Chapter

10

Corrosion Inhibitors

10.1 Introduction

The use of chemical inhibitors to decrease the rate of corrosion processes is quite varied. In the oil extraction and processing industries, inhibitors have always been considered to be the first line of defense against corrosion. A great number of scientific studies have been devoted to the subject of corrosion inhibitors. However, most of what is known has grown from trial and error experiments, both in the laboratories and in the field. Rules, equations, and theories to guide inhibitor development or use are very limited.

By definition, a corrosion inhibitor is a chemical substance that, when added in small concentration to an environment, effectively decreases the corrosion rate. The efficiency of an inhibitor can be expressed by a measure of this improvement:

$$\text{Inhibitor efficiency (\%)} = 100\,\frac{(\text{CR}_{\text{uninhibited}} - \text{CR}_{\text{inhibited}})}{\text{CR}_{\text{uninhibited}}} \tag{10.1}$$

where $\text{CR}_{\text{uninhibited}}$ = corrosion rate of the uninhibited system
$\text{CR}_{\text{inhibited}}$ = corrosion rate of the inhibited system

In general, the efficiency of an inhibitor increases with an increase in inhibitor concentration (e.g., a typically good inhibitor would give 95% inhibition at a concentration of 0.008% and 90% at a concentration of 0.004%). A synergism, or cooperation, is often present between different inhibitors and the environment being controlled, and mixtures are the usual choice in commercial formulations. The scientific and technical corrosion literature has descriptions and lists of numerous chemical compounds that exhibit inhibitive properties. Of these, only very few are actually used in practice. This is partly because the desirable properties of an inhibitor usually extend beyond those simply related to metal protection. Considerations of cost, toxicity, availability, and environmental friendliness are of considerable importance.

Table 10.1 presents some inhibitors that have been used with success in typical corrosive environments to protect the metallic elements of industrial systems. Commercial inhibitors are available under various trade names and labels that usually provide little or no information about their chemical composition. It is sometimes very difficult to distinguish between products from different sources because they may contain the same basic anticorrosion agent. Commercial formulations generally consist of one or more inhibitor compounds with other additives such as surfactants, film enhancers, de-emulsifiers, oxygen scavengers, and so forth. The inhibitor solvent package used can be critical in respect to the solubility/dispersibility characteristics and hence the application and performance of the products.

10.2 Classification of Inhibitors

Inhibitors are chemicals that react with a metallic surface, or the environment this surface is exposed to, giving the surface a certain level of protection. Inhibitors often work by adsorbing themselves on the metallic surface, protecting the metallic surface by forming a film. Inhibitors are normally distributed from a solution or dispersion. Some are included in a protective coating formulation. Inhibitors slow corrosion processes by

- Increasing the anodic or cathodic polarization behavior (Tafel slopes)
- Reducing the movement or diffusion of ions to the metallic surface
- Increasing the electrical resistance of the metallic surface

TABLE 10.1 Some Corrosive Systems and the Inhibitors Used to Protect Them

System	Inhibitor	Metals	Concentration
	Acids		
HCl	Ethylaniline	Fe	0.5%
	MBT*	..	1%
	Pyridine + phenylhydrazine	..	0.5% + 0.5%
	Rosin amine + ethylene oxide	..	0.2%
H_2SO_4	Phenylacridine	..	0.5%
H_3PO_4	NaI	..	200 ppm
Others	Thiourea	..	1%
	Sulfonated castor oil	..	0.5–1.0%
	As_2O_3	..	0.5%
	Na_3AsO_4	..	0.5%
	Water		
Potable	$Ca(HCO_3)_2$	Steel, cast iron	10 ppm
	Polyphosphate	Fe, Zn, Cu, Al	5–10 ppm
	$Ca(OH)_2$	Fe, Zn, Cu	10 ppm
	Na_2SiO_3	..	10–20 ppm
Cooling	$Ca(HCO_3)_2$	Steel, cast iron	10 ppm
	Na_2CrO_4	Fe, Zn, Cu	0.1%
	$NaNO_2$	Fe	0.05%
	NaH_2PO_4	..	1%
	Morpholine	..	0.2%
Boilers	NaH_2PO_4	Fe, Zn, Cu	10 ppm
	Polyphosphate	..	10 ppm
	Morpholine	Fe	Variable
	Hydrazine	..	O_2 scavenger
	Ammonia	..	Neutralizer
	Octadecylamine	..	Variable
Engine coolants	Na_2CrO_4	Fe, Pb, Cu, Zn	0.1–1%
	$NaNO_2$	Fe	0.1–1%
	Borax	..	1%
Glycol/water	Borax + MBT*	All	1% + 0.1%
Oil field brines	Na_2SiO_3	Fe	0.01%
	Quaternaries	..	10–25 ppm
	Imidazoline	..	10–25 ppm
Seawater	Na_2SiO_3	Zn	10 ppm
	$NaNO_2$	Fe	0.5%
	$Ca(HCO_3)_2$	All	pH dependent
	NaH_2PO_4 + $NaNO_2$	Fe	10 ppm + 0.5%

*MBT = mercaptobenzotriazole.

Inhibitors have been classified differently by various authors. Some authors prefer to group inhibitors by their chemical functionality, as follows:[1]

- *Inorganic inhibitors.* Usually crystalline salts such as sodium chromate, phosphate, or molybdate. Only the negative anions of these compounds are involved in reducing metal corrosion. When zinc is used instead of sodium, the zinc cation can add some beneficial effect. These zinc-added compounds are called mixed-charge inhibitors.
- *Organic anionic.* Sodium sulfonates, phosphonates, or mercaptobenzotriazole (MBT) are used commonly in cooling waters and antifreeze solutions.
- *Organic cationic.* In their concentrated forms, these are either liquids or waxlike solids. Their active portions are generally large aliphatic or aromatic compounds with positively charged amine groups.

However, by far the most popular organization scheme consists of regrouping corrosion inhibitors in a functionality scheme as follows.[2]

10.2.1 Passivating (anodic)

Passivating inhibitors cause a large anodic shift of the corrosion potential, forcing the metallic surface into the passivation range. There are two types of passivating inhibitors: oxidizing anions, such as chromate, nitrite, and nitrate, that can passivate steel in the absence of oxygen and the nonoxidizing ions, such as phosphate, tungstate, and molybdate, that require the presence of oxygen to passivate steel.

These inhibitors are the most effective and consequently the most widely used. Chromate-based inhibitors are the least-expensive inhibitors and were used until recently in a variety of application (e.g., recirculation-cooling systems of internal combustion engines, rectifiers, refrigeration units, and cooling towers). Sodium chromate, typically in concentrations of 0.04 to 0.1%, was used for these applications. At higher temperatures or in fresh water with chloride concentrations above 10 ppm higher concentrations are required. If necessary, sodium hydroxide is added to adjust the pH to a range of 7.5 to 9.5. If the concentration of chromate falls below a concentration of 0.016%, corrosion will be accelerated. Therefore, it is essential that periodic colorimetric analysis be conducted to prevent this from occurring. In general, passivation inhibitors can actually cause pitting and accelerate corrosion when concentrations fall below minimum limits. For this reason it is essential that monitoring of the inhibitor concentration be performed.

10.2.2 Cathodic

Cathodic inhibitors either slow the cathodic reaction itself or selectively precipitate on cathodic areas to increase the surface impedance and limit the diffusion of reducible species to these areas. Cathodic inhibitors can provide inhibition by three different mechanisms: (1) as cathodic poisons, (2) as cathodic precipitates, and (3) as oxygen scavengers. Some cathodic inhibitors, such as compounds of arsenic and antimony, work by making the recombination and discharge of hydrogen more difficult. Other cathodic inhibitors, ions such as calcium, zinc, or magnesium, may be precipitated as oxides to form a protective layer on the metal. Oxygen scavengers help to inhibit corrosion by preventing the cathodic depolarization caused by oxygen. The most commonly used oxygen scavenger at ambient temperature is probably sodium sulfite (Na_2SO_3).

