Corrosion in Petroleum industry 2016(Part II)

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Introduction to Corrosion Monitoring
What is Corrosion Monitoring?

The field of corrosion measurement, control, and prevention covers a very broad spectrum of technical activities. Within the sphere of corrosion control and prevention, there are technical options such as

1-cathodic and anodic protection

2-materials selection

3- chemical dosing

4- the application of internal and external coatings. Corrosion measurement employs a variety of techniques to determine how corrosive the environment is and at what rate metal loss is being experienced. Corrosion measurement is the quantitative method by which the effectiveness of corrosion control and prevention techniques can be evaluated and provides the feedback to enable corrosion control and prevention methods to be optimized.

Corrosion measurement

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Corrosion measurement is the quantitative method by which the effectiveness of corrosion control and prevention techniques can be evaluated and provides the feedback to enable corrosion control and prevention methods to be optimized.

A wide variety of corrosion measurement techniques exists, including:

Non Destructive Testing Analytical Chemistry

- Ultrasonic testing
- Radiography
- Thermography
- Eddy current/magnetic flux
- Intelligent pigs

Analytical Chemistry

- pH measurement
- Dissolved gas (O_2, CO_2, H_2S)
- Metal ion count (Fe^{2+}, Fe^{3+})
- Microbiological analysis

Operational Data

- pH
- Flow rate (velocity)
- Pressure
- Temperature

Fluid Electrochemistry

- Potential measurement
- Potentiostatic measurements
- Potentiodynamic measurements
- A.C. impedance

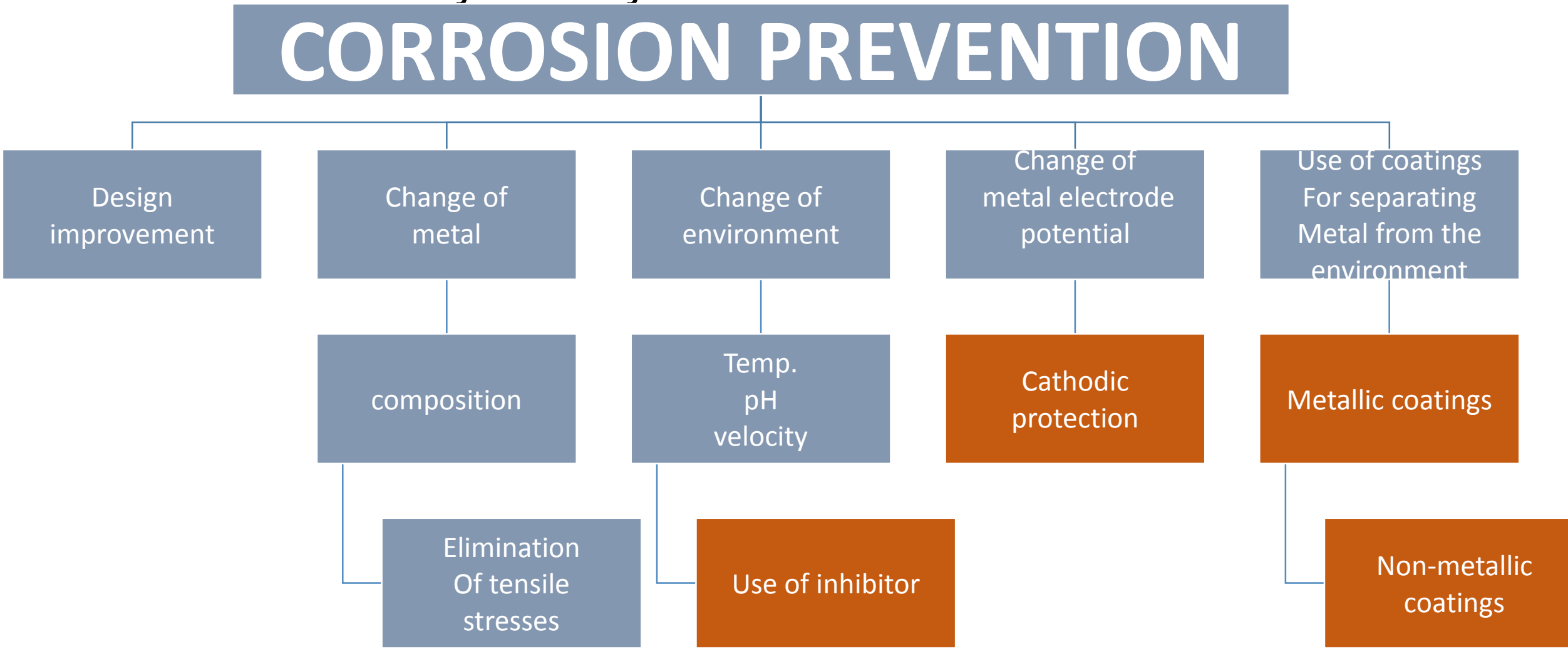
Corrosion Monitoring

- Weight loss coupons
- Electrical resistance
- Linear polarization
- Hydrogen penetration
- Galvanic current

Introduction

- Corrosion of metals occurs when they come in electrical contact with a corrosive environment. Therefore, metallic corrosion can be prevented by :
- **Design Improvement .**
- **Change of Metal.**
- **Change of Environment .**
- **Change of Metal Potential .**
- **Use of Coatings.**

Classification of Corrosion Prevention methods



Classification of Corrosion Prevention Methods in Petroleum industry

A- Change of Metal Potential (Cathodic Protection)

B- Change of Environment Inhibitors

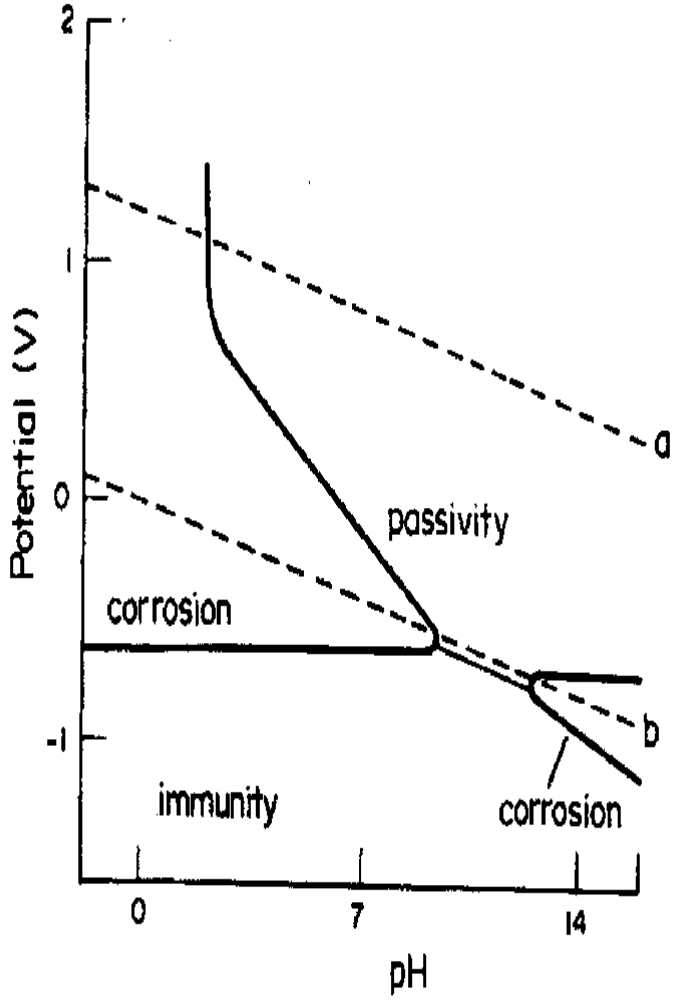
C- Coatings

A- Change of Metal Potential (Cathodic Protection)

Examination of Pourbaix (potential/pH) diagrams indicates that in most cases corrosion can be prevented by changing the electrode potential of the metal. This can be achieved by:

1-Lowering the potential of the metal in the negative (anodic) direction in the domain of immunity. This is called cathodic protection.

2-Increasing the potential of the metal in the positive direction in the domain of passivity. This called anodic protection. These two methods are described below.



Cathodic Protection.

