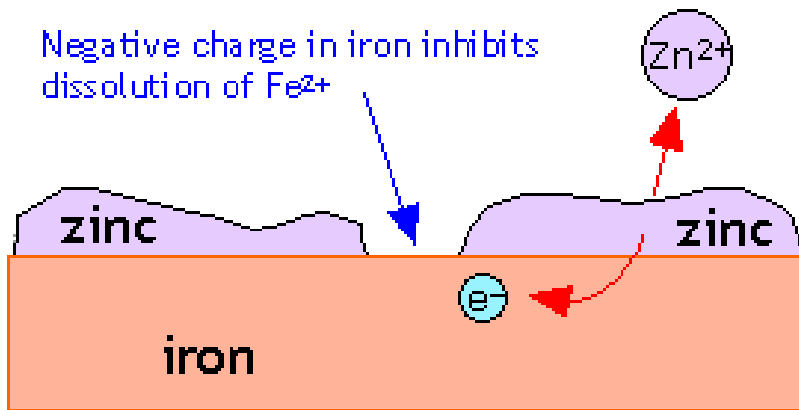
Diagram (cross-section) of a plasma gun.

(III) ANODIC (SACRIFICIAL) COATINGS

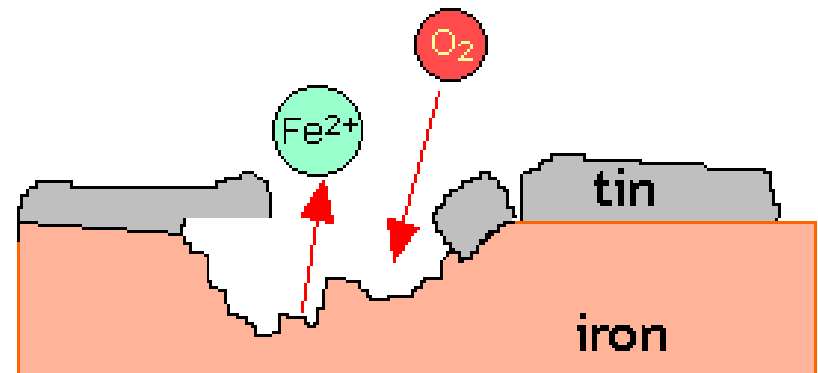
- This is a coating which is anodic to the substrate, such as zinc & aluminum coatings on steel.
- They protect the substrate at the expense of the metallic coating applied. The zinc coatings protect the substrate by acting as a sacrificial anode for the steel which is cathodic to zinc (-0.440 V vs. -0.760 V).
- Any breaks in the coating cause the anodic oxidation of Zn to occur:
$$\text{Zn} = \text{Zn}^{2+} + 2 \text{e}^{-}$$
- The electrons are consumed by the iron substrate which acts as a cathode. The potential is made more negative by electrons and a cathodic reaction is forced to occur on it:
$$2\text{H}^{+} + 2\text{e}^{-} = \text{H}_2$$
- A fine film of H_2 is formed on the surface. Thus, by acting as a sacrificial material, zinc corrodes while the steel substrate is protected.

(VI) CATHODIC (NOBLE) COATINGS

- This coating is electropositive to substrate.
- Example is **copper-coated steel**: Copper ($E = +0.337 \text{ V}$) is positive to steel ($E^\circ = -0.440 \text{ V}$).
- The coatings must be pore-free and thick which can be obtained by *electroplating*.
- Often an intermediate layer is put in between the substrate and the noble coating, such as the nickel-chromium coatings.



Sacrificial coating



Noble coating

CATHODIC (NOBLE) COATINGS

- The use of metallic coatings (cathodic and anodic) is only justified by longer life as they are substantially more expensive than the organic coatings.
- The following are the major methods used for applying metallic coatings:
 - a) Electroplating (See Figure)
 - b) Hot dipping
*(used for galvanizing:
dip steel in molten zinc)*
 - c) Spraying
 - d) Vapour deposition
 - e) Welding.

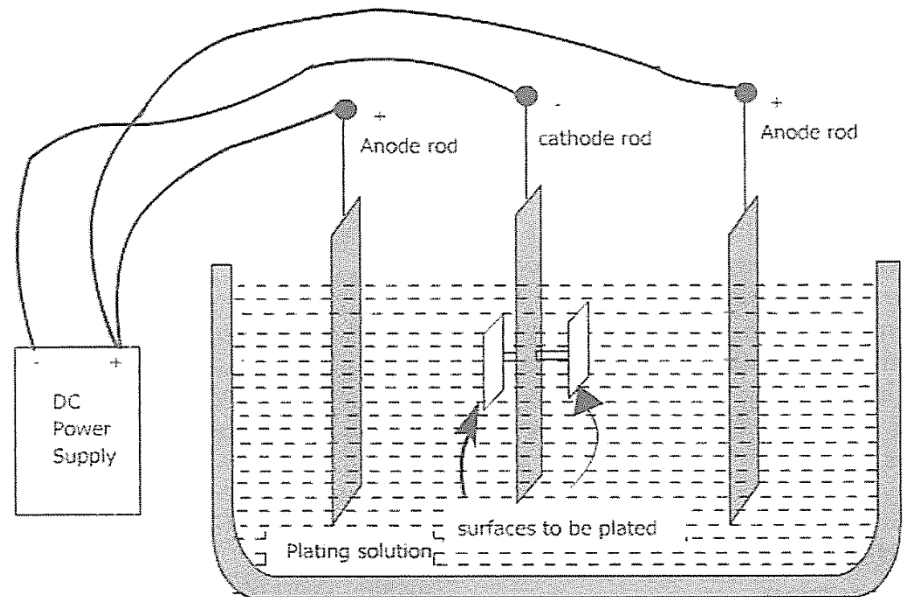


Figure 7.1 Plating bath

SELECTION OF COATINGS

- Selection of an appropriate coating system is a prerequisite for the durability of coating.
- Below is a list of factors which deserve consideration:
 - 1) Cost and life to the first maintenance.
 - 2) Compatibility with the environment.
 - 3) Resistance to atmospheric pollution.
 - 4) Resistance to extreme climates.
 - 3) Ease of maintenance.
 - 6) Safety problem.