10.2.3 Organic

Both anodic and cathodic effects are sometimes observed in the presence of organic inhibitors, but as a general rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration. Organic inhibitors, usually designated as *film-forming,* protect the metal by forming a hydrophobic film on the metal surface. Their effectiveness depends on the chemical composition, their molecular structure, and their affinities for the metal surface. Because film formation is an adsorption process, the temperature and pressure in the system are important factors. Organic inhibitors will be adsorbed according to the ionic charge of the inhibitor and the charge on the surface. Cationic inhibitors, such as amines, or anionic inhibitors, such as sulfonates, will be adsorbed preferentially depending on whether the metal is charged negatively or positively. The strength of the adsorption bond is the dominant factor for soluble organic inhibitors.

These materials build up a protective film of adsorbed molecules on the metal surface, which provides a barrier to the dissolution of the metal in the electrolyte. Because the metal surface covered is proportional to the inhibitor concentrates, the concentration of the inhibitor in the medium is critical. For any specific inhibitor in any given medium there is an optimal concentration. For example, a concentration of 0.05% sodium benzoate or 0.2% sodium cinnamate is effective in water with a pH of 7.5 and containing either 17 ppm sodium chloride or 0.5% by weight of ethyl octanol. The corrosion due to ethylene glycol cooling water systems can be controlled by the use of ethanolamine as an inhibitor.

10.2.4 Precipitation inhibitors

Precipitation-inducing inhibitors are film-forming compounds that have a general action over the metal surface, blocking both anodic and cathodic sites indirectly. Precipitation inhibitors are compounds that cause the formation of precipitates on the surface of the metal, thereby providing a protective film. Hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal and form a protective film.

The most common inhibitors of this category are the silicates and the phosphates. Sodium silicate, for example, is used in many domestic water softeners to prevent the occurrence of *rust water*. In aerated hot water systems, sodium silicate protects steel, copper, and brass. However, protection is not always reliable and depends heavily on pH and a saturation index that depends on water composition and temperature. Phosphates also require oxygen for effective inhibition. Silicates and phosphates do not afford the degree of protection provided by chromates and nitrites; however, they are very useful in situations where nontoxic additives are required.

10.2.5 Volatile corrosion inhibitors

Volatile corrosion inhibitors (VCIs), also called vapor phase inhibitors (VPIs), are compounds transported in a closed environment to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds, such as morpholine or hydrazine, are transported with steam to prevent corrosion in condenser tubes by neutralizing acidic carbon dioxide or by shifting surface pH toward less acidic and corrosive values. In closed vapor spaces, such as shipping containers, volatile solids such as salts of dicyclohexylamine, cyclohexylamine, and hexamethylene-amine are used. On contact with the metal surface, the vapor of these salts condenses and is hydrolyzed by any moisture to liberate protective ions. It is desirable, for an efficient VCI, to provide inhibition rapidly and to last for long periods. Both qualities depend on the volatility of these compounds, fast action wanting high volatility, whereas enduring protection requires low volatility.

10.3 Corrosion Inhibition Mechanism

The majority of inhibitor applications for aqueous, or partly aqueous, systems are concerned with four main types of environment:

1. Aqueous solutions of acids as used in metal-cleaning processes such as pickling for the removal of rust or mill scale during the production and fabrication of metals or in the postservice cleaning of metal surfaces
2. Natural waters, supply waters, and industrial cooling waters in the near-neutral pH range (5 to 9)

3. Primary and secondary production of oil and subsequent refining and transport processes
4. Atmospheric or gaseous corrosion in confined environments, during transport, storage, or any other confined operation

The following sections describe corrosion mechanisms in terms of these four main environments.

10.3.1 Inhibitors for acid solutions

The corrosion of metals in acid solutions can be inhibited by a wide range of substances, such as halide ions, carbon monoxide, and many organic compounds, particularly those containing elements of Groups V and VI of the Periodic Table (i.e., nitrogen, phosphorus, arsenic, oxygen, sulfur, and selenium). Organic compounds containing multiple bonds, especially triple bonds, are effective inhibitors. The primary step in the action of inhibitors in acid solutions is generally agreed to be adsorption onto the metal surface, which is usually oxide-free in acid solutions. The adsorbed inhibitor then acts to retard the cathodic and/or anodic electrochemical corrosion processes.

Inhibitors of corrosion in acid solution can interact with metals and affect the corrosion reaction in a number of ways, some of which may occur simultaneously. It is often not possible to assign a single general mechanism of action to an inhibitor because the mechanism may change with experimental conditions. Thus, the predominant mechanism of action of an inhibitor may vary with factors such as its concentration, the pH of the acid, the nature of the anion of the acid, the presence of other species in the solution, the extent of reaction to form secondary inhibitors, and the nature of the metal. The mechanism of action of inhibitors with the same functional group may additionally vary with factors such as the effect of the molecular structure on the electron density of the functional group and the size of the hydrocarbon portion of the molecule.

Adsorption of corrosion inhibitors onto metals. The inhibitive efficiency is usually proportional to the fraction of the surface θ covered with adsorbed inhibitor. However, at low surface coverage ($\theta<0.1$), the effectiveness of adsorbed inhibitor species in retarding the corrosion reactions may be greater than at high surface coverage. In other cases, adsorption of inhibitors, such as thiourea and amines, from diluted solutions, may stimulate corrosion.

The information on inhibitor adsorption, derived from direct measurements and from inhibitive efficiency measurements, considered in conjunction with general knowledge of adsorption from solution, indicates that inhibitor adsorption on metals is influenced by the following main features.

Surface charge on the metal. Adsorption may be due to electrostatic attractive forces between ionic charges or dipoles on the adsorbed species and the electric charge on the metal at the metal-solution interface. In solution, the charge on a metal can be expressed by its potential with respect to the zero-charge potential. This potential relative to the zero-charge potential, often referred to as the (φ-potential, is more important with respect to adsorption than the potential on the hydrogen scale, and indeed the signs of these two potentials may be different. As the potential of a metallic surface becomes more positive, the adsorption of anions is favored, and as the φ-potential becomes more negative, the adsorption of cations is favored.

The functional group and structure of the inhibitor. Inhibitors can also bond to metal surfaces by electron transfer to the metal to form a coordinate type of link. This process is favored by the presence in the metal of vacant electron orbitals of low energy, such as occurs in the transition metals. Electron transfer from the adsorbed species is favored by the presence of relatively loosely bound electrons, such as may be found in anions, and neutral organic molecules containing lone pair electrons or π-electron systems associated with multiple, especially triple, bonds or aromatic rings. The electron density at the functional group increases as the inhibitive efficiency increases in a series of related compounds. This is consistent with increasing strength of coordinate bonding due to easier electron transfer and hence greater adsorption.

Interaction of the inhibitor with water molecules. Adsorption of inhibitor molecules is often a displacement reaction involving removal of adsorbed water molecules from the surface. During adsorption of a molecule, the change in interaction energy with water molecules in passing from the dissolved to the adsorbed state forms an important part of the free energy change on adsorption. This has been shown to increase with the energy of solvation of the adsorbing species, which in turn increases with increasing size of the hydrocarbon portion of an organic molecule. Thus increasing size leads to decreasing solubility and increasing adsorbability. This is consistent with the increasing inhibitive efficiency observed at constant concentrations with increasing molecular size in a series of related compounds.

Interaction of adsorbed inhibitor species. Lateral interactions between adsorbed inhibitor species may become significant as the surface coverage, and hence the proximity, of the adsorbed species increases. These lateral interactions may be either attractive or repulsive. Attractive interactions occur between molecules containing large hydrocarbon components (e.g., *n*-alkyl chains). As the chain length increases, the increasing Van der Waals attractive force between adjacent molecules leads to stronger adsorption at high coverage. Repulsive interactions occur between ions or molecules containing dipoles and lead to weaker adsorption at high coverage.

In the case of ions, the repulsive interaction can be altered to an attractive interaction if an ion of opposite charge is simultaneously adsorbed. In a solution containing inhibitive anions and cations the adsorption of both ions may be enhanced and the inhibitive efficiency greatly increased compared to solutions of the individual ions. Thus, synergistic inhibitive effects occur in such mixtures of anionic and cationic inhibitors.

Reaction of adsorbed inhibitors. In some cases, the adsorbed corrosion inhibitor may react, usually by electrochemical reduction, to form a product that may also be inhibitive. Inhibition due to the added substance has been termed *primary inhibition* and that due to the reaction product, *secondary inhibition*. In such cases, the inhibitive efficiency may increase or decrease with time according to whether the secondary inhibition is more or less effective than the primary inhibition. Sulfoxides, for example, can be reduced to sulfides, which are more efficient inhibitors.

