Corrosion control by inhibitor

The protection of metals against the corroding action is accomplished by adding chemical substances of small concentration to environment , these chemicals are called "Inhibitors"

Scope of Inhibitor

Corrosion control by use of inhibitors is extremely useful in many environments, however, there are certain exceptions, such as:

➢ equipment and components subjected to turbulent flow.

➢ systems operating above the stability limits of inhibitor.

➢ equipment subjected to high velocity, beyond 4 m/s.

Examples of using of Inhibitors

(1) Corrosion is a serious problem in all cooling water systems. The cooling water may be salt water (35,000 ppm TDS), brackish water (3000-5000 ppm TDS) or fresh water (< 300 ppm TDS). Inhibitor treatment is required for heat exchanger and distribution lines.

(2) Corrosion may be caused in the feed water and boiler sections, if dissolved oxygen and CO_2 is not removed by water treatment. Scales and deposits may also be formed by dissolved and suspended solids. Excessive alkalinity in boilers can lead to caustic cracking. High alkalinity is caused by high TDS (total dissolved solids) and alkalinity. External treatment includes demineralization and reduction of alkalinity, corrosion inhibition and biological control. Morpholine inhibitor is added as inhibitor for treatment of condensate corrosion.

(3) Petroleum Industry. Corrosion phenomena in the petroleum industry occur in a two phase medium of water and hydrocarbon. It is the presence of a thin layer of water which leads to corrosion, and rigorous elimination of water reduces the corrosion rate to a negligible value. The inhibitors used in petroleum industry, both in production and refining are either oil soluble-water insoluble types or oil soluble-water dispersible compounds. New inhibitors are being developed. For instance, traditional filming amines are being replaced by several others, such as propylenedramine, and they work by adsorption on the surface

(4) Sour Gas Systems. A major problem is encountered in steel pipelines in various sour gas environments. Chemical inhibition is one of the effective methods used to mitigate sulfide induced corrosion. Inhibitors containing alkylammonium ions are found to suppress corrosion effectively.

(5) Potable Water Systems. Corrosion is experienced in potable water transportation pipes of steels and cast iron. Inhibitors, such as $Ca(HCO_3)_2$ and polyphosphates are commonly used to combat corrosion.

(6) Engine Coolants. Inhibitors, such as $NaCrO_4$ (sodium chromate), borates and nitrites $(NaNO_2)$ and mercaptabenzothiazole are widely used for protection of automobile engines. Chromates are a health hazard.

(7) Packaging Industry. For transportation of machinery, components and equipment by sea, vapor phase cyclohexylamine and hexamethylamine are used.