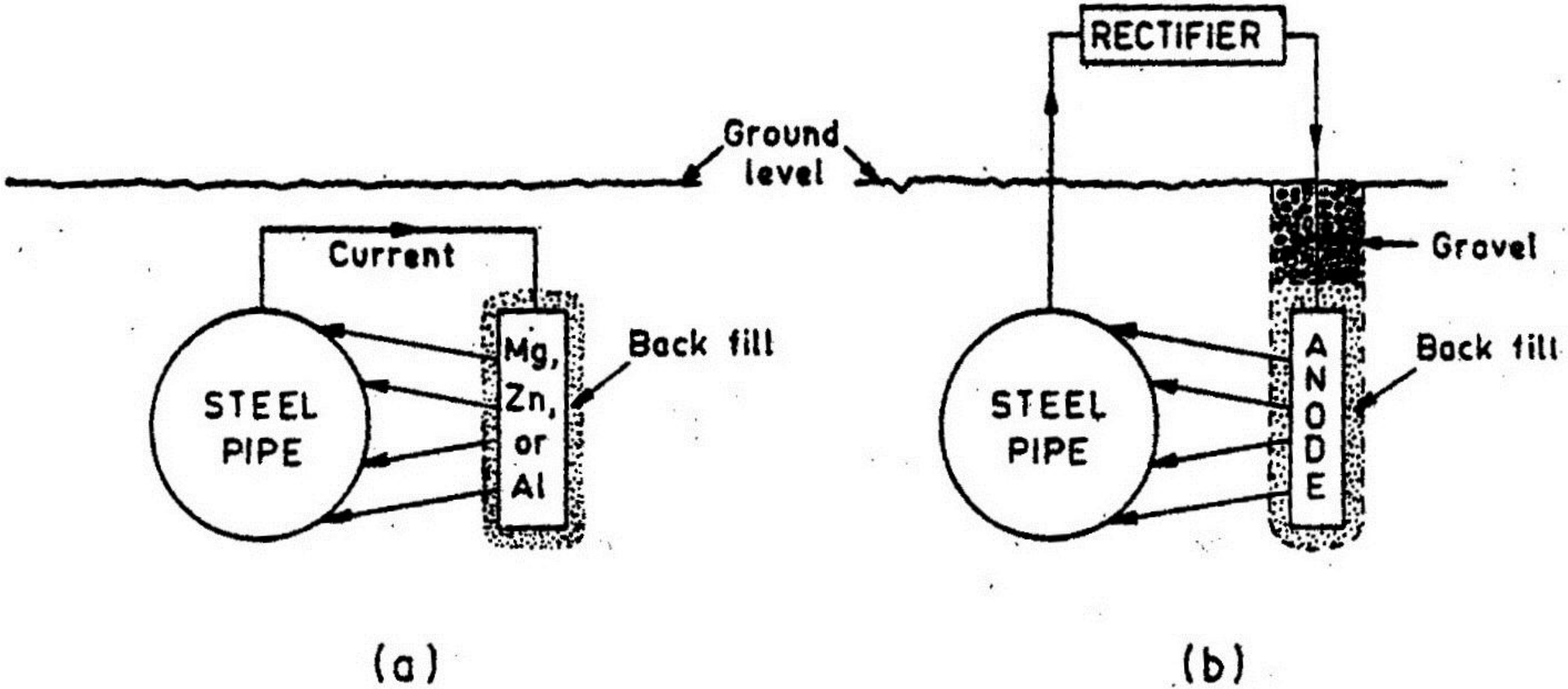
There are two methods of applying cathodic protection to metallic structures :-

A-Galvanic or sacrificial anode method.

B- Impressed current method.

In each method a direct current supply is made available for the protection of metal structures. The choice of the method to be used depends upon a number of economic and technical considerations.

cathodic protection



Galvanic or Sacrificial Anodes Method:

(i) *Anode material*. Factors to be considered in choosing anodes include driving voltage, capacity and cost.

Following materials are in general use.

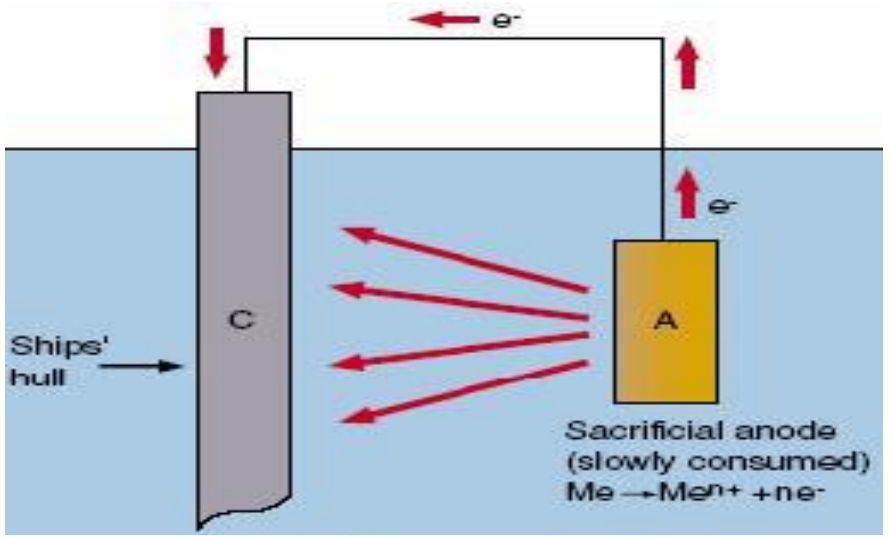
(a) *Magnesium and magnesium alloys*:($E°_{Mg}$ = – 2.3 V)

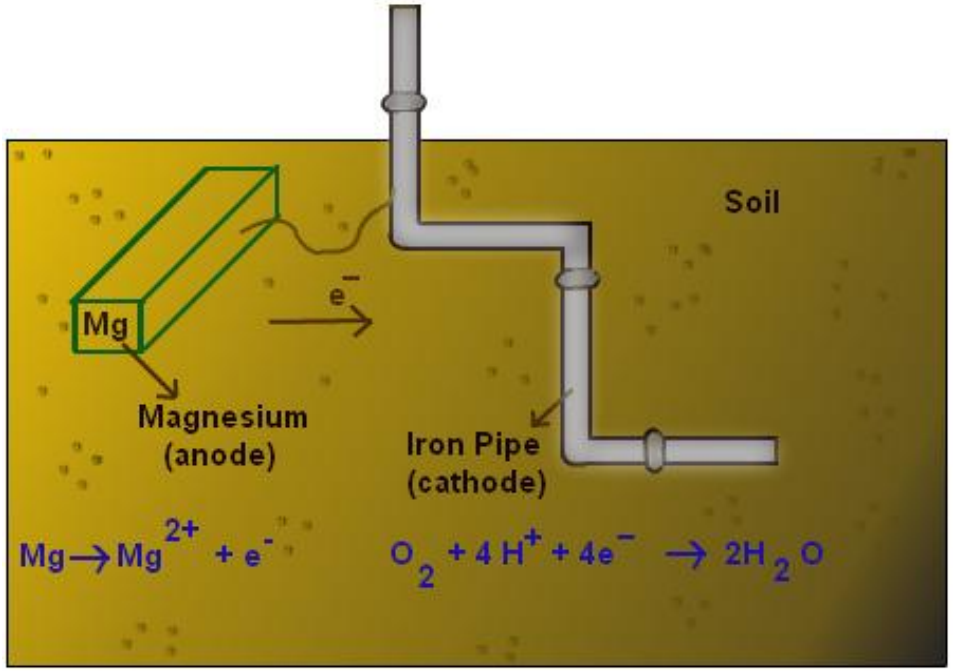
(b)Zinc and zinc alloys. Zinc ($E°_{Zn}$ = – 0.8V)

(c) *Aluminium and aluminium alloys.*

(ii) *Geometry of anode.*

(iii) *Number and spacing of anodes*:





Advantages of galvanic method

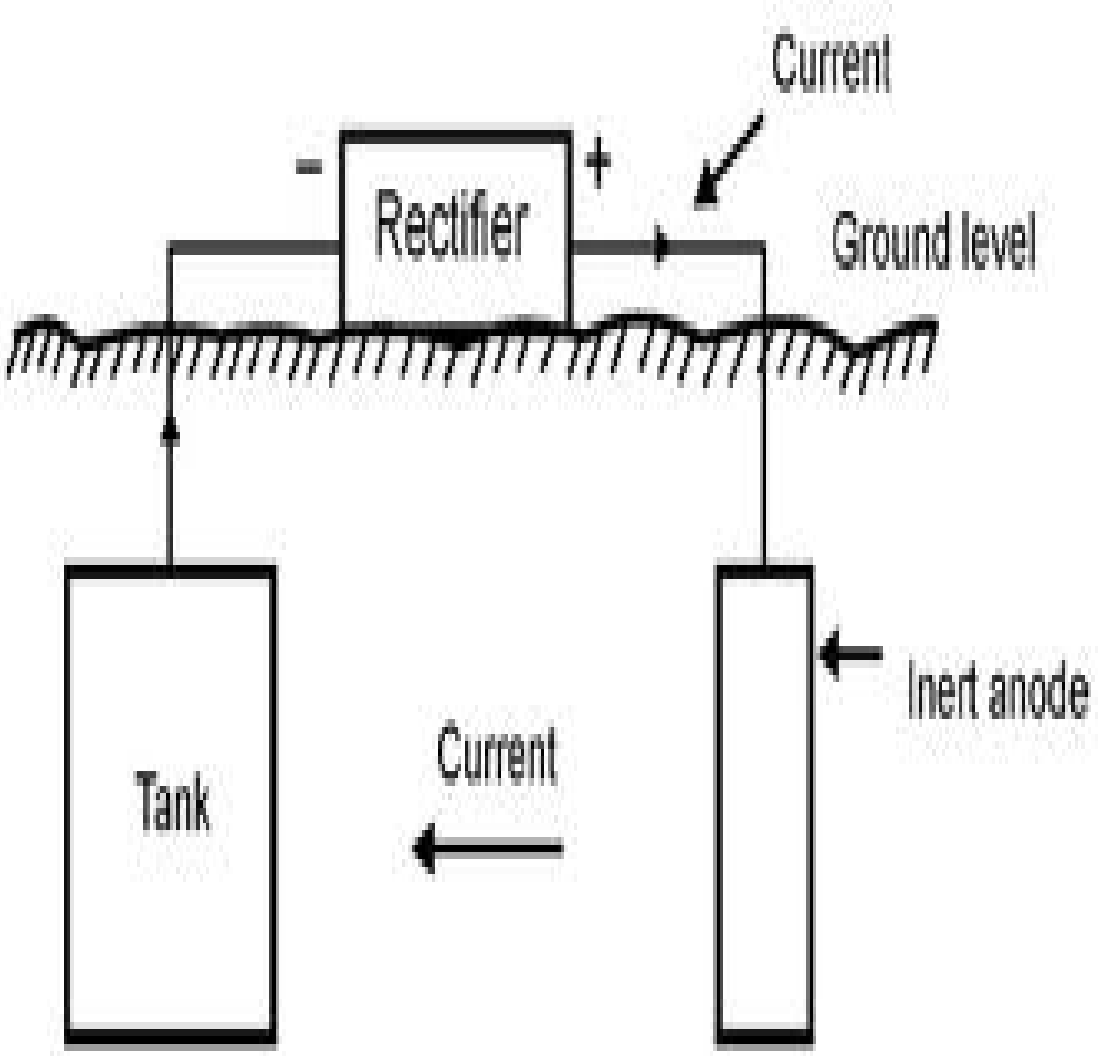
1. **Since no external power supply necessary, this method can be used in remote and difficult to reach areas.**
2. **Low installation cost.**
3. **Minimum maintenance cost.**