Effects of inhibitors on corrosion processes. In acid solutions the anodic process of corrosion is the passage of metal ions from the oxide-free metal surface into the solution, and the principal cathodic process is the discharge of hydrogen ions to produce hydrogen gas. In air-saturated acid solutions, cathodic reduction of dissolved oxygen also occurs, but for iron the rate does not become significant compared to the rate of hydrogen ion discharge until the pH exceeds a value of 3. An inhibitor may decrease the rate of the anodic process, the cathodic process, or both processes. The change in the corrosion potential on addition of the inhibitor is often a useful indication of which process is retarded. Displacement of the corrosion potential in the positive direction indicates mainly retardation of the anodic process (anodic control), whereas displacement in the negative direction indicates mainly retardation of the cathodic process (cathodic control). Little change in the corrosion potential suggests that both anodic and cathodic processes are retarded.

The following discussion illustrates the usage of anodic and cathodic inhibitors for acid cleaning of industrial equipment. The combined action of film growth and deposition from solution results in fouling that has to be removed to restore the efficiency of heat exchangers, boilers, and steam generators. E-pH diagrams indicate that the fouling of iron-based boiler tubes, by Fe_3O_4 and Fe_2O_3, can be dissolved in either the acidic or alkaline corrosion regions. In practice, inhibited hydrochloric acid has been repeatedly proven to be the most efficient method to remove fouling. Four equations are basically needed to explain the chemistry involved in fouling removal. Three of those equations represent cathodic processes [Eqs. (10.2) and (10.3); A, A′ and A" in Figs. 10.1 and 10.2; and Eq. (10.4); B in Figs. 10.1 and 10.2] and one anodic process [i.e., the dissolution of tubular material [Eq. (10.5); C in Figs. 10.1 and 10.2]:[3]

$$Fe_2O_3 + 4\,Cl^- + 6\,H^+ + 2\,e^- \rightarrow 2\,FeCl_{2(aq)} + 3\,H_2O \qquad (10.2)$$

$$Fe_3O_4 + 6\,Cl^- + 8\,H^+ + 2\,e^- \rightarrow 3\,FeCl_{2(aq)} + 4\,H_2O \qquad (10.3)$$

$$2\,H^+ + 2\,e^- \rightarrow H_2 \qquad (10.4)$$

$$Fe + 2\,Cl^- \rightarrow FeCl_{2(aq)} + 2\,e^- \qquad (10.5)$$

These equations indicate that the base iron functions as a reducer to accelerate the dissolution of iron oxides. Because it is difficult to determine the endpoint for the dissolution of fouling oxides, an inhibitor is generally added for safety purpose. Both anodic and cathodic inhibitors could be added to retard the corrosion of the bare metal after dissolution of the fouling oxides. Figures 10.1 and 10.2 illustrate the action that could be played by either an anodic inhibitor (Fig. 10.1) or a cathodic inhibitor (Fig. 10.2). It can be seen that although the anodic inhibitor retards the anodic dissolution of iron at the endpoint, it concurrently decreases the rate of oxide dissolution permitted by the chemical system.

On the other hand, the cathodic inhibitor retards both the reduction of protons into hydrogen and the dissolution of the base, whereas the reduction of the fouling oxides is left unaffected. The E-pH diagrams also indicate that the dissolution of the fouling oxides is also possible in alkaline solutions. But the kinetics of anodic and cathodic reactions in high pH environments are much slower, and therefore these reactions are less useful.

Electrochemical studies have shown that inhibitors in acid solutions may affect the corrosion reactions of metals in the following main ways.

Formation of a diffusion barrier. The absorbed inhibitor may form a surface film that acts as a physical barrier to restrict the diffusion of ions or molecules to or from the metal surface and so retard the rate of corrosion reactions. This effect occurs particularly when the inhibitor species are large molecules (e.g., proteins, such as gelatin or agar agar, polysaccharides, such as dextrin, or compounds containing long hydrocarbon chains). Surface films of these types of inhibitors give rise to resistance polarization and also concentration polarization affecting both anodic and cathodic reactions.

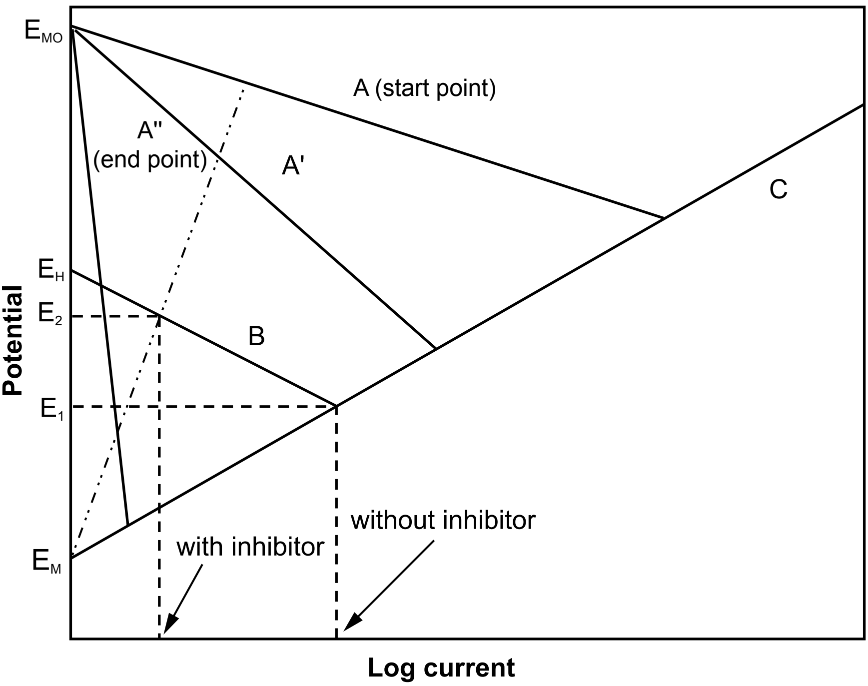

Figure 10.1 The effect of an anodic inhibitor on the dissolution rate of iron and iron oxide.[3]

Blocking of reaction sites. The simple blocking decreases the number of surface metal atoms at which corrosion reactions can occur. The mechanisms of the reactions are not affected, and the Tafel slopes of the polarization curves remain unchanged. It should be noted that the anodic and cathodic processes may be inhibited to different extents. The anodic dissolution process of metal ions is considered to occur at steps or emergent dislocations in the metal surface, where metal atoms are less firmly held to their neighbors than in the plane surface. These favored sites occupy a relatively small proportion of the metal surface. The cathodic process of hydrogen evolution is thought to occur on the plane crystal faces that form most of the metal surface area. Adsorption of inhibitors at low surface coverage tends to occur preferentially at anodic sites, causing retardation of the anodic reaction. At higher surface coverage, adsorption occurs on both anodic and cathodic sites, and both reactions are inhibited.

Participation in the electrode reactions. Corrosion reactions often involve the formation of adsorbed intermediate species with surface metal atoms [e.g., adsorbed hydrogen atoms in the hydrogen evolution reaction and adsorbed (FeOH) in the anodic dissolution of iron].