(8) Construction Industry. Corrosion of rebar in concrete poses a serious threat to building structures. Inhibitors, such as chromates, liquid form and controls their viscosity. phosphates, nitrates and sodium metasilicates are used to suppress corrosion. Addition of sodium tetraborate and zinc borate has shown promising results. Commercial inhibitors, such as MCI 2022, MCI 2000 and Rheocrete 222, have shown good promise. Baker Petrolite, Du-Pont and NALCC are some of the known names in inhibitor manufacturing.
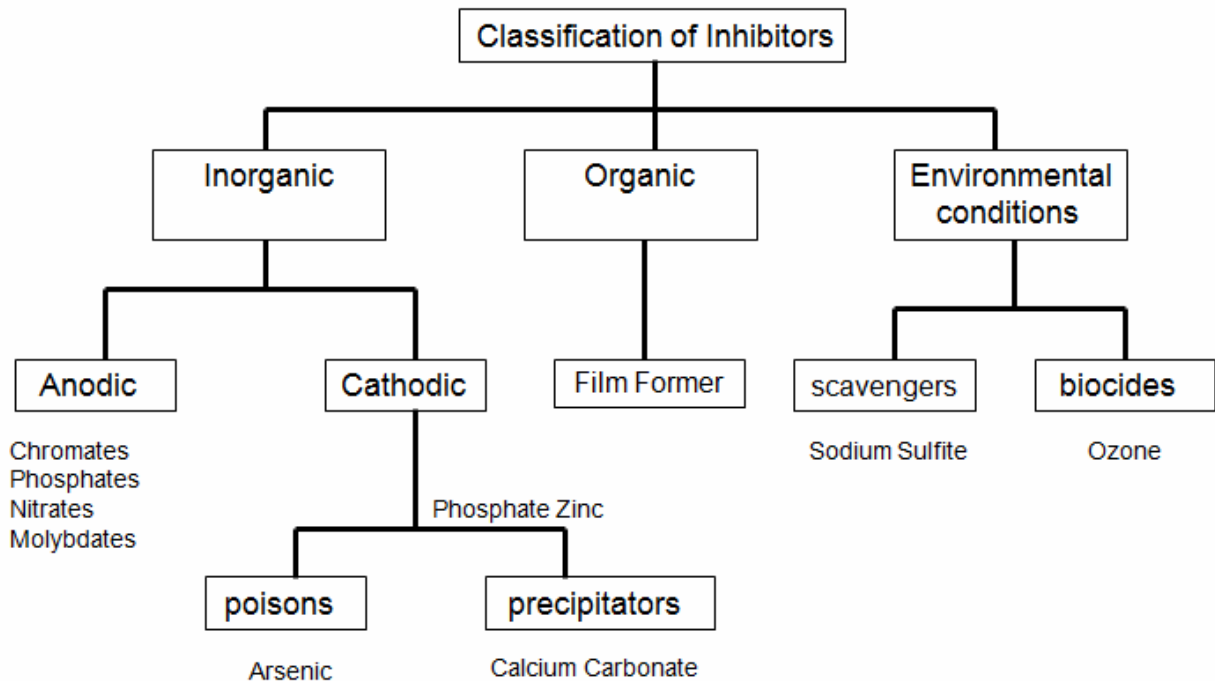
Anodic inhibitor also called "dangerous inhibitors" because they caused a large shift in corrosion potential as well as if they used in insufficient corrosion lead to pitting or increase corrosion rate , also they are called : *passivators* .Cathodic inhibitors either slow the cathodic reaction itself or they selectively participate on cathodic area to increase circuit resistance and restrict diffusion of reducible species
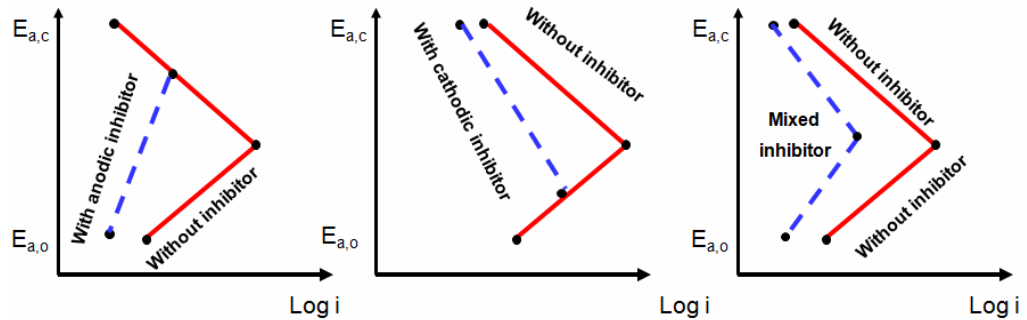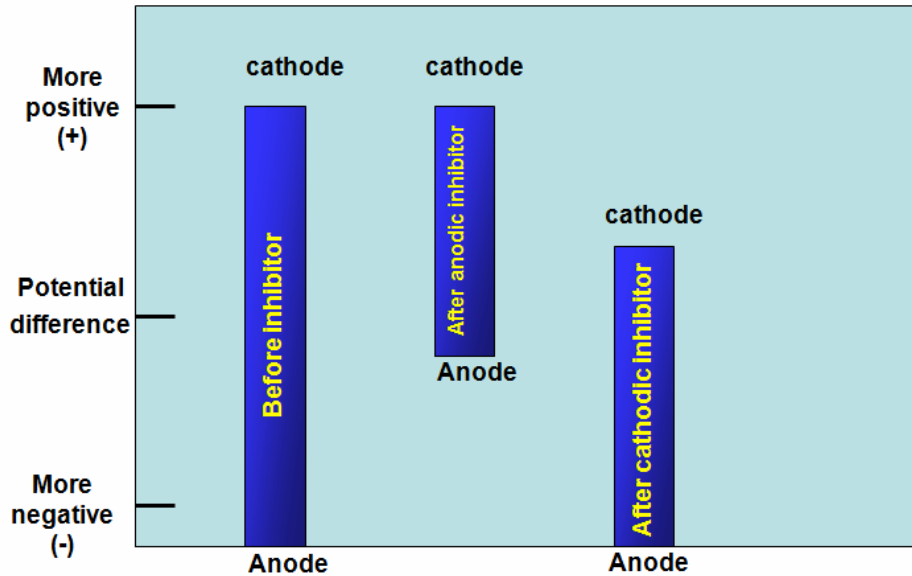