Exercise (coating /penetration rate)

- Electroplated nickel coatings are sometimes used to coat materials that are susceptible to corrosion (e.g. Ni coatings on steel auto bumpers).
- Tests have shown that the weight loss of such a Ni coating after being in service for one year is 0.089 g of Ni per cm² of surface area.
 - a) Calculate the equivalent corrosion rate in $\mu\text{A}/\text{cm}^2$.
 - b) If a coating of thickness 0.005 cm is used, how long will it last?

Example: Copper Plating Process

Design a process to electroplate a 0.1-cm-thick layer of copper onto a 1 cm × 1 cm cathode surface.

SOLUTION

In order for us to produce a 0.1-cm-thick layer on a 1 cm² surface area, the weight of copper must be:

$$\rho_{\text{Cu}} = 8.96 \text{ g/cm}^3 \quad A = 1 \text{ cm}^2$$

$$\text{Volume of copper} = (1 \text{ cm}^2)(0.1 \text{ cm}) = 0.1 \text{ cm}^3$$

$$\text{Weight of copper} = (8.96 \text{ g/cm}^3)(0.1 \text{ cm}^3) = 0.896 \text{ g}$$

From Faraday's equation, where $M_{\text{Cu}} = 63.54 \text{ g/mol}$ and $n = 2$:

$$It = \frac{wnF}{M} = \frac{(0.896)(2)(96,500)}{63.54} = 2722 \text{ A} \cdot \text{s}$$

SOLUTION (Cont'd)

Therefore, we might use several different combinations of current and time to produce the copper plate:

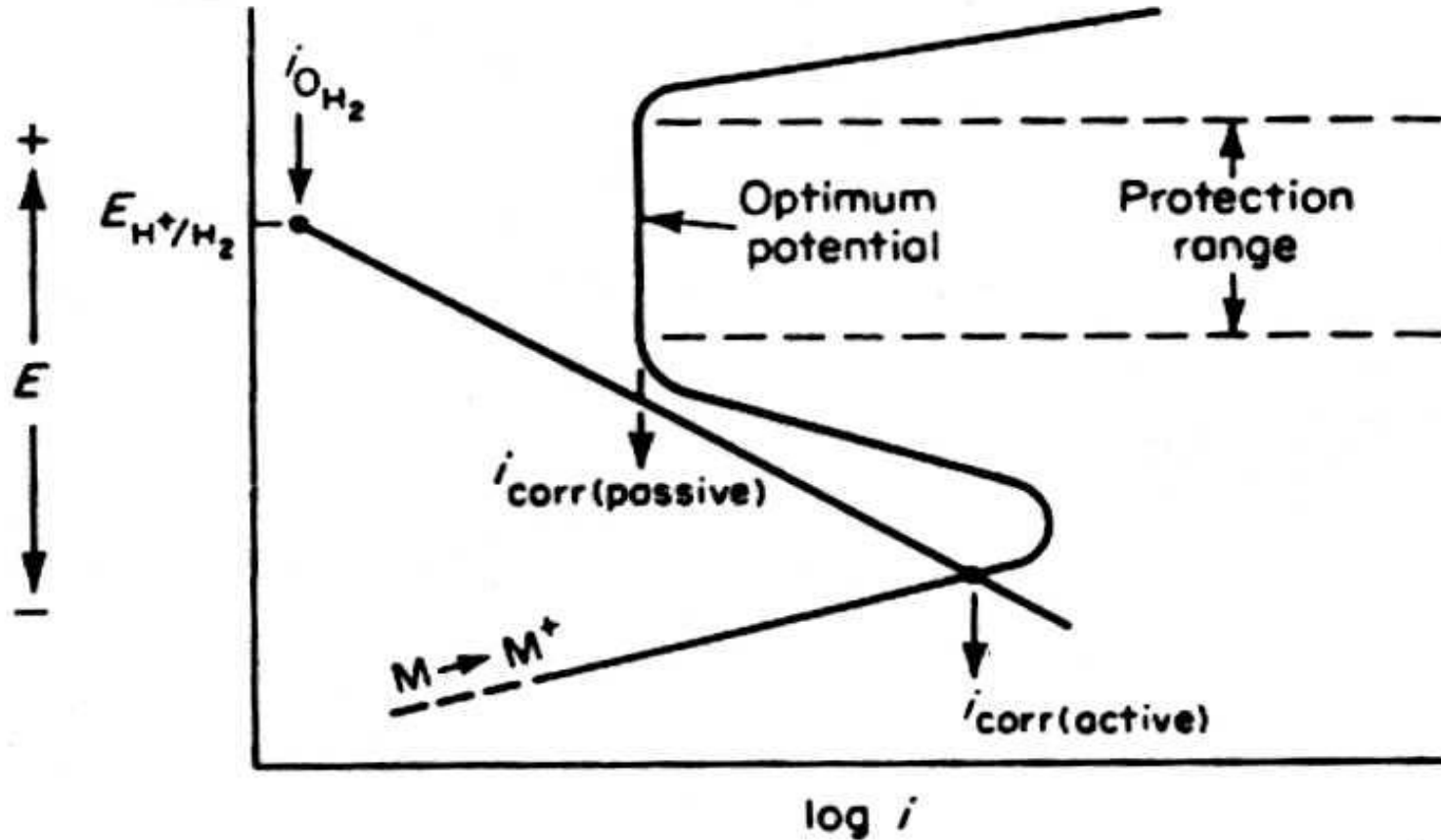
Current	Time
0.1 A	27,220 s = 7.6 h
1.0 A	2,722 s = 45.4 min
10.0 A	272.2 s = 4.5 min
100.0 A	27.22 s = 0.45 min

Our choice of the exact combination of current and time might be made on the basis of the rate of production and quality of the copper plate.