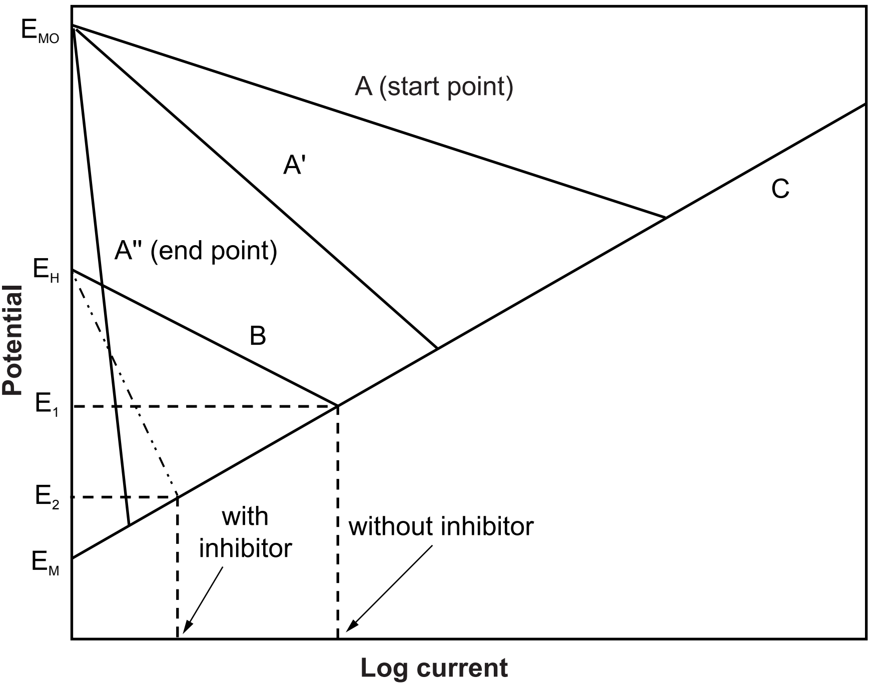

Figure 10.2 The effect of a cathodic inhibitor on the dissolution rate of iron and iron oxide.[3]

The presence of adsorbed inhibitors will interfere with the formation of these adsorbed intermediates, but the electrode processes may then proceed by alternative paths through intermediates containing the inhibitor. In these processes the inhibitor species act in a catalytic manner and remain unchanged. Such participation by the inhibitor is generally characterized by an increase in the Tafel slope of the anodic dissolution of the metal.

Inhibitors may also retard the rate of hydrogen evolution on metals by affecting the mechanism of the reaction, as indicated by increases in the Tafel slopes of cathodic polarization curves. This effect has been observed on iron in the presence of inhibitors such as phenyl-thiourea, acetylenic hydrocarbons, aniline derivatives, benzaldehyde derivatives. and pyrilium salts.

Alteration of the electrical double layer. The adsorption of ions or species that can form ions on metal surfaces will change the electrical double layer at the metal-solution interface, and this in turn will affect the rates of the electrochemical reactions. The adsorption of cations, such as quaternary ammonium ions and protonated amines, makes the potential more positive in the plane of the closest approach to the metal of ions from the solution. This positive potential displacement retards the discharge of the positively charged hydrogen ion.

Conversely, the adsorption of anions makes the potential more negative on the metal side of the electrical double layer, and this will tend to accelerate the rate of discharge of hydrogen ions. This effect has been observed for the sulfosalicylate ion and the benzoate ion.

Measuring the efficiency of a acid inhibitor. The following example illustrates how the corrosion efficiency of an inhibitor can be evaluated with a relatively simple corrosion test. Trans-cinnamaldehyde (TCA) corrosion inhibiting efficiency was evaluated with an electrochemical technique called linear polarization resistance (LPR). TCA can be used to reduce the corrosion of steel during pickling or oil field acidizing treatments. Nearly 40 years ago, Hugel tested a variety of inhibitors for steel in 6 M HCl at 60°C and found that alkenyl and aromatic aldehydes were very effective.[4] Cinnamaldehyde was one of the best, providing almost 99% protection. Numerous patents have been issued since then on the use of aldhydes, and cinnamaldehyde in particular, as steel corrosion inhibitors in acid media.

The LPR polarization resistance (R_p) is typically calculated from the slope of a polarization curve where

$$R_p = \frac{\Delta E}{\Delta I_{\text{app}}}$$

and where ΔE is the voltage change for an applied current (ΔI_{app}). R_p itself can be converted in a corrosion current (I_{corr}) using the Stern Geary approximation written as:[5,6]

$$I_{\text{corr}} = \frac{\beta_a \beta_c}{2.3\,(\beta_a + \beta_c)\,R_p}$$

where β_a and β_c are, respectively, the anodic and cathodic Tafel slopes.

The polarization curves presented in Figs. 10.3 to 10.5 were obtained with carbon steel exposed to a solution containing, respectively, 250, 1000, and 5000 ppm of TCA in a 6 M HCl solution. Assuming, for this example, that β_a and β_c are both equal to 0.1 V decade^{-1} and that the R_p of uninhibited carbon steel in 6 M HCl is equal to 14 $\Omega\cdot\text{cm}^2$, it is possible to obtain the inhibitor efficiency values presented in Table 10.2.

10.3.2 Inhibitors in near-neutral solutions

Corrosion of metals in neutral solutions differs from that in acid solutions in two important respects. In air-saturated solutions, the main

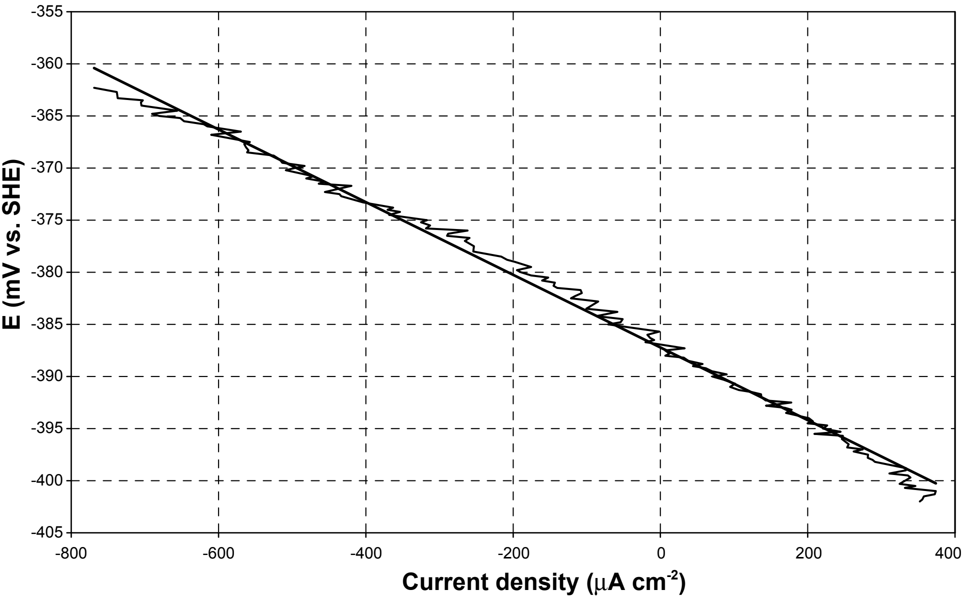

Figure 10.3 Corrosion of AISI 1018 carbon steel in 6 M HCl containing 250 ppm trans-cinnamaldehyde

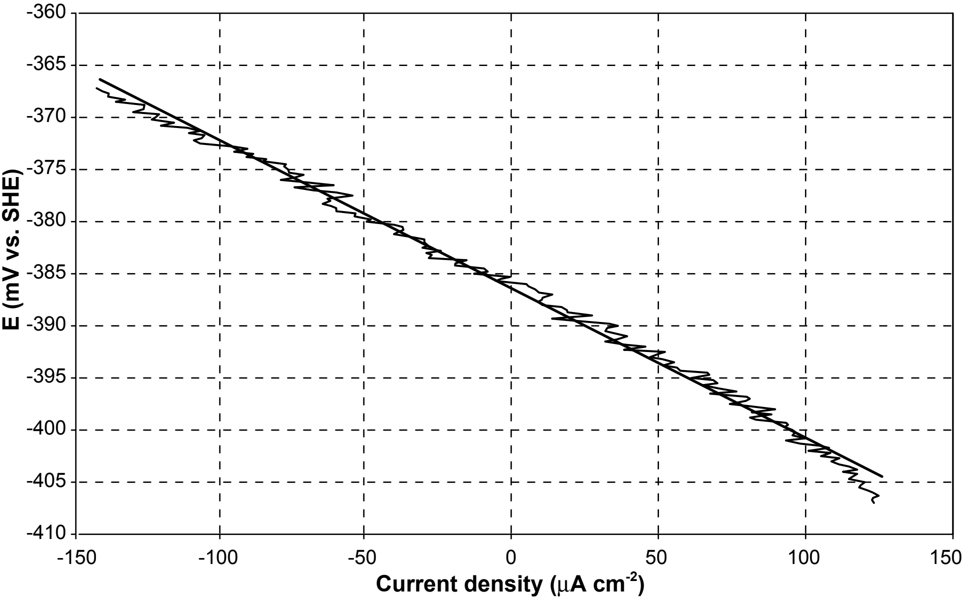

Figure 10.4 Corrosion of AISI 1018 carbon steel in 6 M HCl containing 500 ppm trans-cinnamaldehyde.