Action of corrosion inhibitors: (a) anodic inhibitors examples: chromate, nitrite, molybdate, tungstate, orthophosphate, silicate, benzoate, (b) cathodic inhibitors examples: $Cu(HCO_3)_2$, $ZnSO_4$, $Cr_4(SO_4)_3$, $NiSO_4$, polyphosphate, aminoethylene phosphate and (c) mixed inhibitors examples: organic inhibitors containing nitrogen and/or sulfur, like amines, triazoles, alkythiourea

Characteristics of Cathodic Inhibitors

(A) Polyphosphates The structure molecule is of a sodium polyphosphate

$$NaO-P(=O)(ONa)-\left[O-P(=O)(O)-ONa\right]_n$$

O= orthophosphate n=1
Pyrophosphate n=2
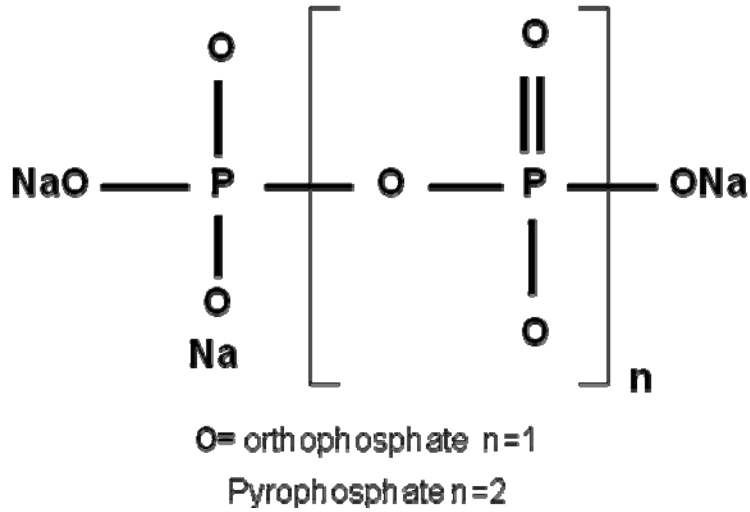
The polyphosphate molecule bonds with divalent calcium and other ions to form positively charged colloidal particles which are attracted to the cathode and form a protective film. As some metal ions, such as iron, may also be adsorbed on the film, polyphosphate also shows a partial anodic behavior although basically they are cathodic inhibitors. The mechanism of corrosion prevention by polyphosphates is shown in below figure
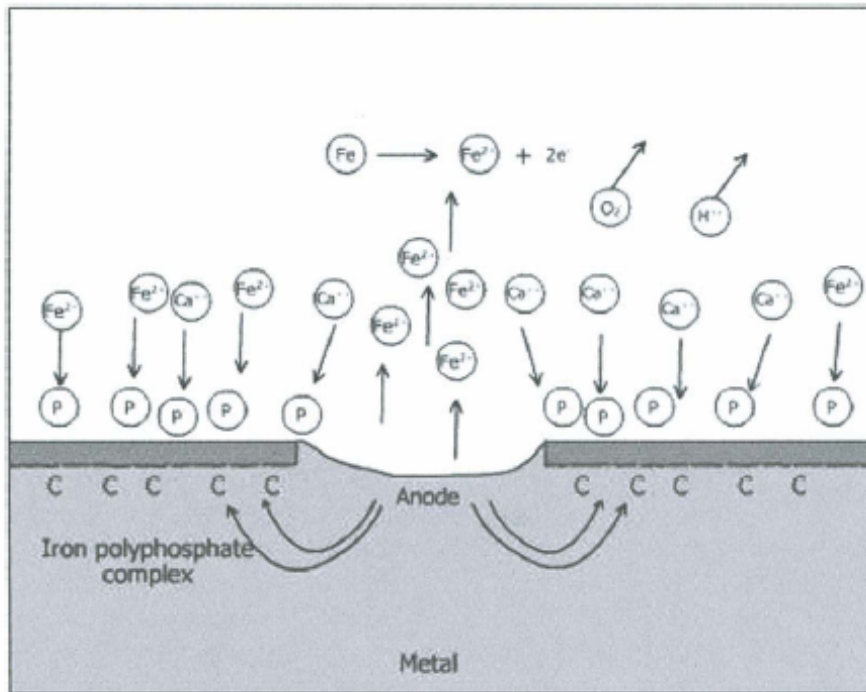
One major disadvantage of using polyphosphate is the hydrolysis of the phosphorus oxygen bond which converts the polyphosphate to orthophosphate, which is a proven weak inhibitor. A pH range of 6.5-7.5 is considered generally suitable to avoid reversion to orthophosphate which allows undesirable algae growth.Polyphosphates are blended with silicates and ferrocyanide to overcome this limitation.