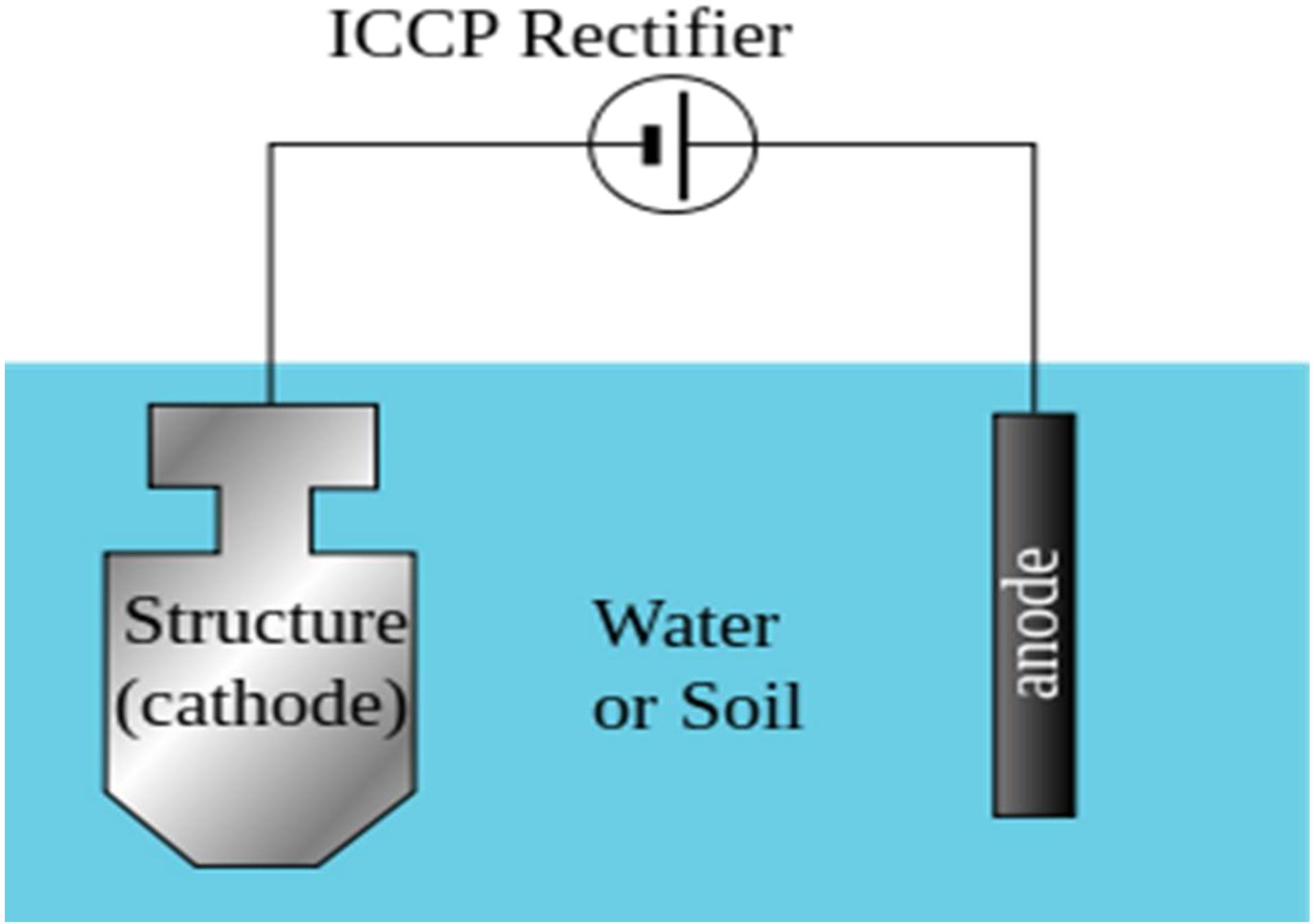
Limitations of galvanic method

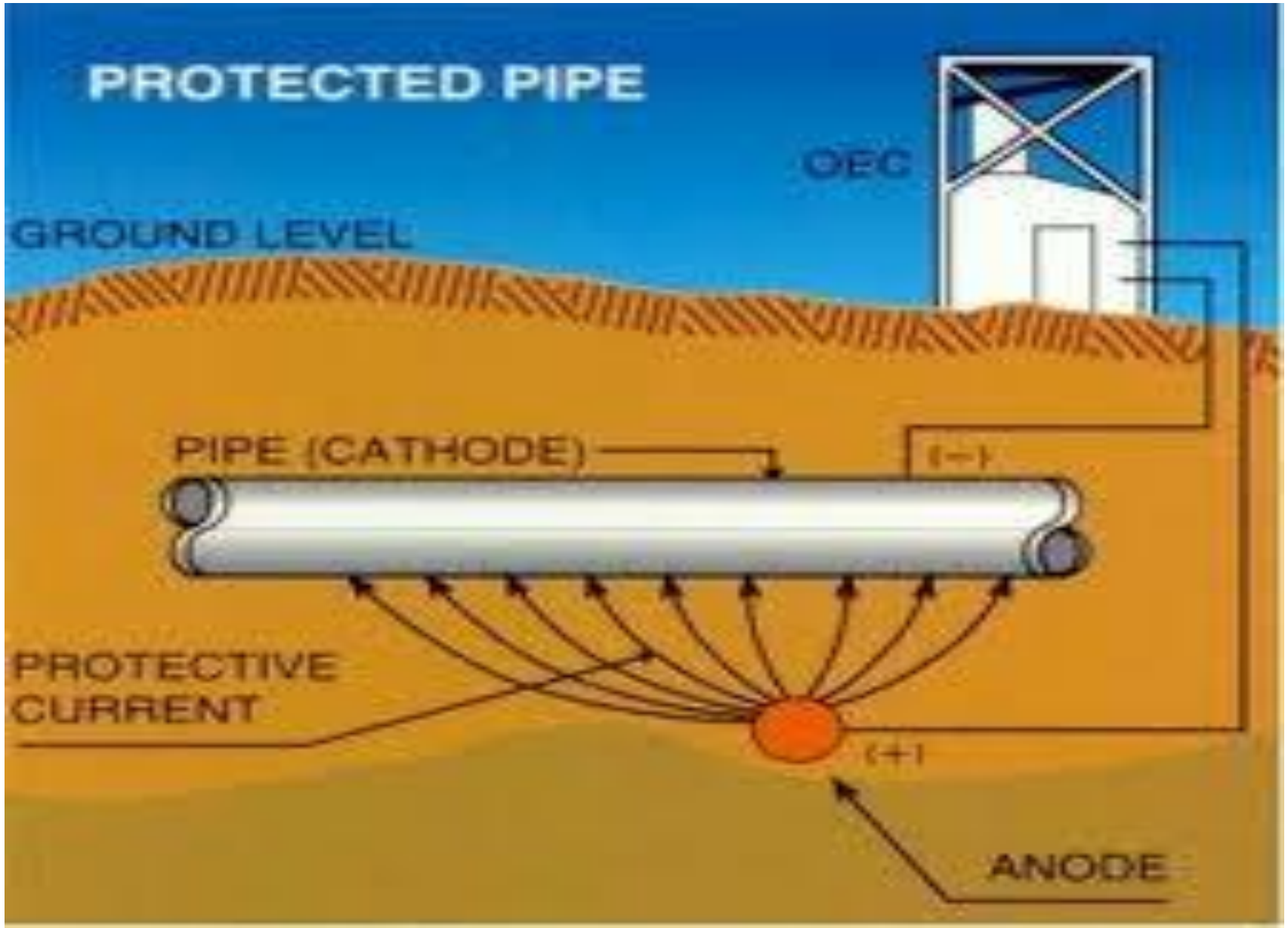
1. **Limited driving potential and current output.**
2. **Soil resistivity limitation.**
3. **Not applicable for large diameter bars or poorly coated pipe.**
4. **Mutual interference in multiple or parallel installation.**