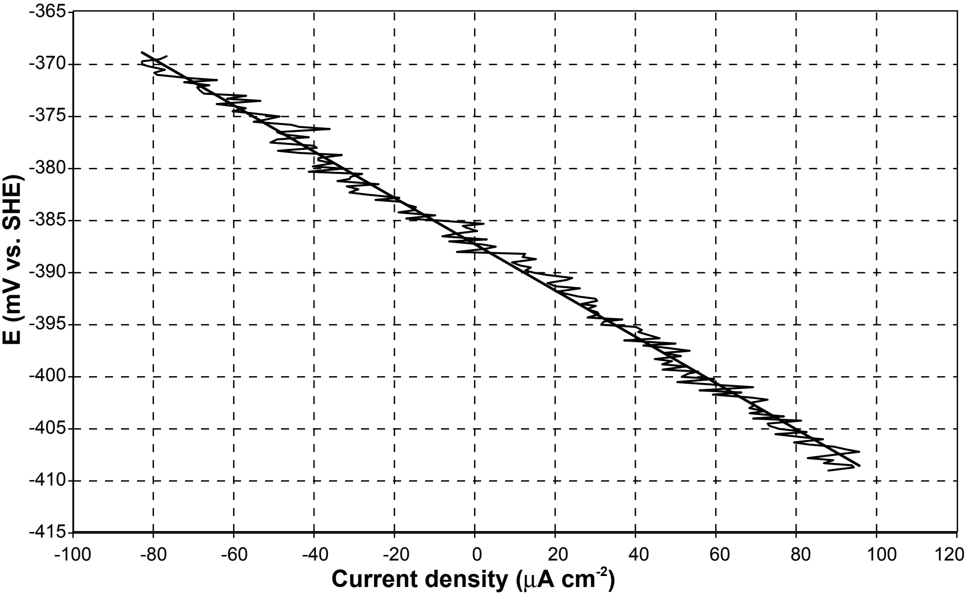

Figure 10.5 Corrosion of AISI 1018 carbon steel in 6 M HCl containing 1000 ppm trans-cinnamaldehyde.

TABLE 10.2 Inhibitor Efficiency of Trans-Cinnamaldehyde (TCA) to the Corrosion of Carbon Steel Exposed to a 6 M HCl Solution

TCA, ppm	R_p, $\Omega \cdot cm^2$	Corrosion current, $mA \cdot cm^{-2}$	Corrosion rate, $mm \cdot y^{-1}$	Efficiency, %
0	14	1.55	18.0	0
250	35	0.62	7.2	60
1000	143	0.152	1.76	90
5000	223	0.097	1.13	94

cathodic reaction in neutral solutions is the reduction of dissolved oxygen, whereas in acid solution it is hydrogen evolution. Corroding metal surfaces in acid solution are oxide-free, whereas in neutral solutions metal surfaces are covered with films of oxides, hydroxides, or salts, owing to the reduced solubility of these species. Because of these differences, substances that inhibit corrosion in acid solution by adsorption on oxide-free surfaces do not generally inhibit corrosion in neutral solution.

Typical inhibitors for near-neutral solutions are the anions of weak acids, some of the most important in practice being chromate, nitrite, benzoate, silicate, phosphate, and borate. Passivating oxide films on metals offer high resistance to the diffusion of metal ions, and the anodic reaction of metal dissolution is inhibited. These inhibitive anions are often referred to as anodic inhibitors, and they are more generally used than cathodic inhibitors to inhibit the corrosion of iron, zinc, aluminum, copper, and their alloys in near-neutral solutions. The action of inhibitive anions on the corrosion of metals in near-neutral solution involves the following important functions:

1. Reduction of the dissolution rate of the passivating oxide film
2. Repair of the oxide film by promotion of the reformation of oxide
3. Repair of the oxide film by plugging pores with insoluble compounds
4. Prevention of the adsorption of aggressive anions

Of these functions, the most important appears to be the stabilization of the passivating oxide film by decreasing its dissolution rate (function 1). Inhibitive anions probably form a surface complex with the metal ion of the oxide (i.e., Fe^{3+}, Zn^{2+}, Al^{3+}), such that the stability of this complex is higher than that of the analogous complexes with water, hydroxyl ions, or aggressive anions.

Stabilization of the oxide films by repassivation is also important (function 2). The plugging of pores by formation of insoluble compounds (function 3) does not appear to be an essential function but is valuable in extending the range of conditions under which inhibition can be achieved. The suppression of the adsorption of aggressive anions (function 4) by participation in a dynamic reversible competitive adsorption equilibrium at the metal surface appears to be related to the general adsorption behavior of anions rather than to a specific property of inhibitive anions.

Inhibition in neutral solutions can also be due to the precipitation of compounds, on a metallic surface, that can form or stabilize protective films. The inhibitor may form a surface film of an insoluble salt by precipitation or reaction. Inhibitors forming films of this type include

- Salts of metals such as zinc, magnesium, manganese, and nickel, which form insoluble hydroxides, especially at cathodic areas, which are more alkaline due to the hydroxyl ions produced by reduction of oxygen
- Soluble calcium salts, which can precipitate as calcium carbonate in waters containing carbon dioxide, again at cathodic areas where the high pH permits a sufficiently high concentration of carbonate ions
- Polyphosphates in the presence of zinc or calcium, which produce a thin amorphous salt film

These salt films, which are often quite thick and may even be visible, restrict diffusion, particularly of dissolved oxygen to the metal surface. They are poor electronic conductors, and so oxygen reduction does not occur on the film surface. These inhibitors are referred to as cathodic inhibitors.

The following sections discuss the mechanism of action of inhibitive anions on iron, zinc, aluminum, and copper.

Iron. Corrosion of iron (or steel) can be inhibited by the anions of most weak acids under suitable conditions. However, other anions, particularly those of strong acids, tend to prevent the action of inhibitive anions and stimulate breakdown of the protective oxide film. Examples of such aggressive anions include the halides, sulfate, and nitrate. The balance between the inhibitive and aggressive properties of a specific anion depends on the following main factors (which are themselves interdependent):

- *Concentration.* Inhibition of iron corrosion in distilled water occurs only when the anion concentration exceeds a critical value. At concentrations below the critical value, inhibitive anions may act aggressively and stimulate breakdown of the oxide films. Effective inhibitive anions have low critical concentrations for inhibition. A number of anions have been classified in order of their inhibitive power toward steel, judged from their critical inhibitive concentrations. The order of decreasing inhibitive efficiency is azide, ferricyanide, nitrite, chromate, benzoate, ferrocyanide, phosphate, tellurate, hydroxide, carbonate, chlorate, *o*-chlorbenzoate, bicarbonates fluoride, nitrate, and formate.
- *pH.* Inhibitive anions are effective in preventing iron corrosion only at pH values more alkaline than a critical value. This critical pH depends on the anion.
- *Dissolved oxygen concentration and supply.* Inhibition of the corrosion of iron by anions requires a critical minimum degree of oxidizing power in the solution. This is normally supplied by the dissolved oxygen present in air-saturated solutions.
- *Aggressive anion concentration.* When aggressive anions are present in the solution, the critical concentrations of inhibitive anions required for protection of iron are increased. It has been shown that the relationship between the maximum concentration of aggressive anion C_{agg} permitting full protection by a given concentration of inhibitive anion C_{inh} is of the form

  $$\log C_{\mathrm{inh}} = n \log C_{\mathrm{agg}} + K$$

  where K is a constant dependent on the nature of the inhibitive and aggressive anions, and n is an exponent that is approximately the ratio of the valency of the inhibitive anion to the valency of the aggressive anion

- *Nature of the metal surface.* The critical concentration of an anion required to inhibit the corrosion of iron may increase with increasing surface roughness.
- *Temperature.* In general, the critical concentrations of anions (e.g., benzoate, chromate, and nitrite) required for the protection of steel increase as the temperature increases.