Note : In actual operation, two or three inhibitors are blended to maximize the advantage of each other and to minimize their limitations. Frequently anodic and cathodic inhibitors are combined to maximize metal protection. The process is called 'synergistic blending.'

(B) Zinc

Zinc salts are well-known cathodic inhibitors in cooling water systems. They are, however, not used alone as the films formed by them are unstable. They are, however, used very effectively with polyphosphate as a synergistic blend to maximize the effect of inhibition. These synergistic blends minimize the inhibitor concentration. Chromates can also be used in synergistic blends with polyphosphates. Zinc and chromate inhibitors are toxic and not environmentally friendly. They also need a careful pH control as they have a tendency to form scales above a pH of 8.00.

Inorganic Anodic Inhibitors

The addition of inorganic inhibitors causes suppression of electrochemical reaction at anodic-cathodic areas. Most of the times, inhibitors are used in a blended form. These inhibitors only react at an adequate level of concentration.

(A) Chromate Inhibitors

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 $Na_2Cr_2O_7$. The protective passive film which is formed contains iron oxide and chromium oxide which makes the chromate inhibitors very effective Chromates are reduced to form chromium (III) according to the following reaction:

$Fe \rightarrow Fe^{+2}+2e^-$ (oxidation of iron)

$CrO_4^- +8H^+ +3e^- \rightarrow Cr^{+3}+4H_2O$ (formation of Cr^{+3})
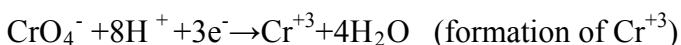
A mixed potential is created by the oxidation of iron and reduction of chromium and this potential lies somewhere in the passivation range, which accounts for the passivating effect of chromate inhibitor.
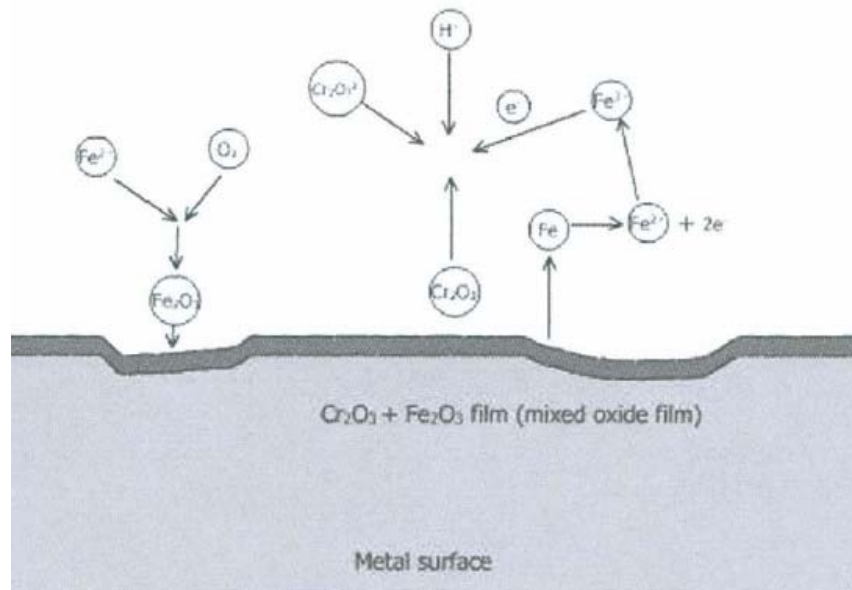
Formation of a mixed iron oxide and chromium oxide film