A current of ~ 1 A and a time of ~ 45 minutes are not uncommon in electroplating operations.

Electrical Protection

I. ANODIC PROTECTION



Schematic diagram showing protection range and optimum potential for anodically protecting an active-passive metal.

ANODIC POLARIZATION

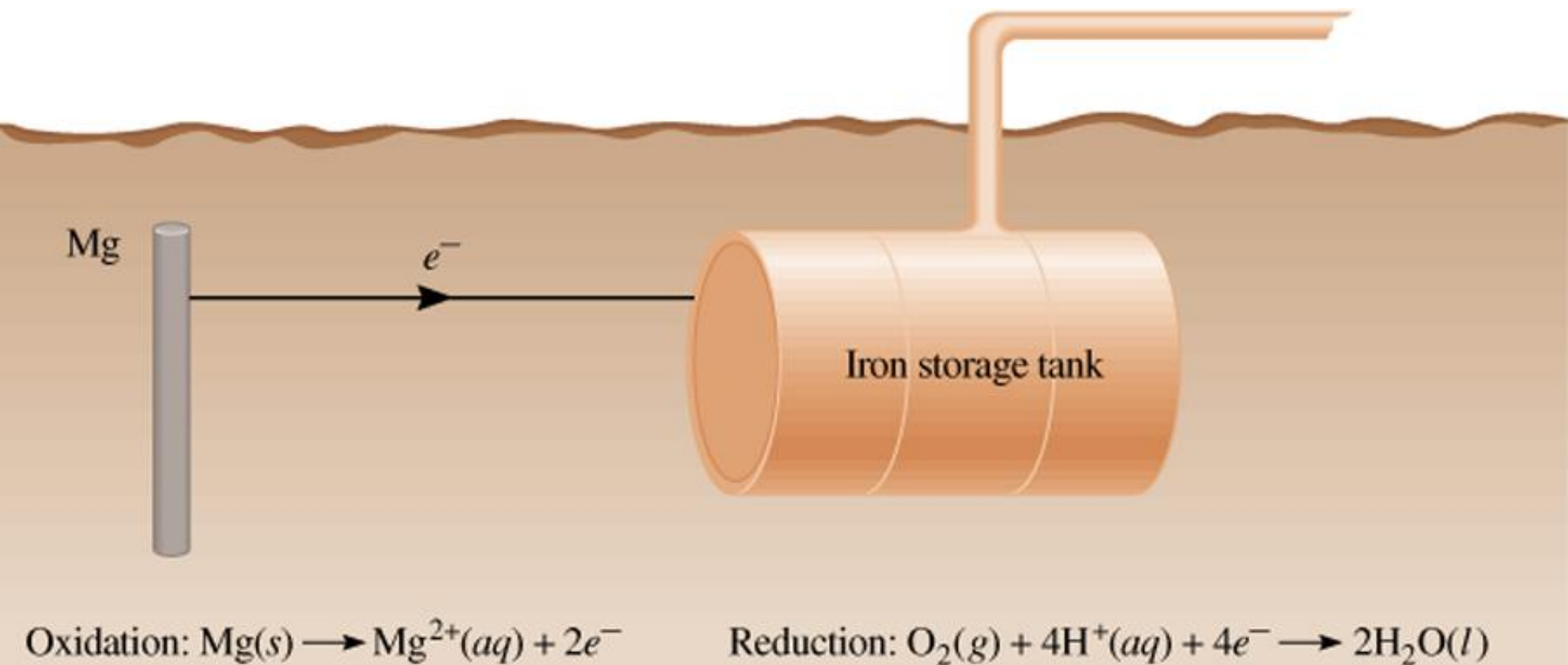
- For some metals, positive polarization forms an oxide / hydroxide surface film protective from corrosion.
- By this method called *anodic protection*, it is possible to passivate active-passive metals,
 - e.g. iron, chromium and nickel.
- The potential must be maintained in the region of passivity using a potentiostat.
- Anodic protection is achieved by making the metal to be protected an anode in an electrolytic cell.
 - The cell is supported by suitable potential from a power source, e.g. battery.
 - This would cause the metal to passivate at some high voltage.
- Application:

Anodic protection is widely used in *transport of acids and corrosives in metal containers* and similar applications.