Zinc. The effects of inhibitive and aggressive anions on the corrosion of zinc are broadly similar to the effects observed with iron. Thus with increasing concentration, anions tend to promote corrosion but may give inhibition above a critical concentration. Inhibition of zinc corrosion is somewhat more difficult than that of iron (e.g., nitrite and benzoate are not efficient inhibitors for zinc). However, inhibition of zinc corrosion is observed in the presence of anions such as chromates, borate, and nitrocinnamate, which are also good inhibitors for the corrosion of iron. Anions such as sulfate, chloride, and nitrate are aggressive toward zinc and prevent protection by inhibitive anions. The presence of dissolved oxygen in the solution is essential for protection by inhibitive anions. As in the case of iron, pressures of oxygen greater than atmospheric or an increase in oxygen supply by rapid stirring can lead to the protection of zinc in distilled water. Inhibition of zinc corrosion occurs most readily in the pH range of 9 to 12, which corresponds approximately to the region of minimum solubility of zinc hydroxide.

The ways in which inhibitive anions affect the corrosion of zinc are mainly similar to those described above for iron. In inhibition by chromate, localized uptake of chromium has been shown to occur at low chromate concentrations and in the presence of chloride ions. Inhibitive anions also promote the passivation of zinc (e.g., passivation is much easier in solutions of the inhibitive anion, borate, than in solutions of the noninhibitive anions, carbonate and bicarbonate). A critical inhibition potential, analogous to that on iron, has been observed for zinc in borate solutions. Thus inhibitive anions promote repair of the oxide film on zinc by repassivation with zinc oxide.

Aluminum. When aluminum is immersed in water, the air-formed oxide film of amorphous γ-alumina initially thickens (at a faster rate than in air) and then an outer layer of crystalline hydrated alumina forms, which eventually tends to stifle the reaction. In near-neutral air-saturated solutions, the corrosion of aluminum is generally inhibited by anions that are inhibitive for iron (e.g., chromate, benzoate, phosphate, and acetate). Inhibition also occurs in solutions containing sulfate or nitrate ions, which are aggressive toward iron. Aggressive anions for aluminum include the halide ions, F^-, Cl^-, Br^-, I^-, which cause pitting attack, and anions that form soluble complexes with aluminum (e.g., citrate and tartrate), which cause general attack. Competitive effects, similar to those observed on iron, are observed in the action of mixtures of inhibitive anions and chloride ions on aluminum.

In near-neutral and deaerated solutions, the oxide film on anodized aluminum is stable and protective in distilled water and chloride solutions, as well as in solutions of inhibitive anions. Thus the inhibition of aluminum corrosion by anions differs from that of iron or zinc in that the presence of dissolved oxygen in the solution is not necessary to stabilize the oxide film. In corrosion inhibition by chromate ions, their interaction with the oxide film on aluminum has been shown to result in the formation of an outer layer of the film that is more protective due to its high electronic resistance and low dissolution rate. Chromate ions were also found to prevent the uptake and penetration of chloride ions into the aluminum oxide film.

Copper. Little work has been carried out on the mechanism of inhibition by anions of copper corrosion in neutral solutions. Inhibition occurs in solutions containing chromate, benzoate, or nitrite ions. Chloride and sulfide ions are aggressive, and there is some evidence that chloride ions can be taken up into the cuprous oxide film on copper to replace oxide ions and create cuprous ion vacancies that permit easier diffusion of cuprous ions through the film, thus increasing the corrosion rate.

Copper corrosion can also be effectively inhibited in neutral solution by organic compounds of low molecular weight, such as benzotriazole and 2-mercaptobenzothiazole. Benzotriazole is particularly effective in preventing the tarnishing and dissolution of copper in chloride solutions. In the presence of benzotriazole, the anodic dissolution, oxide film growth, and dissolved oxygen reduction reactions are all inhibited, indicating strong adsorption of the inhibitor on the cuprous oxide surface.

10.3.3 Inhibitors for oil and gas systems

Even in early days, oil producers applied numerous chemical compounds, sometimes with success, to minimize corrosion damage in the oil wells themselves and in surface handling equipment. Once amines and imidazolines came into use, corrosion inhibition in oil wells became dramatically more effective. Modern inhibitors are applied in the field, continuously or by periodic batch, at concentrations of 15 to

50 ppm, based on total liquid production. A much wider variety of inhibitor chemistry is available today for combating oil-field corrosion than existed only a decade ago. In recent years, organic molecules containing sulfur, phosphorus, and nitrogen in various combinations have been developed. These inhibitor types have extended the performance of oil-field inhibitors, particularly in the directions of being tolerant of oxygen contamination and of controlling corrosion associated with high CO_2, low H_2S conditions.[7]

Most of the inhibitors currently used in producing wells are organic nitrogenous compounds. The basic types have long-chain hydrocarbons (usually C_{18}) as a part of the structure. Most inhibitors in successful use today are either based on the long-chain aliphatic diamine, or on long carbon chain imidazolines. Various modifications of these structures have been made to change the physical properties of the material (e.g., ethylene oxide is commonly reacted with these compounds in various molecular percentages to give polyoxy-ethylene derivatives that have varying degrees of brine dispersibility). Many carboxylic acids are used to make salts of these amines or imidazolines. Inhibitors in general petroleum production can be classified as follows:[8]

- Amides/imidazolines
- Salts of nitrogenous molecules with carboxylic acids
- Nitrogen quaternaries
- Polyoxyalkylated amines, amides, and imidazolines
- Nitrogen heterocyclics and compounds containing P, S, O

There are several hypotheses and theories concerning the inhibitive action of the long-chain nitrogenous compounds. One of the classical concepts is the so-called sandwich theory in which the bottom part of the sandwich is the bond between the polar end of the molecule and the metal surface. The strength of the protective action depends on this bond. The center portion of the sandwich is the nonpolar end of the molecule and its contribution toward protection is the degree to which this portion of the molecule can cover or wet the surface. The top portion of the protective sandwich is the hydrophobic layer of oil attached to the long carbon tail of the inhibitor. This oil layer serves as the external protective film, covering the inhibitor film and creating a barrier to both outward diffusion of ferrous ion and inward diffusion of corrosive species.

Water or water solutions of salts alone will not cause damaging corrosion unless they contain specific corrodents, such as CO_2, H_2S, and their products of dissolution. Oil and gas wells are either sweet or sour.

Sweet wells do not contain hydrogen sulfide, whereas sour wells do. The source of CO_2 can be mineral dissolution or a by-product of the petroleum-forming process. The source of H_2S can be dissolution of mineral deposits in the rocks, a by-product of the petroleum-forming process, or bacterial action at any time in the history of the petroleum deposit. Oxygen always originates from air and can only come in contact with petroleum fluids after the recovery process begins. It does not exist in the undisturbed hydrocarbon deposit.

The dissolution products of H_2S in oil-field waters will be dissolved hydrogen sulfide molecules (H_2S) and bisulfide ions (HS^-), and the dissolution products of CO_2 will be dissolved CO_2 molecules (some hydrate to form H_2CO_3) and bicarbonate (HCO_3^-) ions. The pH of these waters is not basic enough to produce appreciable amounts of sulfide or carbonate ions. However, damaging corrosion in the oil field nearly always takes localized forms, often pitting. Corrosion pits in oil-field steels typically penetrate at 10 to 100 times the rate of uniform corrosion. Pit growth in steels exposed to brine, an active corrosion system, occurs because of a galvanic couple between filmed metal and relatively bare metal.

Sweet corrosion. Corrosion in CO_2 gas wells can be divided into three temperature regimes. Below 60°C, the corrosion product is nonprotective and high corrosion rates will occur. Above approximately 150°C, magnetite is formed, and the wells are not corrosive except in the presence of high brine levels. In the middle temperature regime, in which most gas well conditions lie, the iron carbonate corrosion product layer is protective but is affected adversely by chlorides and fluid velocity.[7]

One of the important physical properties of oil-field inhibitors is their volubility or dispersibility characteristic in the oil and the brine being produced. An inhibitor, properly chosen on the basis of the corrosion mechanism, will not be effective if it does not have access to the corroding metal. When it comes to treating oil and gas wells, there are also some important differences. The distinction between an oil well and a gas well is not clear cut. Often the distinction is made on the basis of economics or workload balance within a producing company. The facts that many oil wells produce a considerable volume of gas and many gas wells produce a considerable volume of liquid, plus the fact that wells often experience a shift in production during their lifetime, make a technical distinction difficult. However, there are more important differences. Typical gas wells are much hotter than oil wells, and the hydrocarbon liquids are much lighter. Gas wells are normally much deeper and usually produce lower total dissolved solids (TDS) brines. Oxygen is not a factor to consider in gas well corrosion but can cause major problems in artificial lift oil wells.