(B) Nitrites

They are effective inhibitors for iron and a number of metals in a wide variety of waters. Like chromates, nitrites are anodic inhibitors and they inhibit the system by forming a passive film with ferric oxide. These are environmentally-friendly inhibitors. Besides steel, nitrites also inhibit the corrosion of copper, tin and nickel alloys at pH levels 9-10. Chromate is an extremely effective inhibitor for corrosion prevention of aluminum alloys. Nitrites should not be used in open systems as they would oxidize to nitrates in the presence of oxygen.:" $2NO_2 + O_2 = 2NO_3$

Nitrites are not effective inhibitors. The presence of chloride and sulfate ions can damage the protective film formed by nitrites. They are often blended with borax in closed recirculation system.

(C) Nitrates

They protect solder and aluminum. They are not very effective and limited to use only in closes recirculation systems.

(D) Phosphate Inhibitors

Phosphate retards corrosion by promoting the growth of protective iron oxide films and by healing the defects in protective films. The effectiveness of phosphate inhibitor is reduced by chloride ions which damage the protective film formed by phosphate.

(E) Molybdates

Molybdenum is an alloying element which is known to increase passivation of stainless steels. Steels of type 316 contain molybdenum as a minor constituent and promote passivation. Sodium molybdate forms a complex passivation film at the iron anode of ferrous-ferric molybdenum oxide. The passive film can only be formed in the presence of oxygen. They are very expensive and used with other inhibitors in synergistic blends.

(F) Silicates

They have been used with success for years in potable water systems. The complex silicon ion has a tendency to form negatively charged colloidal particles which migrate to anodic areas and form passive films. Silicates are strong anodic inhibitors and passive films can be formed even on the corroded surface. The monomeric silica does not provide any protection. In waters below pH levels of 6.0, the silicate used is $Na_2O.2SiO_3$ and with a pH greater than 6.0, it is $Na_2Cr_3.3SiO_3$. Silicate inhibitors are also useful to prevent red water formation in plumbing systems by oxidation of ferrous carbonate in natural water or steel pipes encountering soft water. Red water formation seriously affects plumbing fixtures and the problem appears particularly in galvanized pipes if the temperature exceeds 65°C, due to reversal of polarity. Silicate treatment also prevents dezincification in brass and corrosion of copper. Mixtures of silicates and phosphates have been effectively used as inhibitors.

ORGANIC INHIBITORS

Phosphate retards corrosion by promoting the growth of protective iron oxide films and by healing the defects in protective films. The effectiveness of phosphate inhibitor is reduced by chloride ions which damage the protective film formed by phosphate. Organic inhibitors are abundantly used in the oil industry to control oil and gas well corrosion. Most common types are long chain (Cis) hydrogen and nitrogen containing compounds.

Organic inhibitors are neither anodic nor cathodic, but they inhibit both the anodic and cathodic areas to varying degrees depending on the type of inhibition. The most common types of organic inhibitors are shown below:

(1) Monoamine: Primary amine, RNH2

                Secondary amine, R2NH
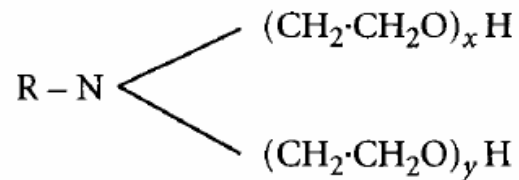
                Tertiary amine, R-N(CH3)2