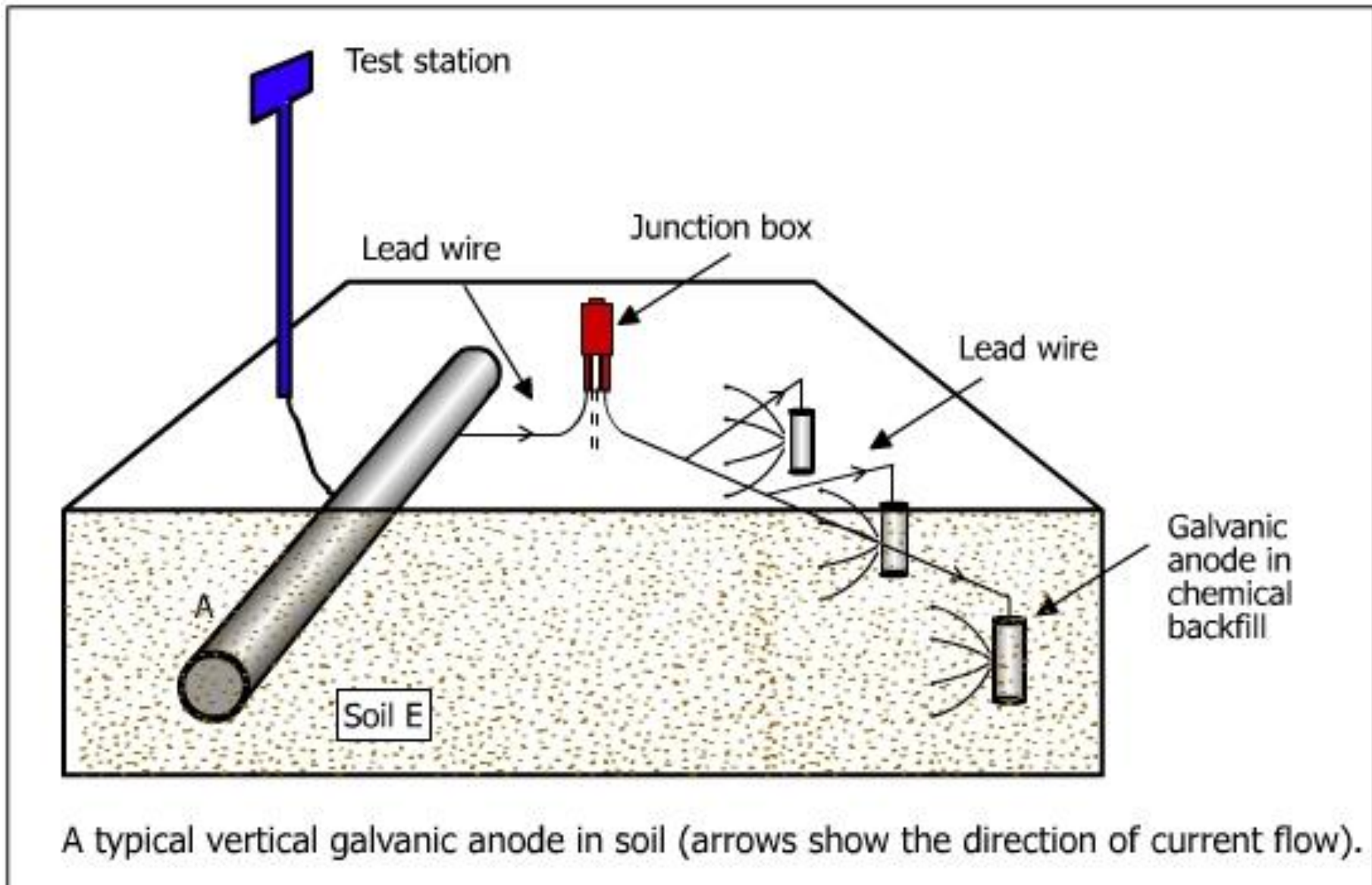
II. CATHODIC PROTECTION

- Cathodic protection system design is based upon protecting the bare surface area of the buried / submerged metallic structure.
- Typically a well coated pipeline will be protected over 90% of its surface.
- In this case, only 10% of the pipeline surface will require cathodic protection current.
- Two types of cathodic protection systems exist:
 - a) Galvanic anode system (or Sacrificial anode system).
 - b) Impressed current anode system.
- In both systems, the metallic structure is made the cathode (negative) by connecting it to galvanic anodes, which are less noble than the metallic structure to be protected.

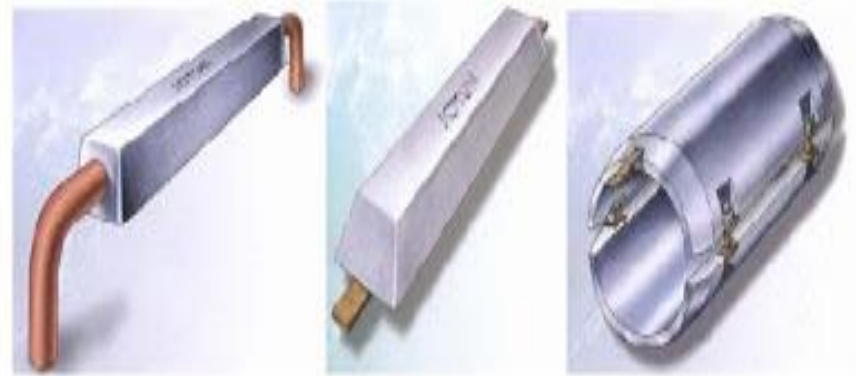
Cathodic Protection of an Iron Storage Tank



A galvanic anode cathodic protection system is shown below.



Sacrificial Anode Types



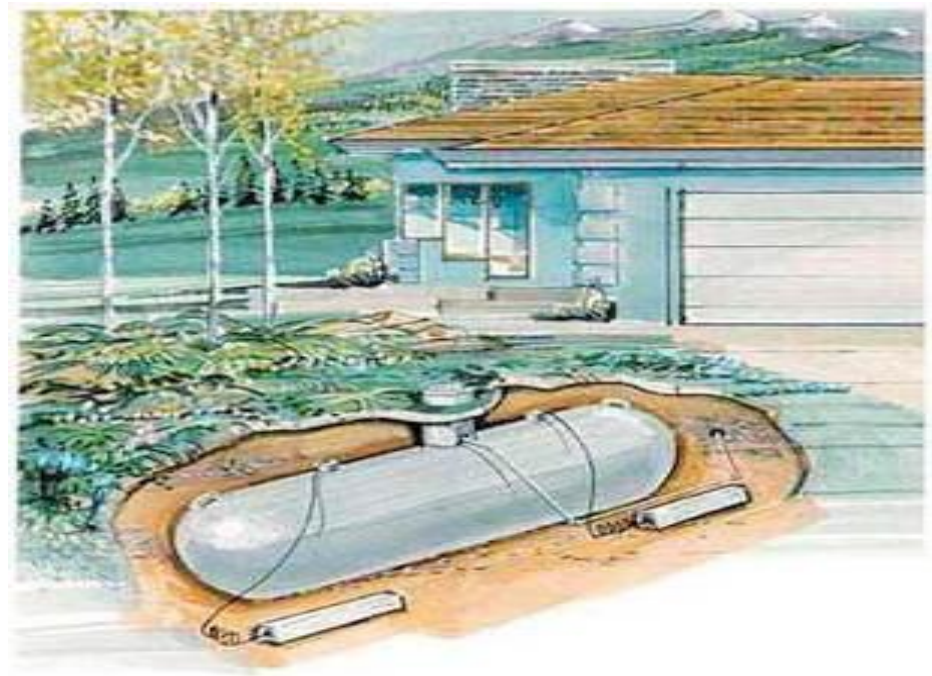
Sacrificial Anodes: New and Old



Small sacrificial anode packed in calico bag containing chemical backfill



CATHODIC PROTECTION Applications



- Cathodic protection can be achieved in two ways:

1) Sacrificial Anode

2) Impressed current

a) Galvanic – sacrificial anode protection

- In this technique, the current is generated by the corrosion of active metals, such as magnesium, zinc and also aluminum:



- A suitable anode is buried adjacent to and level with the invert (lowest part) of a pipeline.
- The anode Mg or Zn, is connected to the pipeline or any buried metallic structure by an insulated cable.