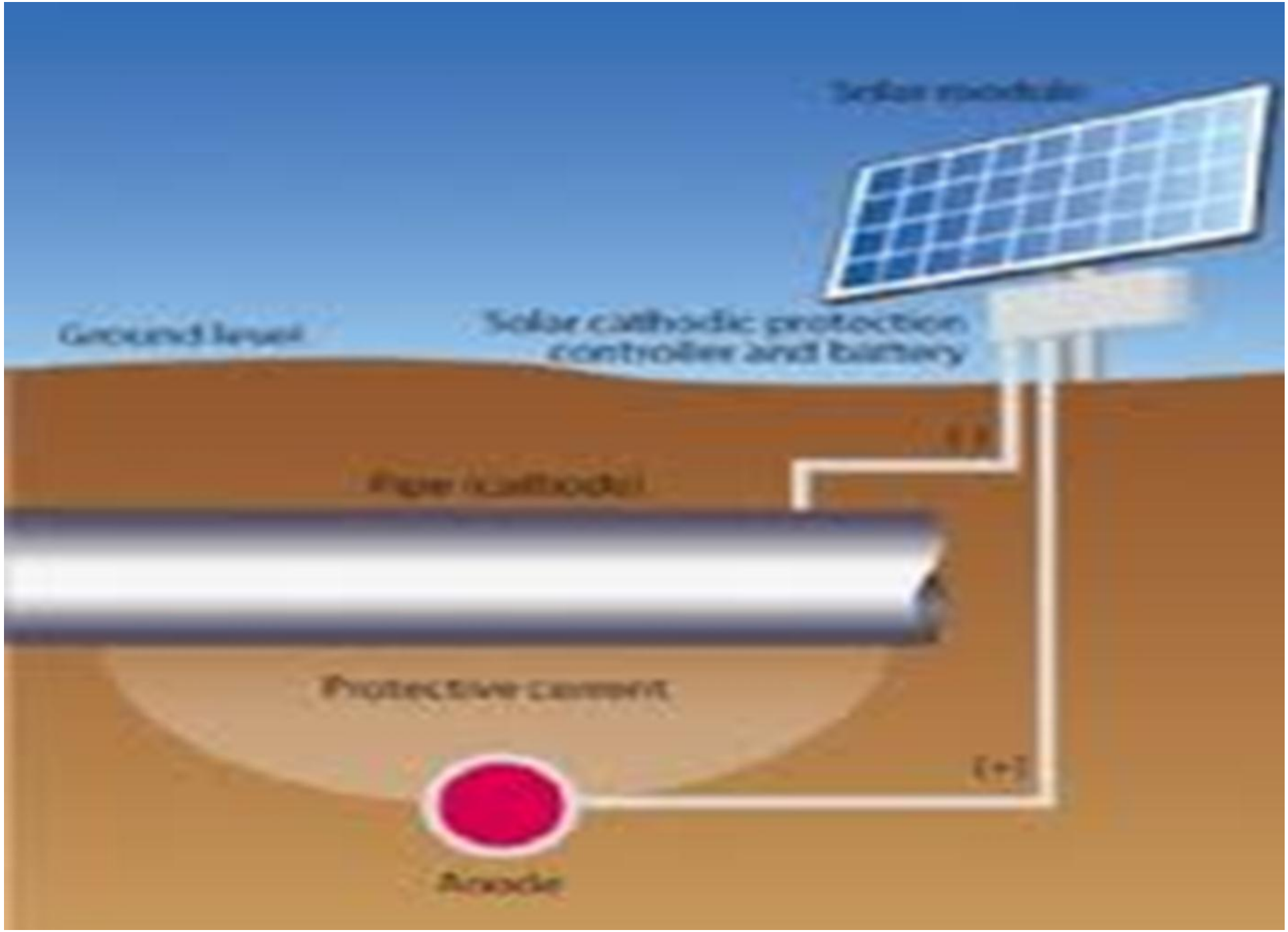
Impressed current method

In this method the metallic structure is made cathode with the use of impressed current by connecting the negative terminal of the external power supply source to the metallic structure to be protected and positive to an inert anode




ICCP Rectifier
Structure
(cathode)
Water
or Soil
anode


PROTECTED PIPE
OEC
GROUND LEVEL
PIPE (CATHODE)
(−)
PROTECTIVE CURRENT
(+)
ANODE


Solar module
Ground level
Solar cathodic protection
controller and battery
(-)
Pipe (cathode)
Protective casement
(+)
Anode

Advantages of impressed current method

1. Larger driving voltage
2. Larger flexibility of control.
3. Applicable to large objects.
4. Uncoated part can be protected.