Due to the large temperature gradient in many gas wells, corrosion mechanisms can change, resulting in different types of corrosion in the same well, whereas oil wells do not exhibit this behavior. Normally, oil wells produce more liquid than gas wells, resulting in a shorter treatment life when batch treated. Because corrosion in oil wells is electrochemical in nature, an electrolyte must be present for corrosion to occur. In oil wells, the source of the water is nearly always the producing formation, and the water will contain dissolved salts in concentrations ranging from traces to saturation. Water associated with corrosion may be in a thin layer, in droplets, or even the major phase.

Results of the study of corrosion control by inhibitors in producing oil wells in carbon dioxide flooded fields[8] showed imidazolines are successful in protection in CO_2 brines. The inhibitor was found to be incorporated in the carbonate corrosion product layer but was still more effective if the surface film contained sulfide. Also, better results were obtained with inhibitors, such as nitrogen-phosphorus compounds or compounds with sulfur in the organic molecules.

Sour corrosion. In sour wells, hydrogen sulfide is the primary corrosive agent, and frequently carbon dioxide is present as well. The presence of various iron sulfides in the corrosion products at different concentrations of hydrogen sulfide has been identified. Based on this evidence the net corrosion reaction due to hydrogen sulfide can be written as follows:

$$\mathrm{Fe} + \mathrm{H_2S} \rightarrow \mathrm{FeS} + 2\,\mathrm{H}^+ + 2\,e^- \tag{10.6}$$

The most probable mechanism to explain the accelerating effect of hydrogen sulfide involves the formation of a molecular surface complex that can yield hydrogen atoms according to Eqs. (10.7) to (10.9). Some of the hydrogen produced in the process [Eq. (10.9)] may recombine to form molecular gaseous hydrogen, whereas some can diffuse in the metal and eventually cause blistering or hydrogen induced cracking.[9]

$$\mathrm{Fe} + \mathrm{HS}^- \rightarrow \mathrm{Fe}\,(\mathrm{HS}^-)_{\mathrm{ads}} \tag{10.7}$$

$$\mathrm{Fe}\,(\mathrm{HS}^-)_{\mathrm{ads}} + \mathrm{H}^+ \rightarrow \mathrm{Fe}\,(\mathrm{H\text{-}S\text{-}H})_{\mathrm{ads}} \tag{10.8}$$

$$\mathrm{Fe}\,(\mathrm{H\text{-}S\text{-}H})_{\mathrm{ads}} + e^- \rightarrow \mathrm{Fe}\,(\mathrm{HS}^-)_{\mathrm{ads}} + \mathrm{H}_{\mathrm{ads}} \tag{10.9}$$

Corrosion inhibitors used in the past to combat corrosion in sour wells include aldehydes, cyanamide thiourea, and urea derivatives. The most widely used inhibitors are organic amines. Although organic amines are known to be less effective inhibitors in acid solution, inhibition by amines in the presence of hydrogen sulfide is greatly enhanced.[9] Oil-field inhibitors function by incorporating into a thin layer of corrosion product on the metal surface. This surface film may be a sulfide or a carbonate and may be anaerobic or partially oxidized. Some types of inhibitor molecules incorporate better in one type of film than others. For example, amine inhibitors are not effective when oxygen is present. Inhibitor molecules containing nitrogen (e.g., imidazolines) will incorporate into either sulfide or carbonate films but are more effective when the film contains some sulfide.

Acidizing. An important procedure for stimulation of oil and gas well production is acidizing. Because of the very low permeability of certain formations containing hydrocarbons, these are not able to flow readily into the well. Formations composed of limestone or dolomite may be treated with HCl or, if the rock is sandstone, a mixture containing HF. In the acidizing treatment, the acid (e.g., HCl, at a concentration of 7 to 28%) is pumped down the tubing into the well where it enters the perforations and contacts the formation; the acid etches channels that provide a way for oil and gas to enter the well.[8] Many inhibitors are used for well acidizing operations, mainly high molecular weight nitrogenous compounds such as those used in primary production or the reaction products of these compounds with unsaturated alcohols. Many of those commercial inhibitors contain alkyl or alkylaryl nitrogen compounds and acetylenic alcohols, such as 1-octyn-3-ol. These products present serious handling problems because they are very toxic; this can determine which product is actually used by an operator. Furthermore, their effectiveness is limited both in efficiency and time. Acid soaks normally last between 12 and 24 h, after which time inhibitor efficiency can start to fall off alarmingly.

Oxygen-containing inhibitors that are successful in concentrated HCl include cinnamaldehyde and the alkynols containing unsaturated groups conjugated with the oxygen function described as alpha-alkenylphenones.[8] They provide, especially when mixed with small amounts of surfactants, protection similar to that obtained with acetylenic alcohols.

Oxygen-influenced corrosion. Oil-producing formations originally contain no oxygen. During the process of bringing oil to the surface, oxygen from air contamination may dissolve into produced fluids. This oxygen has three consequences:

1. Oxygen can readily accept electrons, so it increases the rate of corrosion.
2. The nature of the surface corrosion product changes, so the chemical properties required for effective inhibitor incorporation change.

3. Oxidation of certain ions in solution leads to increased precipitation of solid phases.

Air may be pulled into the annuli of wells having little gas pressure as a consequence of the artificial lift process or of negative-pressure gas gathering systems. In some cases, in situ combustion stimulation can introduce oxygen into the formation itself. On the surface, small amounts of oxygen can be introduced into production liquids by leaking pump packing or direct contact during storage.[10]

In water flooding, the same types of inhibitors as described for primary production are currently used. The most effective and most frequently used are the quaternary ions of the fatty or the imidazoline types. They are also good bactericides and dispersive agents. Combination of amino-methylene phosphonate and zinc salts have been used successfully in circulating water systems and have provided more effective protection than the inorganic phosphate-zinc salts. Organic sulfonates have recently been introduced into practice.

Oxygen is practically always present in drilling muds. The most effective control of oxygen corrosion would be to keep it out of the system, but this is difficult because the drilling fluid is exposed to the atmosphere as it circulates through the pit. The attack is almost always in the form of pitting, which in a short time can produce irreversible damage to drilling equipment. Oxygen activity in drilling muds is determined by the interplay of a number of factors. For example, phosphorus compounds such as sodium hexametaphosphate, phosphate esters of organic alcohol, and organic phosphonates may act as anodic inhibitors, but a precaution is required in their use because they have a strong tendency to thin nondispersed muds. Tannins and lignins are thinners for high-solid muds, and they also have a certain inhibitive influence.

Application methods. The selection of an inhibitor is of prime importance, but the proper application of an inhibitor is even more important. If an inhibitor does not reach the corrosive areas, it cannot be effective. Maximum corrosion protection can be achieved by continuous injection of inhibitor through a dual tubing string (kill string), a capillary tubing, a side mandrel valve, or even perforated tubing. Any of these methods will supply a continuous residual of inhibitor to maintain corrosion protection. Treating rates or inhibitor concentrations are best based on the volume of fluid produced and can range from near 50 ppm to over 1000 ppm, depending on the severity of the conditions.[7]

Many gas wells are not equipped with facilities for continuous treatment and must be treated by some type of batch or slug treatment. The most commonly used method is the batch or short-batch treatment in which a volume of inhibitor solution (typically 2 to 10%) is injected into a shut-in well and allowed to fall to the bottom. Fall rates are a function of solution viscosity. The common failure of this method is not allowing sufficient time for the inhibitor to reach the hole bottom. A variation on this method is the tubing displacement treatment in which the inhibitor solution is pushed to the bottom by diesel or condensate. This guarantees the inhibitor reaching bottom hole, but it can kill low-pressure wells and is more costly.

Sometimes a short batch is forced down with a nitrogen displacement or compressed gas to speed up the fall rate and reduce shut-in time. An inhibitor squeeze is sometimes used to try to get a longer return time and simulate a continuous treatment. However, there is always the concern of formation damage with squeezes and with tubing displacements.