Magnesium & Zinc Sacrificial Anodes

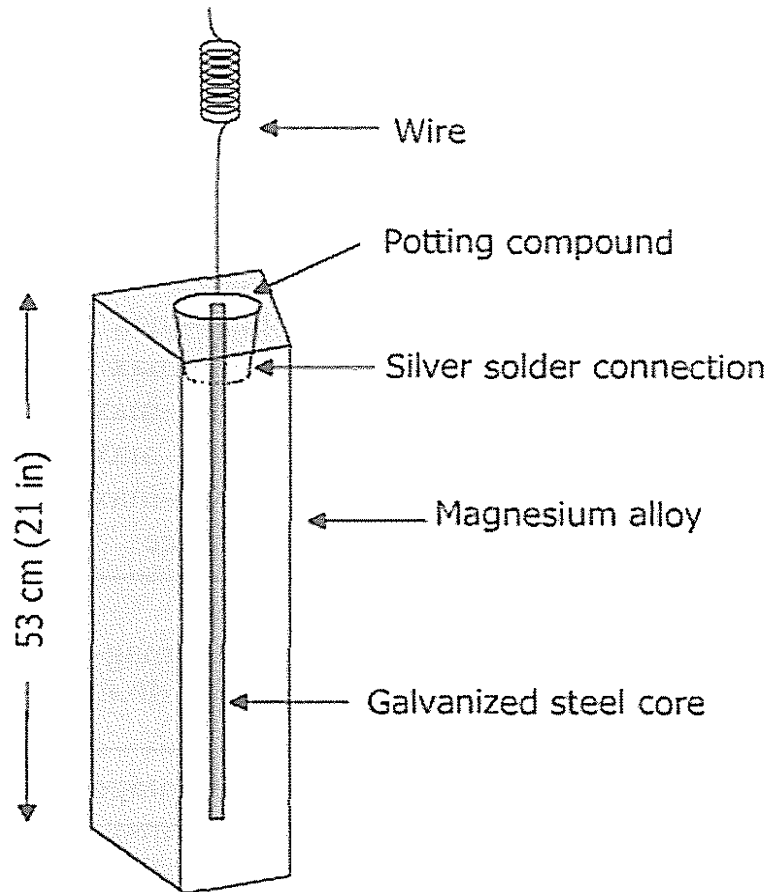


Figure 5.18 Typical 14.5 kg magnesium galvanic anode

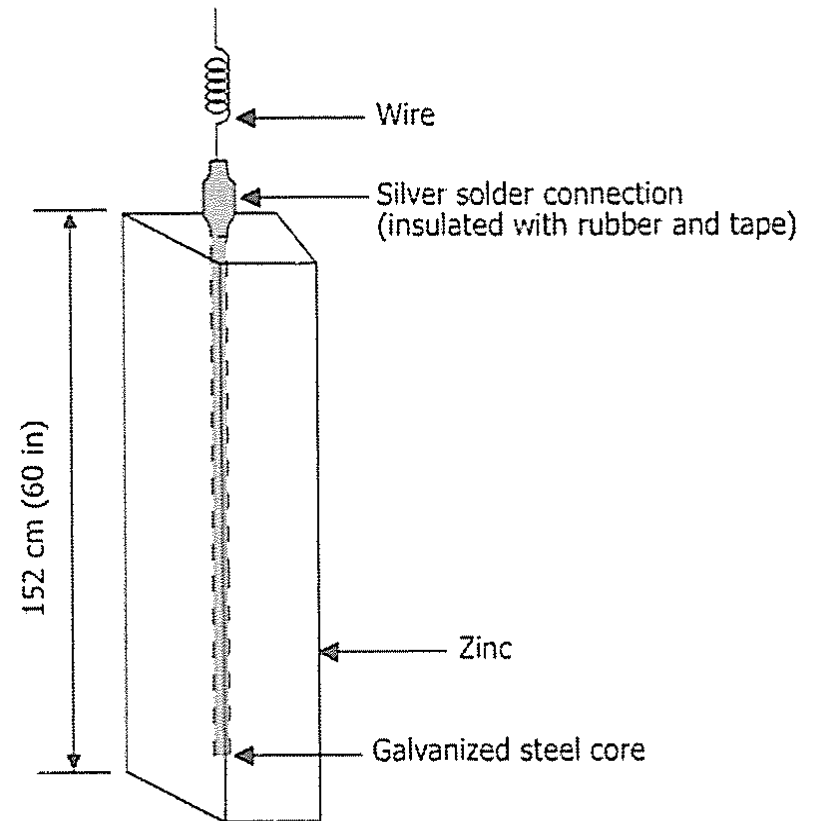


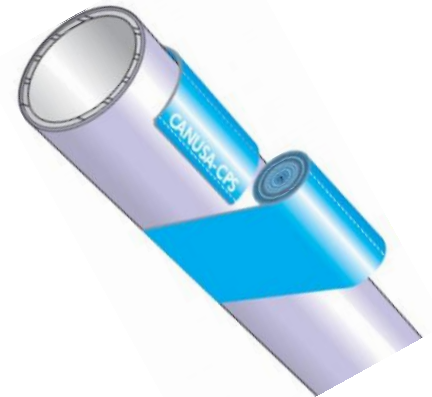
Figure 5.19 Typical 13.6 kg (30 lb) zinc anode