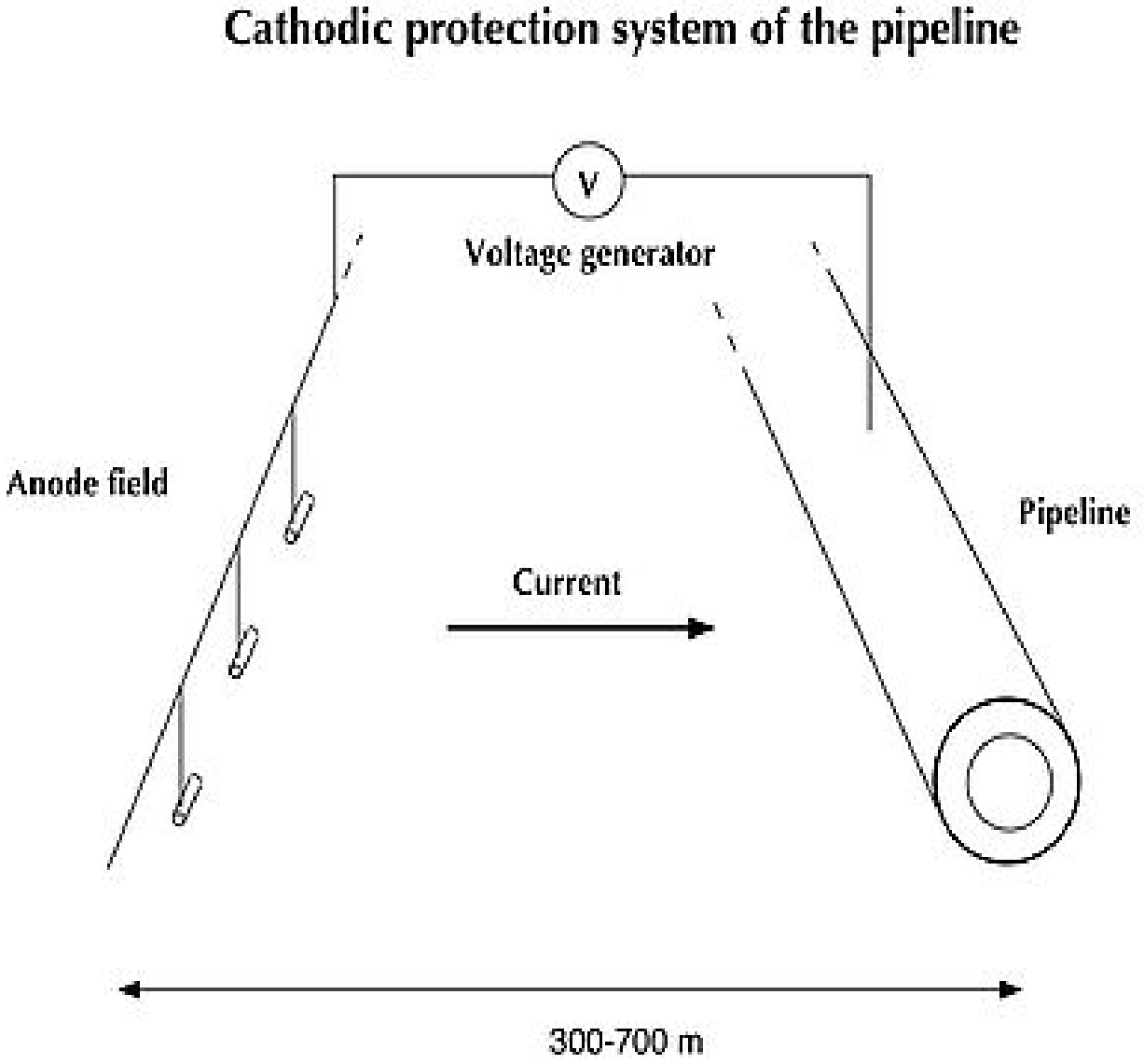
Limitations of impressed current method

1. Larger installation cost
2. Higher maintenance cost.
3. Interference problem with parallel currents.

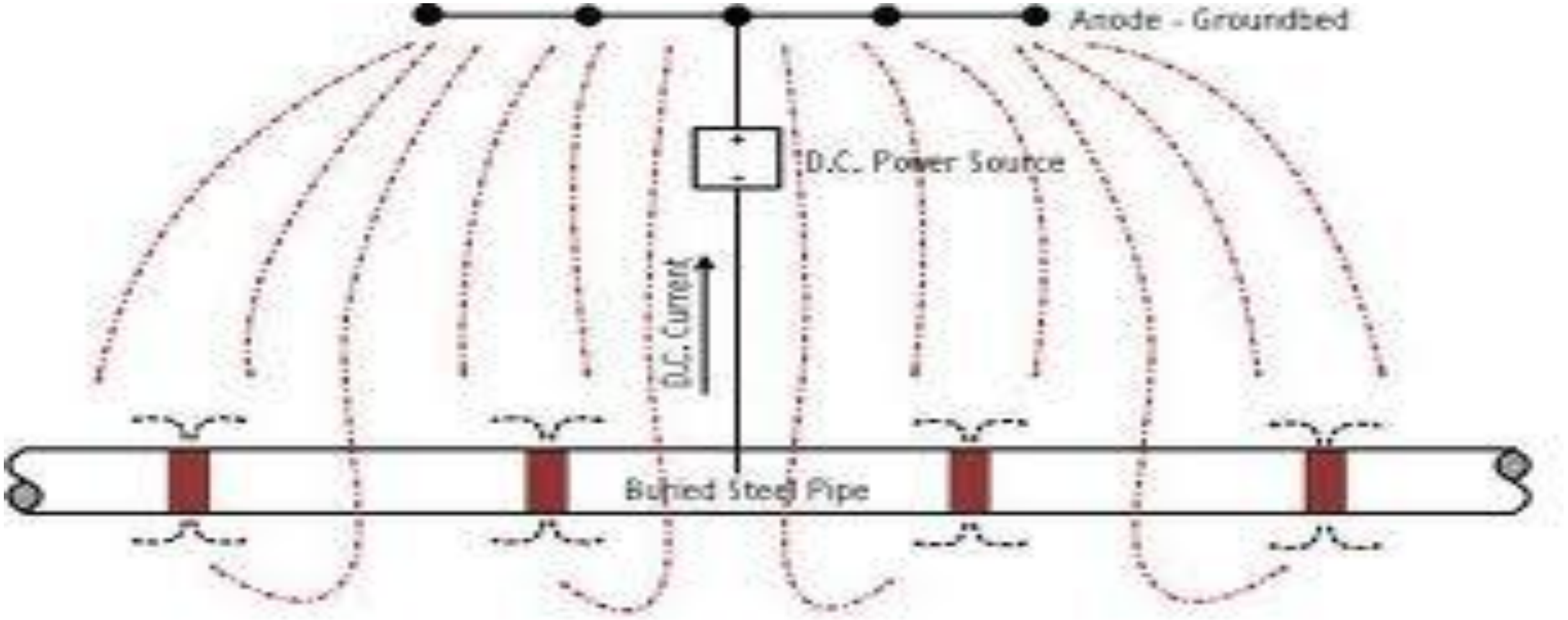
Typical Application of Cathodic Protection

Cathodic protection is effective in reducing various types of electrochemical corrosion such as **aqueous corrosion, erosion corrosion, cavitation corrosion, corrosion fatigue and stress corrosion**. However, process applications are quite specific and usually require laboratory development. **Some typical examples of cathodic protections are given below.**

Pipes lines


Cathodic protection system of the pipeline
V
Voltage generator
Anode field
Pipeline
Current
300-700 m

Underground cables



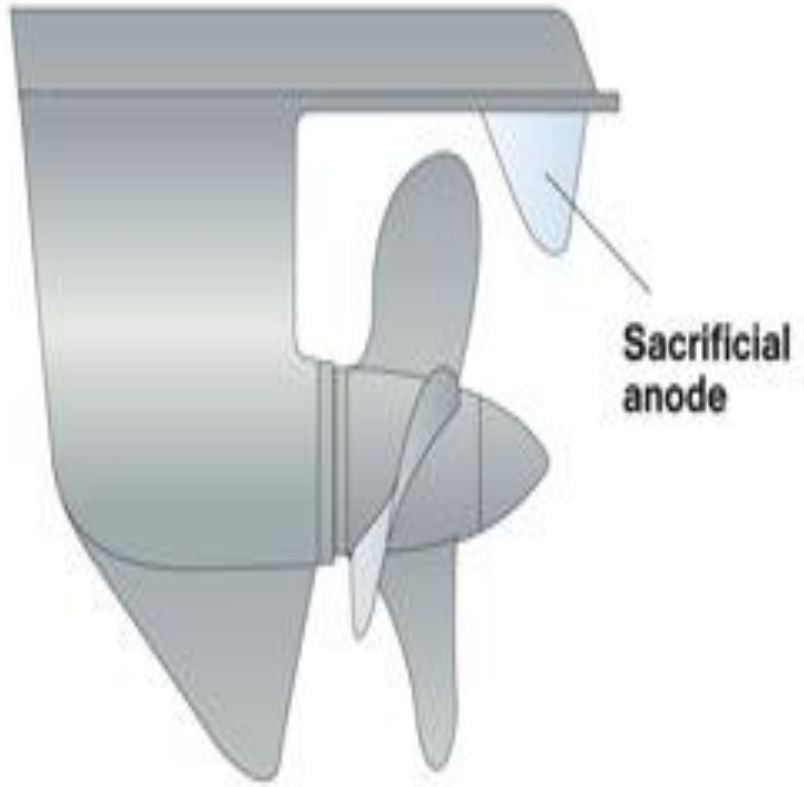
Chemical equipment

Marine


Rudder Bonding
Reference Cell
Control Panel
Linear Loop Anode
Shaft Earthing Assembly
Remote Monitoring
Control Panel
Elliptical Anode
Reference Cell

Hulls of ships.

These are protected by installing evenly distributed magnesium or zinc alloy anodes. Impressed current methods are not successful.



Oil-cargo-ballast tanks.

These are protected by the use of sacrificial anodes.

B- Change of Environment {Inhibitors}

Inhibitors are substances which when added in small quantity to a corrosive environment lower the corrosion rate. They reduce corrosion by either acting as a barrier by forming an adsorbed layer or retarding the cathodic and/or anodic process. **A cathodic inhibitor** increases the cathodic polarization and hence moves the corrosion potential in the anodic direction, whereas an **anodic inhibitor** increases anodic polarization and displaces the corrosion potential in the negative direction. **Substances which increase both the cathodic and the anodic polarizations are called mixed inhibitors**, the potential change in these cases is small and its direction is determined by the relative degree of the cathodic and anodic effects

EFFECTIVENESS OF THE CORROSION INHIBITORS FOR THE PETROLEUM INDUSTRY UNDER VARIOUS FLOW CONDITIONS

Several types of corrosion inhibitors were evaluated. Active ingredients of those inhibitors included long chain amines, fatty amides, imidazolines, fatty acids and their salts.

Inhibitors were tested at the concentration range of 50 - 200 ppm in the electrolyte and electrolyte/hydrocarbon mixture in the presence of CO_2 and H_2S in static and dynamic conditions. Several evaluations were performed when corrosion inhibitors were added into electrolyte containing flow modifiers. The results, which include the corrosion and electrochemical testing data, show that generally tested corrosion inhibitors are effective in studied range of flow rates and compatible

Inhibitors function by adsorption of ions or molecules onto metal surface

They reduce the corrosion rate by,

1-Increasing or decreasing the anodic and or cathodic reaction

2-Decreasing the electrical resistance of metals surface

3-Decreasing the diffusion rate for reactions to the surface of the metal.

Inhibitors are often easy to apply and offer the advantage of in-situ application without causing any significant disruption to process

However, there several consideration when choosing an inhibitor.

WHEN CHOOSING AN INHIBITOR

1. Cost of inhibitor can be sometimes very high when the material involved is expensive or when the amount needed is huge
2. Toxicity of the inhibitor can cause jeopardizing effects on human beings, and other living species
3. Availability of the inhibitor will determine the selection of it and if the availability is low, the inhibitor becomes often expensive.
4. Environment friendliness.

Depending upon the mechanism and mode of protection inhibitors can be classified under the following groups:

A. Chemical passivators . (Nitrites,Chromates,Zinc molybdate)

B. Adsorption inhibitors.(Hexamethylene tetramine,Thiourea)

C. Film forming inhibitors.

(i) Anodic filming inhibitors (ii) Cathodic filming inhibitors.

A. Vpour phase inhibitors(VPI) or Volatile corrosion inhibitors (VCI).

(Dicyclohexylamine nitrite)

Organic Inhibitors:

Corrosion inhibition by organic compounds takes effect generally by mechanism of adsorption of molecules and ions at metal surface.