(2) Diamines
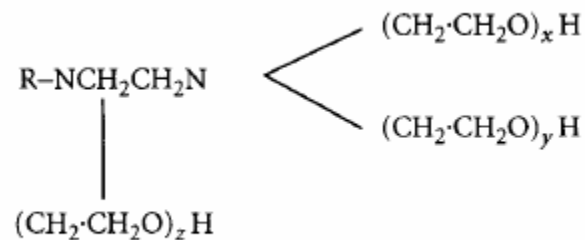
R-NHCH2CH2CH2NH2

(3) Amides

R-CONH2

(4) Polyethoxylated compounds

(a) Amines

$$R-N \begin{cases} (CH_2 \cdot CH_2O)_x H \\ (CH_2 \cdot CH_2O)_y H \end{cases}$$

(x and y vary between 2 and 50)

(b) Diamines

$$R-NCH_2CH_2N \begin{cases} (CH_2 \cdot CH_2O)_x H \\ (CH_2 \cdot CH_2O)_y H \end{cases}$$
$$| \quad (CH_2 \cdot CH_2O)_z H$$

(x + y + z varies between 3–10)

Organic inhibitors react by adsorption on a metallic surface. Cationic inhibitors (+), like amines, or anionic inhibitors (—), like sulfonates, are preferentially adsorbed depending on the charge of the metal surface (+) or (-).

Organic molecules inhibits corrosion by adsorption at the metal – solution interface , however the mode of adsorption depends upon

1 – chemical structure of molecules

2 – chemical composion

3 – nature of metal surface , and etc.

Adsorption isotherms

The usual methods for evaluating the adsorption mechanism is through the adsorption isotherm . Interpretation of adsorbent type organic inhibitors performance data to one of the following adsorption isotherms:

1 – Langmuir isotherm

Mathematically can be expressed as : $\theta = \dfrac{Kc}{1+Kc}$

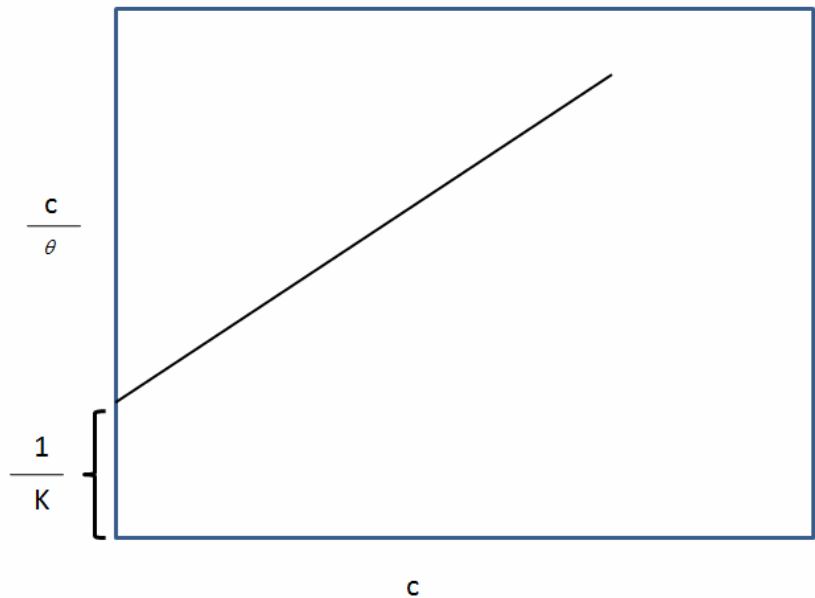Where θ : is surface coverage

K : adsorption constant

c :concentration of inhibitor

$\theta + \theta Kc = Kc$

$(1+Kc) = \dfrac{Kc}{\theta}$

$\dfrac{1}{K} + c = \dfrac{c}{\theta}$

$\dfrac{c}{\theta} = c + \dfrac{1}{K}$

Where K is indicate the degree of adsorption i.e. higher the value of K the higher indication that the inhibitor strongly adsorbed on the metal surface .