Magnesium & Zinc Sacrificial Anodes

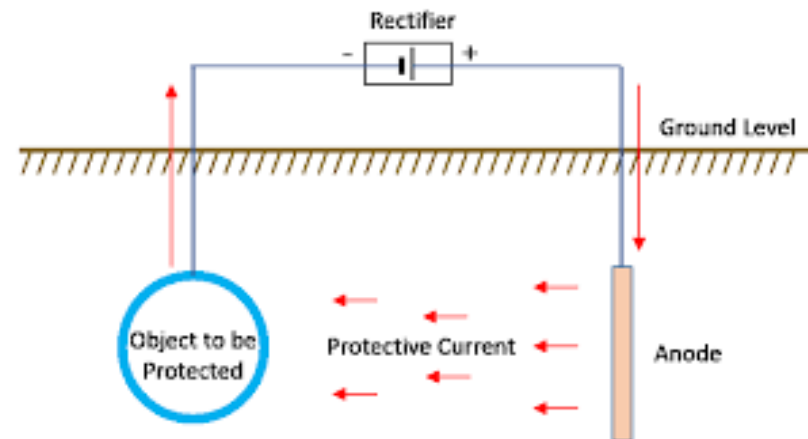
- The anodic installation is often designed for **ten years** but may last much longer if current demand is low.
- The potential of the pipe must be continuously monitored and the value should **not be allowed to fall below -0.85 V** (CuSO_4 reference electrode).
- A 70 lb Mg anode practically gives a current of more than 300 mA in a soil of average resistivity of 2000 ohm.cm. Bare steel sometimes requires about 15 mA/ft².
- A single anode can protect about 2 square feet of the pipe.

Magnesium & Zinc Sacrificial Anodes

- By applying a coating:
the current requirement is reduced to $0.5 \mu\text{A}/\text{cm}^2$, hence one Mg anode can protect up to 6000 square feet of the pipe surface.
- Chemical backfill:
mixture of clay and gypsum *to help dissolve anode and reduce soil resistivity* for electrochemical reactions.
- It has been shown that a combination of cathodic protection & coating is the most economical means of protecting steel structures

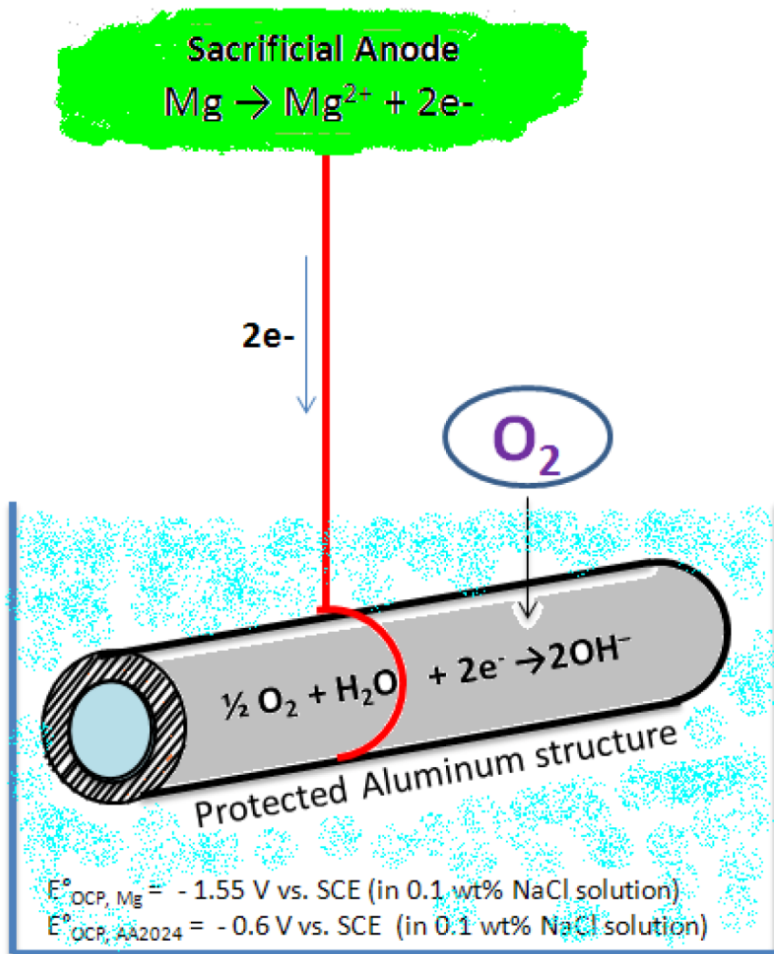


b) Impressed Current anode cathodic protection (ICCP)