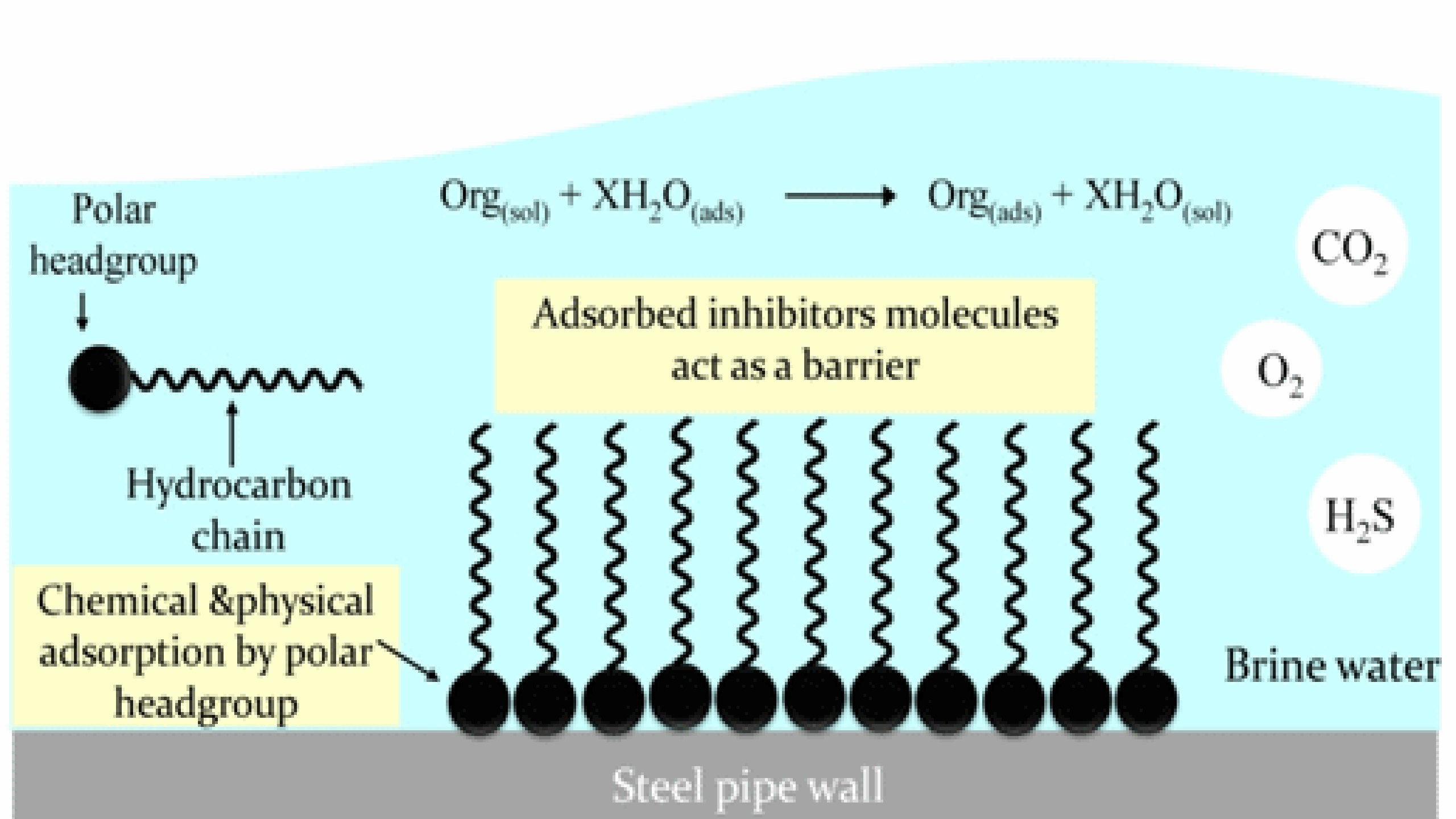
Adsorption can be:

Physisorption due to electrostatic attractive force between the inhibiting ions or dipoles and the electrically charged metal surface.

Chemisorption caused by the interaction between unshared electron pairs or electrons with metals to form a coordinate type of bond.

This type of absorption takes place when there are heteratoms such as P, Se, S, N and O present with lone pair electrons and/or aromatic rings in the adsorbed molecules.

A combination of both


$Org_{(sol)} + XH_2O_{(ads)} \longrightarrow Org_{(ads)} + XH_2O_{(sol)}$
Polar headgroup
Hydrocarbon chain
Adsorbed inhibitors molecules act as a barrier
CO_2
O_2
H_2S
Chemical &physical adsorption by polar headgroup
Brine water
Steel pipe wall

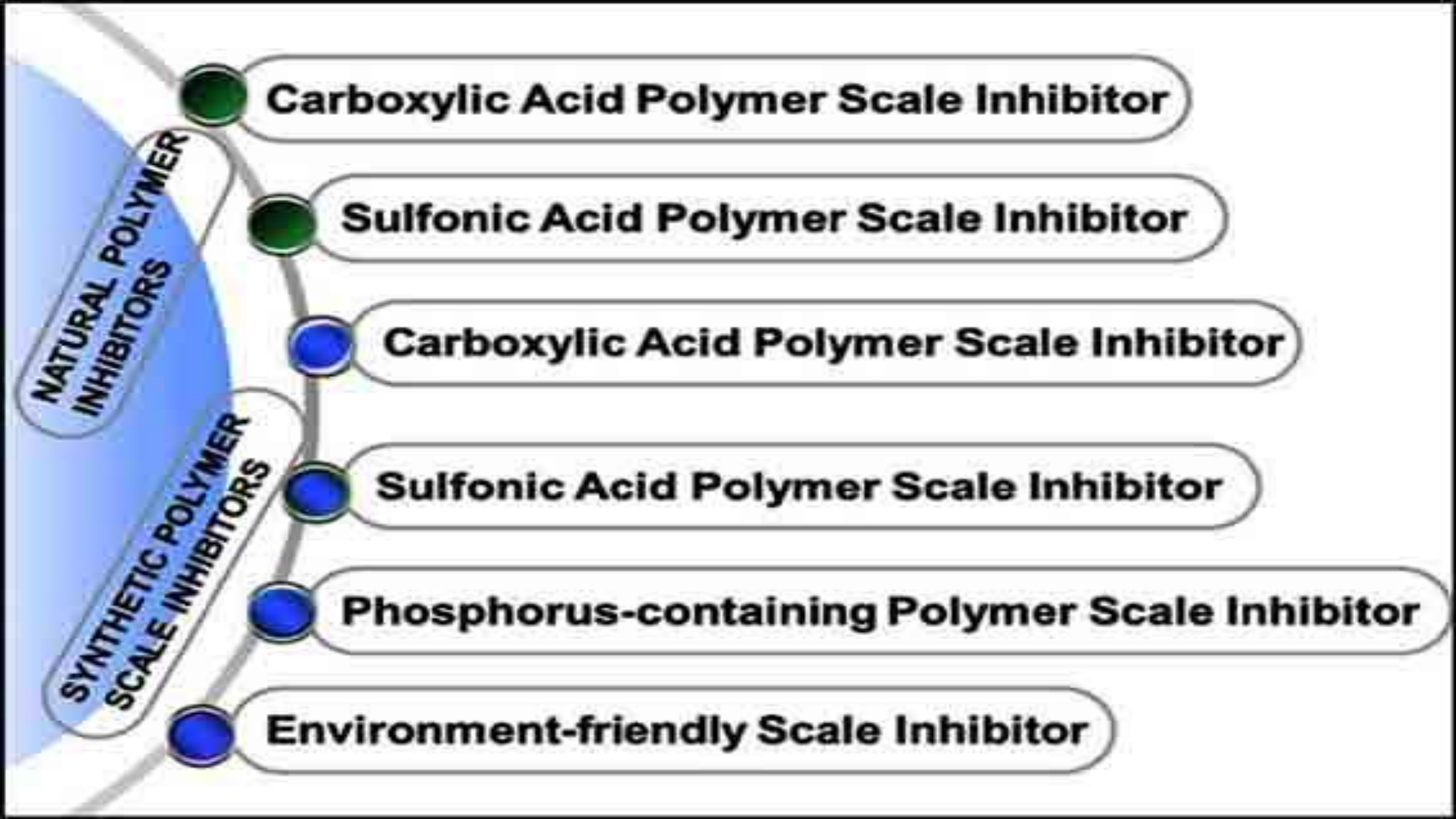
GREEN INHIBITORS

The safety and environmental issues of corrosion inhibitors arisen in industries has always been a global concern .

Chromates for example are both toxic and carcinogenic ,many alternative corrosion inhibitors are developed to reduce jeopardizing effects on humans, animals and environment.

These environmentally green corrosion inhibitors range from rare earth elements to organic compounds

Research has been conducted using some rare earth metals such as lanthanide compounds (lanthanum, cerium).