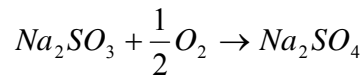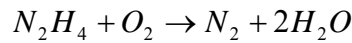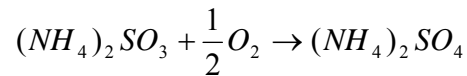2 – Freundlich isotherm , can be expressed mathematically as

$\theta = Kc^{n}$

$\log \theta = \log K + n \log c$

K, n: are constants

SCAVENGERS

Oxygen, even in very small amounts, may cause serious corrosion in feedwater lines, stage heaters, economizers, boiler metal, steam operated equipment and condensable piping. It must, therefore, be removed from the closed system. The solubility of oxygen varies with both pressure and temperature. Oxygen is the main cause of corrosion. It reacts by consuming electrons at the cathode causing cathodic depolarization and enhancing the rate of corrosion. Chemicals which eliminate oxygen from the closed systems are called *scavengers*. Ammonium sulfite $(NH_4)_2SO_3$, and hydrazine (N_2H_4) have been successfully used over the years to eliminate oxygen. Oxygen scavengers remove oxygen as shown below:

$$(NH_4)_2SO_3 + \frac{1}{2}O_2 \rightarrow (NH_4)_2SO_4$$

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

$$Na_2SO_3 + \frac{1}{2}O_2 \rightarrow Na_2SO_4$$

The oxygen scavenger reaction rate changes by a factor of 2 for every change in temperature by 10°C as shown by reaction (1). Sodium sulfite reacts to form sodium sulfate and increases the total dissolved solid contents of the boiler water. Generally, eight parts by weight of Na_2SO_3 are needed to scavenge one part of O_2, but dosage depends on the purity.

NEUTRALIZERS

Neutralizing inhibitors reduce corrosion by reducing the concentration of H^+ ions in solution. Neutralizers   control a small amount of HCl, CO_2, SO_2, H_2S, organic acids and other similar species that react with water to produce H+ ions. The most commonly used neutralizing inhibitors are morpholine, cyclohexylamine and

diethylamine-ethanol. The formation of H^+ by CO_2 is shown below:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$H_2CO_3 \rightarrow H^+ + HCO_3$$
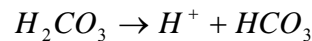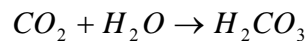
(Carbonic acid) → (hydrogen ions) + (Bicarbonate ions)

Inhibitor effect

The effectiveness of action of inhibitor is often expressed as 'inhibitor effect' (Z) which represent the ratio of the metal dissolution rate in an unhabited corrosion medium (S_o) to the dissolution rate of the same metal under the condition but in an inhibited corrosion medium (S)

$$Z = \frac{S_o}{S}$$

Percentage Inhibitive Efficiency

It can be calculated by one from the below forms:

1) Weight loss technique measurements $\eta\% = \dfrac{w_u - w_i}{w_u} \times 100 = \left[1 - \dfrac{w_i}{w_u}\right] \times 100$

   Where w_u and w_i are the weight losses in uninhibited and inhibited condition respectively

2) Polarization technique measurements $\eta\% = \dfrac{i_u - i_i}{i_u} \times 100 = \left[1 - \dfrac{i_i}{i_u}\right] \times 100$

   Where i_{un} and i_{in} are the corrosion current densities for uninhibited and inhibited condition respectively

3) Gas evolution technique $\eta\% = \dfrac{v_o - v}{v_o} \times 100 = \left[1 - \dfrac{v}{v_o}\right] \times 100$

Where v and v_o are the volume of Hydrogen gas liberation at uninhibited and inhibited condition respectively

Example: Mild steel corroded in a seawater at rate of 60 mpy, when 10ppm of an inhibitor was added the corrosion rate dropped to 15 mpy ,what is the inhibition efficiency ?

$$\eta = \left[1 - \frac{v}{v_o}\right] \times 100 = \left[1 - \frac{15}{60}\right] \times 100 = 0.75$$

To use the corrosion inhibition effectively the corrosion engineer must

1. Be able to identify those problems that can be solved by use of corrosion inhibitors

2. The economics involved must be considered that is , whether or not the loss due to corrosion exceed the cost of inhibitor

3. The compatibility of inhibitors with the process being used must be considered to avoid effects such as foaming , decrease in catalytic activity , degradation of other material , loss of heat transfer , etc

4. The inhibitor must be applied under conditions that produce maximum effect

Application of inhibitors

- Solid forms : most solids are relatively pure , but sometimes a solid inhibitor is fused with another ingredient which controlled rate of solubility is required inhibitor concentration for solids are expressed in weight basis.

- Liquid forms : are usually preferred because of the ease with which can be transported , measured and dispersed