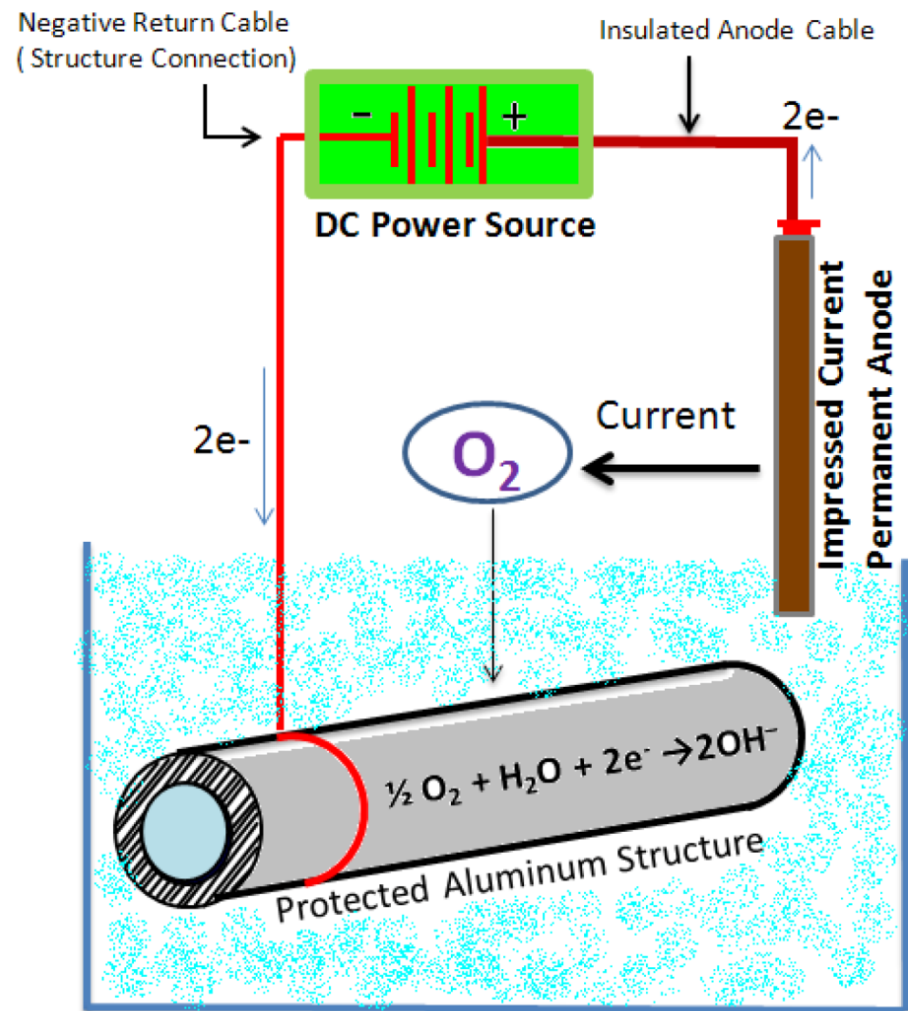


- Impressed current cathodic protection systems (ICCP) are used to provide cathodic protection for pipelines, ship hulls, offshore production platforms, water and wastewater treatment equipment, tank farm and of course underground storage tanks.
- The principle advantage of ICCP is its much greater output capacity as compared to galvanic anode systems. Therefore when protection is desired for large, poorly coated and bare structures ICCP is often the choice.
- ICCP systems require external DC power source that is energized by standard AC current.
- There are many anode materials available and most of them provide 100-10000 times current provided by galvanic anodes.
- The amount of Metal exposed in UST's is very large, so to inhibit corrosion, current required is typically in excess of 4-8 amps per service station.