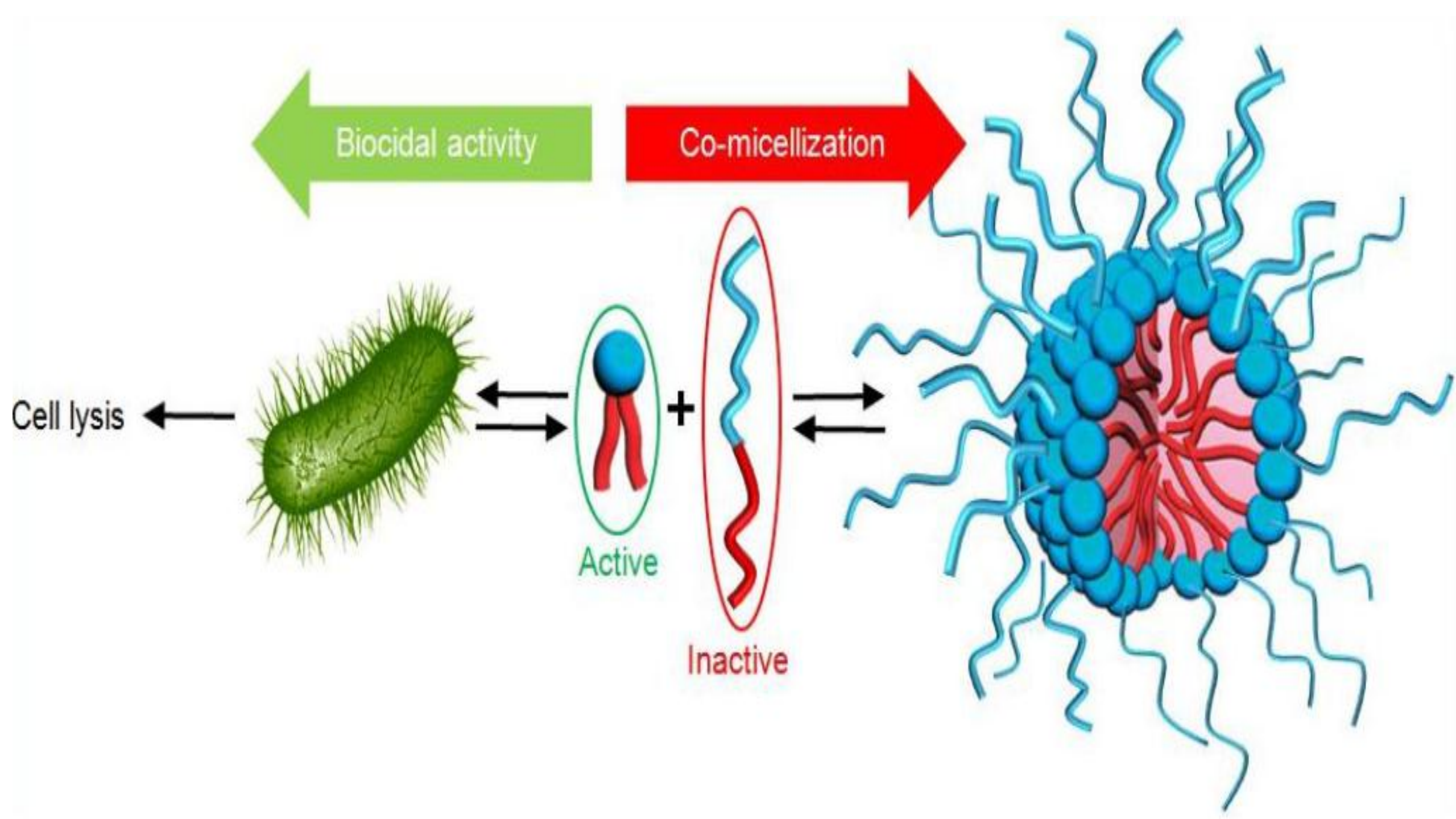

NATURAL POLYMER INHIBITORS
SYNTHETIC POLYMER SCALE INHIBITORS
Carboxylic Acid Polymer Scale Inhibitor
Sulfonic Acid Polymer Scale Inhibitor
Carboxylic Acid Polymer Scale Inhibitor
Sulfonic Acid Polymer Scale Inhibitor
Phosphorus-containing Polymer Scale Inhibitor
Environment-friendly Scale Inhibitor

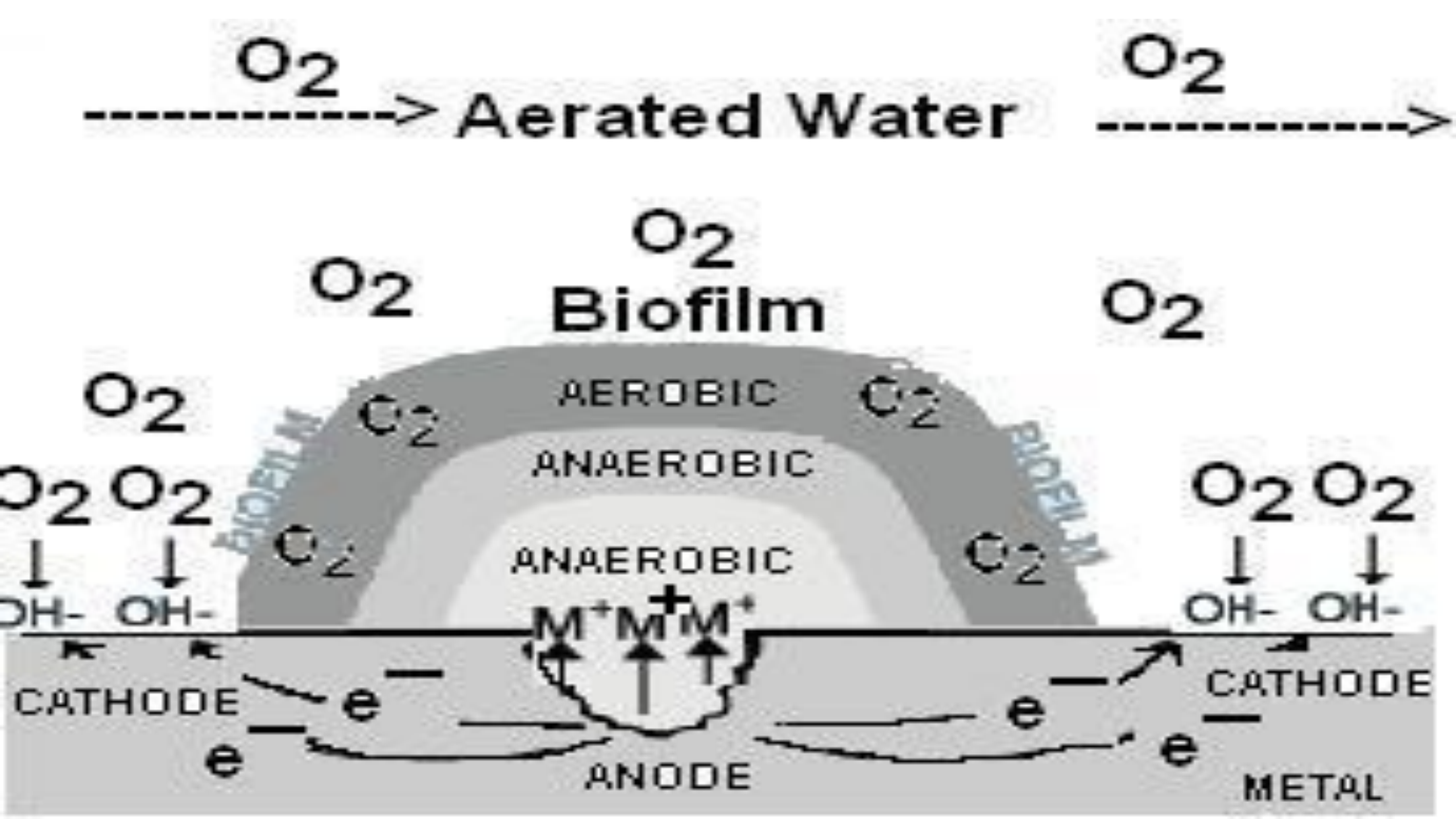
Various inhibitors are used in petroleum industries in various stages.

A) Green Inhibitors. Medicinal plants as green corrosion inhibitors.

B) Biocidal Inhibitors Microbial control strategies and treatments.

C)Inhibitors for biological corrosion.


Biocidal activity
Co-micellization
Cell lysis
Active
Inactive


O2
Aerated Water
O2
O2
Biofilm
O2
O2
AEROBIC
O2
ANAEROBIC
O2
O2
O2
O2
O2
ANAEROBIC
O2
O2
OH-
OH-
OH-
OH-
M+ M+ M+
CATHODE
CATHODE
e
e
e
e
ANODE
METAL

Corrosion resistant coatings for metals and alloys

One of the most common ways of preventing corrosion to steel surfaces is to apply protective coatings.

The coatings we apply may be inhibitive , barrier, or sacrificial.

The key to a successful coating project is surface preparation. We want a surface that is clean and suitably roughened.

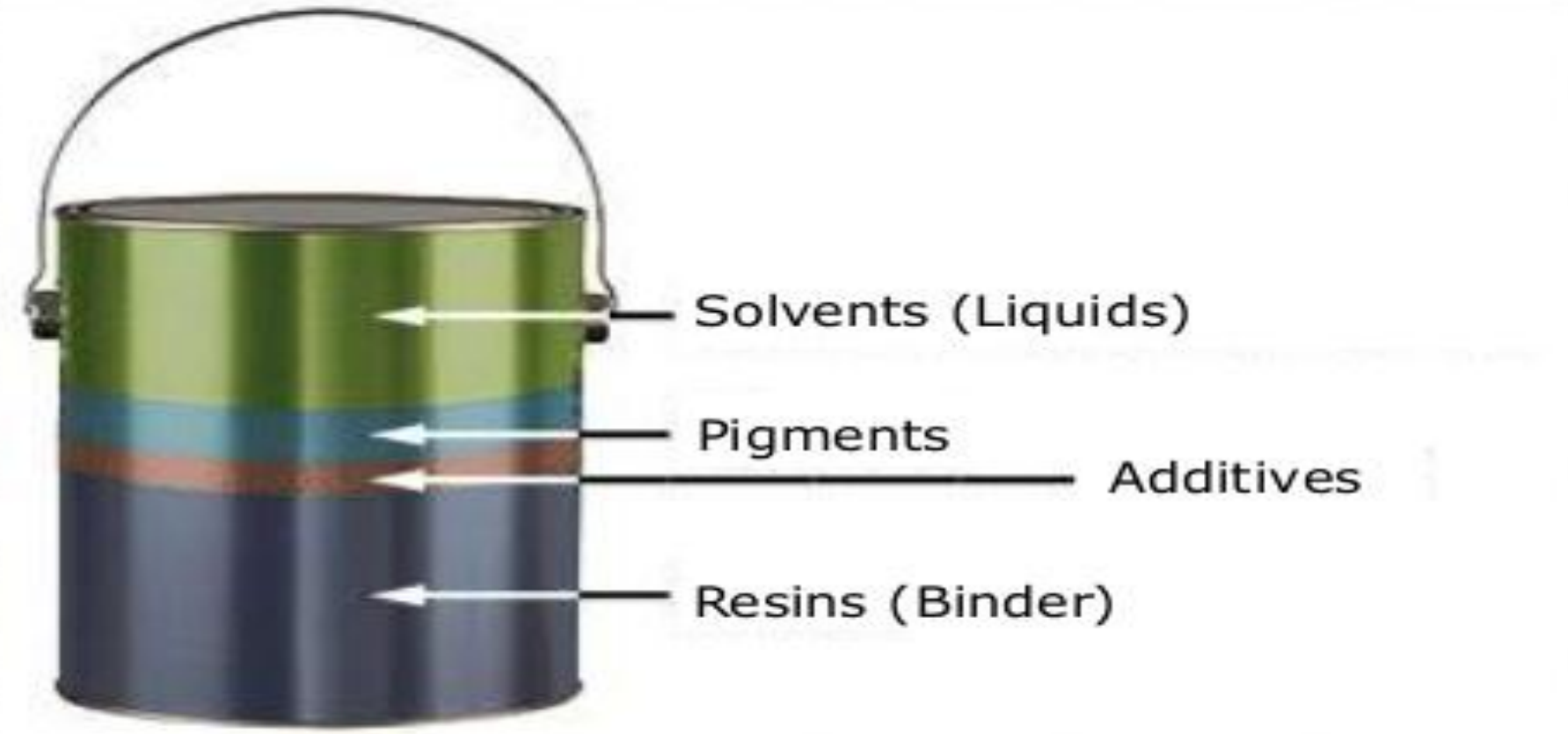
Adhesion is the most important attribute of a coating. A clean surface with the proper profile provides a surface to which a coating can adhere.