Sacrificial Anode CP Method

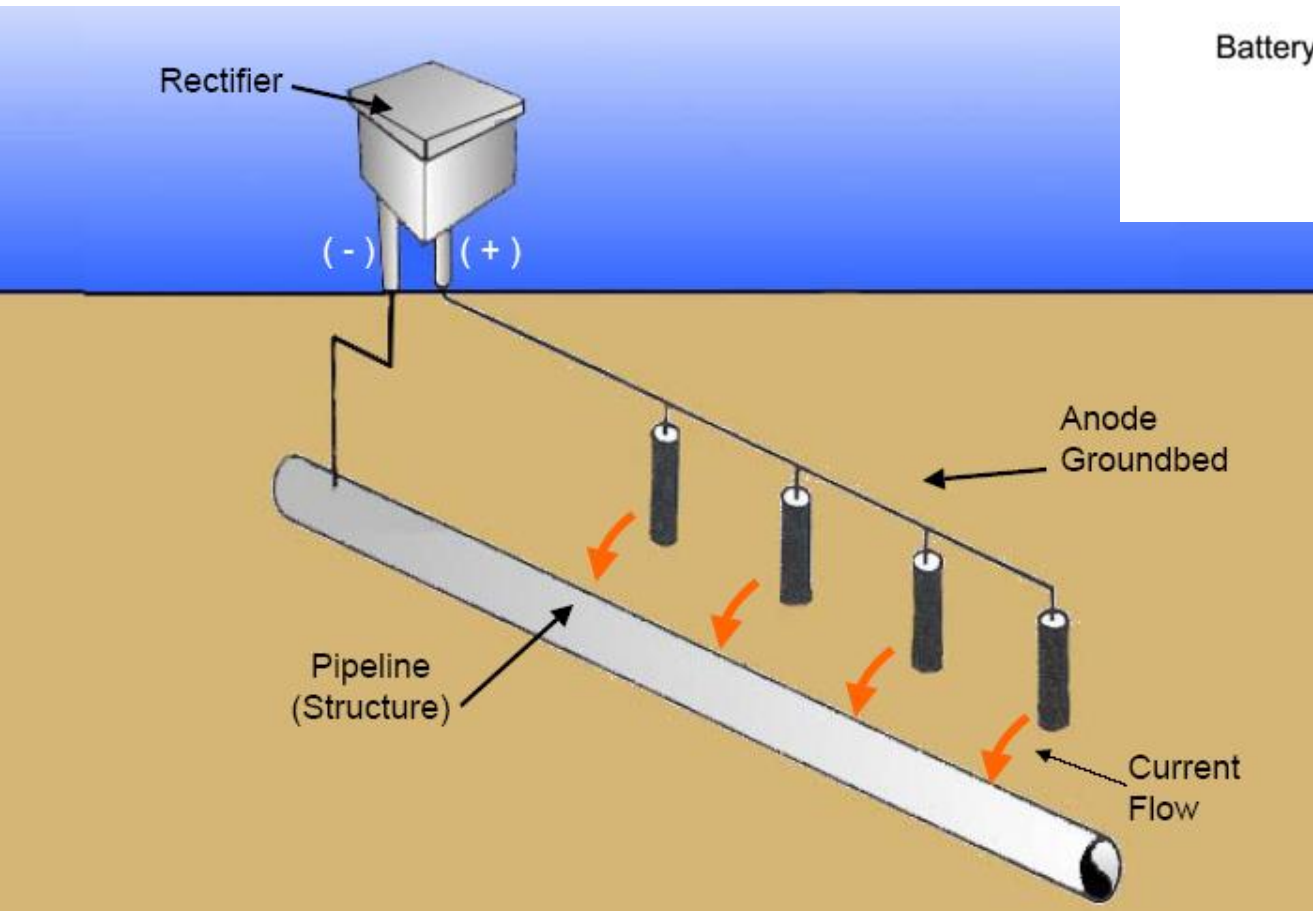


Impressed Current CP Method



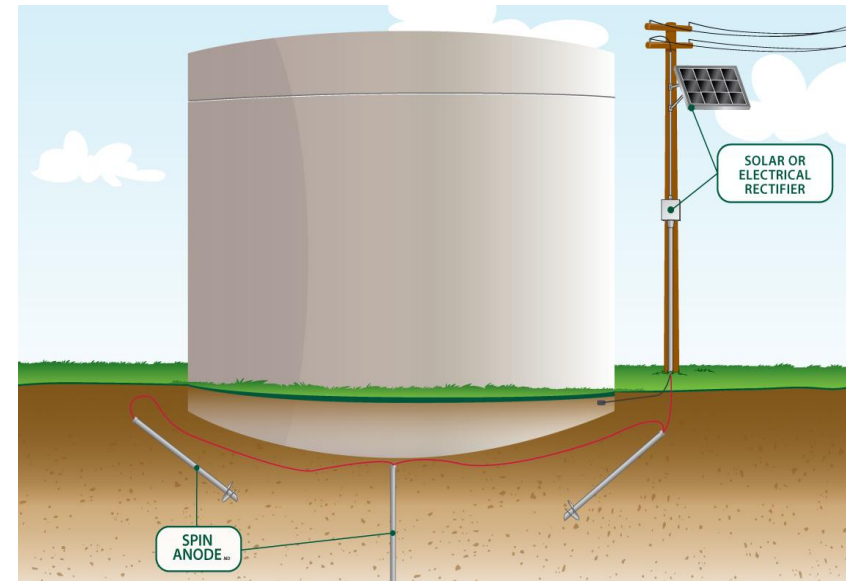
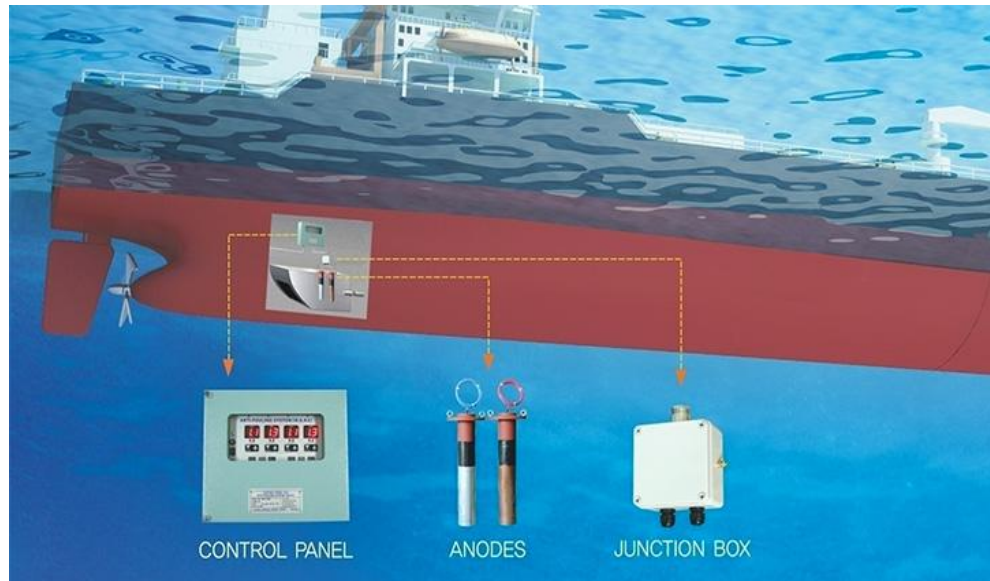
Cathodic Protection (CP) Methods

Impressed Current anode

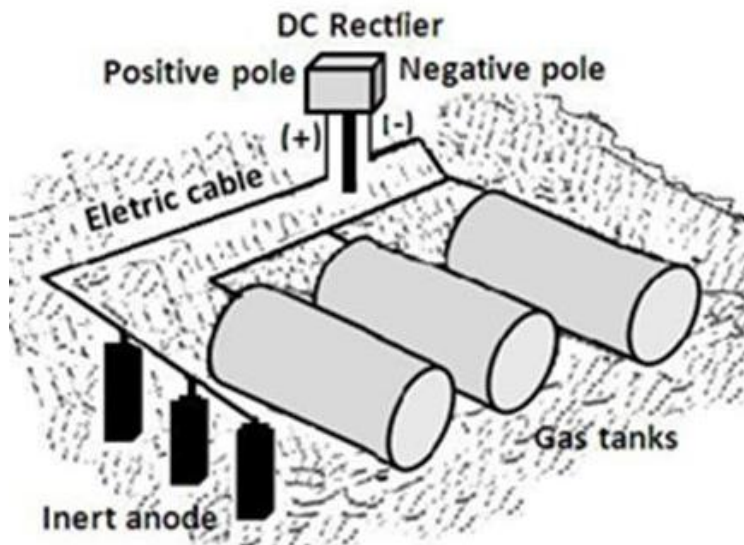


**solar power for
cathodic protection**

Impressed Current Applications

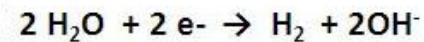


Above-ground storage tank



Electrolytic reactions:

Cathode



Inert anode



Comparison of Cathodic Protection Systems

General Disadvantages:

Sacrificial anode systems

- Large weight for large capacity, long life systems.
- Response to varying operating conditions is limited.
- Hydrodynamic loadings can be high (Seawater drag)

Impressed current systems

- Relative complexity of system demands high level of design expertise.
- In-service operator surveillance required.
- Vulnerable to component failure or loss of power.