A clean steel surface should be free of all:

- Oil
- Grease
- Dust
- Dirt
- Mill scale
- Rust
- Coating

Oxides
Corrosion Products
Other foreign matter

Basic Composition of Paint



Most coatings are named after the binder (resin).

Examples:

Alkyds
Epoxies
Urethanes
Acrylics

Other coatings may be named after the pigment such as zinc rich primer or red lead primer.

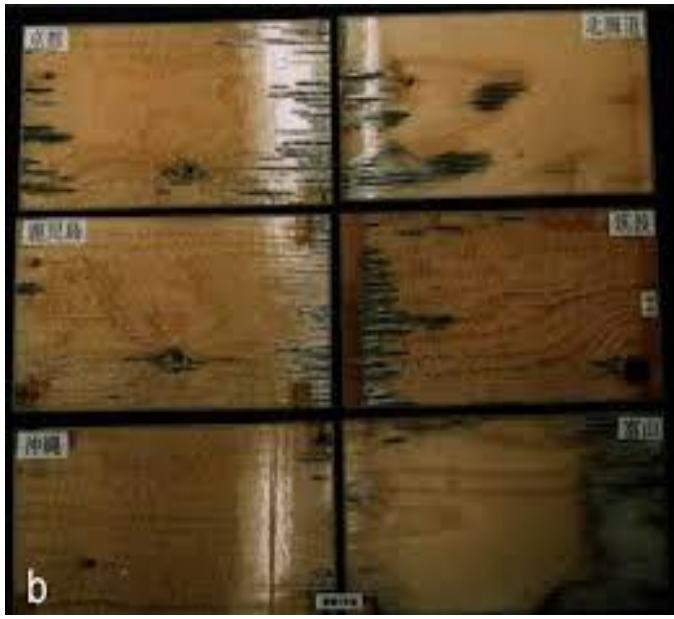
Some general classifications of coatings are:

Organic

Inorganic

Non-Convertible

Convertible



Organic resins are made of something that was once alive such as vegetable oil or fish oil.
A lot of our coatings are made from petroleum products.
Most resins in use in today's industrial coatings are synthetic or man made.

Non-convertible coatings are those coatings that dry and cure by solvent evaporation. When they are dry they are cured. Examples are:

- **Vinyl**
- **Chlorinated Rubber**
- **Asphalt**
- **Bitumen**

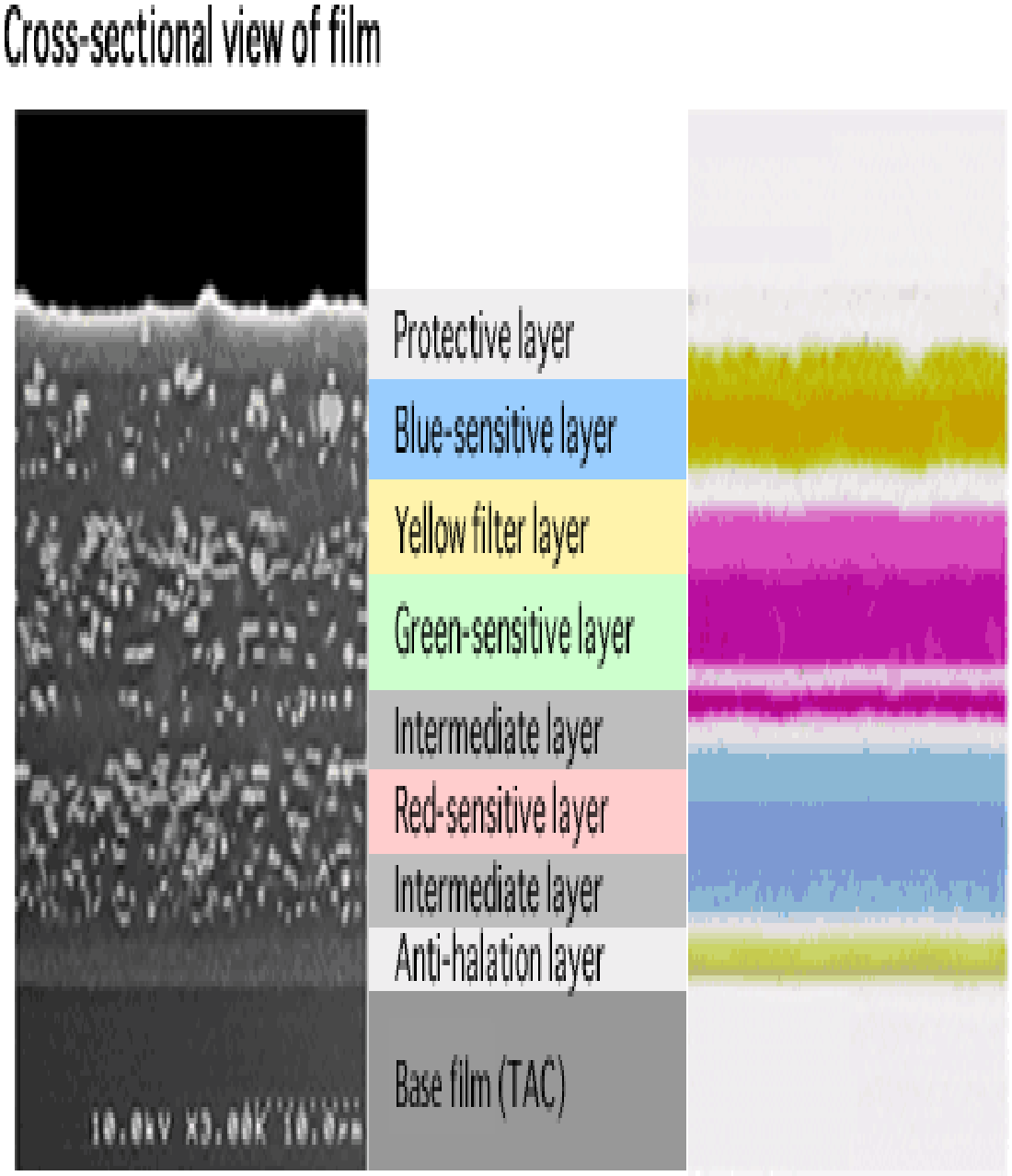
Convertible coatings are those that cure principally by some type of polymerization. The solvent must evaporate before the polymerization takes place. After polymerization it is a different chemical compound. Examples are:

- **Epoxies**
- **2-Pack Urethanes**
- **Polyesters**
- **Vinyl Esters**

Coatings are generally applied as systems. These systems consist of one or more coating layers.

Coating systems may be:

- Single layer
- Multiple layers of the same generic type.
- Multiple layers of different generic types.



A typical coating system consists of a primer, an intermediate coat, and one, or more, topcoats.

An example of a coating system for a bridge might be:

Zinc Rich Primer
Epoxy Intermediate Coat
Urethane Topcoat

There are three basic types of primers. They are:

- **Sacrificial**
- **Inhibitive**
- **Barrier**

Sacrificial primers protect the steel substrate by containing metallic pigments that are anodic to the steel. The most common sacrificial primer is a zinc rich primer. Zinc is a more active metal than steel and will become an anode when in direct contact with the less active steel substrate.

Inhibitive primers contain pigments that passivate the steel and therefore mitigate corrosion. Red lead primer is one of the best of the inhibitive primers. Unfortunately we do not see much red lead used any more because of health concerns.

Barrier type primers create a barrier to the passage of moisture through the film to the substrate, thus preventing the electrolyte from getting to the steel. Without electrolyte we cannot have corrosion. Barrier type primers often contain lamellar type pigments.

Intermediate coats also serve as barriers in the coating system, as well as adding film thickness.
Intermediate coats must be compatible with the primer as well as the topcoat.

Topcoats in the system must protect the substrate, and previous coats, from the environment in which the coating will be exposed. This may be simply atmospheric exposure, or a more severe environment such as immersion or chemical.

Protective coatings have been used to mitigate corrosion for years and new technology is making coatings better and better every year.

This has been a very basic and simple explanation of how coatings help to protect steel and concrete from corrosion. The subject is much more complex that what I have presented here.


THANK
YOU!