10.3.4 Atmospheric and gaseous corrosion

VCIs represent a very economical and powerful tool in combating the atmospheric or gaseous corrosion damage done to metals and alloys. Volatile corrosion inhibition is based on conditioning of the environment with trace amounts of inhibitive material to achieve a protective effect. A VCI compound, in addition to being volatile, is required to promote electrochemical effects such as change of the potential in the diffuse part of the double layer that controls the migration of components of the electrode reactions.

The first condition for good efficiency of a vapor phase inhibitor is its capability to reach the metallic surface to be protected. The second is that the rate of transfer of the molecule should not be too slow to prevent an initial attack of the metal surface by the aggressive environment before the inhibitor can act. These two conditions are related partly to the vapor pressure of the inhibitor, partly to the distance between the source(s) of the inhibitor and the metal surfaces, and partly to the accessibility of the surfaces.[11]

The vapor pressure of a chemical compound will depend upon the structure of the crystal lattice and the character of the atomic bonds in the molecule. In this respect, organic components of the molecule will generally ensure its volatility. A convenient volatile inhibitor should not have too high a vapor pressure, because it will be lost as a result of the fact that enclosures are generally not airtight; protection will then drop. A convenient partial vapor pressure for efficient compounds will lie between 10^{-5} and 10^{-1} mm·Hg (i.e., 10^{-3} to 10 Pa).

By definition, only compounds that have an appreciable vapor pressure under atmospheric conditions and can act as electrolyte layer inhibitors by electrochemically changing the kinetics of electrode reactions should be classified as VCIs. Neutralizing amines have an appreciable vapor pressure and are effective inhibitors for ferrous metals, but their mechanism is based on adjusting the pH value of the electrolyte, thus creating conditions that are inhospitable for rust formation. Hence, they should not necessarily be classified as volatile corrosion inhibitors .

Volatile compounds reach the protective vapor concentration rapidly, but in the case of enclosures that are not airtight, the consumption of inhibitor is excessive and the effective protective period is short. Low vapor pressure inhibitors are not rapidly exhausted and can ensure more durable protection. However, more time is required to achieve a protective vapor concentration. Furthermore, there is a possibility of corrosion occurring during the initial period of saturation, and if the space is not hermetically sealed, an effective inhibitor concentration may never be obtained. Therefore, the chemical compound used as a volatile inhibitor must not have too high or too low a vapor pressure, but some optimum vapor pressure.[12]

The comparison between the vapor pressure of a compound and its molecular heat of sublimation shows a marked decrease in vapor pressure values with an increase in heat of sublimation. A plausible explanation is that a decrease in vapor pressure is caused by steric intermolecular actions between functional groups and by an increase in molecular weight of the compound (Table 10.3).[12]

It is significant that the most effective volatile corrosion inhibitors are the products of the reaction of a weak volatile base with a weak volatile acid. Such substances, although ionized in aqueous solutions, undergo substantial hydrolysis, the extent of which is almost indepen-

TABLE 10.3 Saturated Vapor Pressures of Common VCIs

Substance	Temperature, °C	Vapor pressure, mm·Hg	Melting point, °C
Morpholine	20	8.0	
Benzylamine	29	1.0	
Cyclohexylamine carbonate	25.3	0.397	
Diisopropylamine nitrite	21	4.84×10^{-3}	139
Morpholine nitrite	21	3×10^{-3}	
Dicyclohexylamine nitrite	21	1.3×10^{-4}	179
Cyclohexylamine benzoate	21	8×10^{-5}	
Dicyclohexylamine caprylate	21	5.5×10^{-4}	
Guanadine chromate	21	1×10^{-5}	
Hexamethyleneimine benzoate	41	8×10^{-4}	64
Hexamethyleneamine nitrobenzoate	41	1×10^{-6}	136
Dicyclohexylamine benzoate	41	1.2×10^{-6}	210

dent of concentration. In the case of the amine nitrites and amine carboxylates, the net result of those reactions may be expressed as

$$H_2O + R_2NH_2NO_2 \rightarrow (R_2NH_2)^+{:}OH^- + H^+{:}(NO_2^-) \qquad (10.10)$$

The nature of the adsorbed film formed at the steel-water interface is an important factor controlling the efficiency of VCIs. Metal surfaces exposed to vapors from VCIs in closed containers give evidence of having been covered by a hydrophobic-adsorbed layer. The contact angle of distilled water on such surfaces increases with time of exposure. Experimental studies on the adsorption of volatile inhibitors from the gas phase confirm the assumption that the VCIs react with the metal surface, thus providing corrosion protection. When a steel electrode is exposed to vapors of a VCI, the steady-state electrode potential shifts considerably into the region of positive values. The higher the vapor pressure, the stronger the shift of the electrode potential in the positive direction. Inhibitor adsorption is not a momentary process and requires much time for completion. This indicates that the adsorption is chemical and not physical in nature, resulting in a chemisorbed layer on the metal surface. In proper conditions, the inhibitor molecule will become dissociated or undissociated from the vapor phase and will dissolve into the water layer, with several possible effects (i.e., on the pH, surface wetting, and electrochemical processes at the metal/aqueous film interface).

It is well known, and shown in potential-pH diagrams, that an alkalization of the corrosive medium has a beneficial effect on the corrosion resistance of some metals, notably ferrous metals. Cyclohexylamine and dicyclohexylamine are moderately strong bases ($pK_a = 10.66$ and 11.25, respectively). The pH of the solutions of their salts with weak acids will depend on the pK_a of the acid. For example, cyclohexylamine carbonate will have a rather alkaline pH (pK_a for carbonic acid: 6.37), whereas dicyclohexyl ammonium nitrite will have a neutral pH ($pK_a = 3.37$ for nitrous acid). Guanidine is a strong base ($pK_a = 13.54$) and is mainly used as an additive in VCI formulations to adjust the alkalinity. Buffers (sodium tetraborate, etc.) may have to be used to maintain the pH of a VCI formulation at a convenient level.

The effect of a volatile inhibitor on the electrochemical processes at the metal surface is first evidenced by the shift in the steady-state electrode potential when an electrode is exposed to vapors of the volatile inhibitor.[11] The positive shift generally observed with most of the VCIs on ferrous metals is indicative of a preferentially anodic effect of the inhibitors. This anodic effect may be related either to a simple blocking effect of the anodic sites by the amine part of the inhibitors or to the contribution of the anionic component (i.e., the weak acid component).

In the case of nitrobenzoates, for example, it has been claimed that an acceleration of the cathodic partial process by reduction of the nitro group may lead, in addition to the effect of oxygen in the thin electrolyte layer, to a complete passivation of iron or ordinary steels. Contributions from the two parts of the dissociated molecule to the inhibitive effect is very likely and explains a synergistic effect of the inhibitor at the cathodic and anodic sites, as was suggested long ago. For example, it was shown by autoradiographic studies that the dissociation products of cyclohexylamine carbonate act separately on anodic and cathodic sites, with the former effect predominating.[11]

10.4 Selection of an Inhibitor System

Proper choices of inhibitors should be made by matching the appropriate inhibitor chemistry with the corrosion conditions and by selection of appropriate physical properties for the application conditions. Method of application and system characteristics must be considered when selecting physical properties of an inhibitor.

Inhibitor selection begins with the choice of physical properties. Must the inhibitor be a solid or liquid? Are melting and freezing points of importance? Is degradation with time and temperature critical? Must it be compatible with other system additives? Are specific solubility characteristics required? This list can be extensive but is important because it defines the domain of possible inhibitors. It must be the first step of the inhibitor evaluation for any new system. The physical measurements are those routinely done as part of minimal quality acceptance testing.

In choosing between possible inhibitors, the simplest corrosion tests should be done first to screen out unsuitable candidates. The philosophy of initial screening tests should be that poorly performing candidates are not carried forward. An inhibitor that does poorly in early screening tests might actually do well in the actual system, but the user seldom has the resources to test all possible inhibitors. The inhibitor user must employ test procedures that rigorously exclude inferior inhibitors even though some good inhibitors may also be excluded.

The challenge in inhibitor evaluation is to design experiments that simulate the conditions of the real-world system. The variables that must be considered include temperature, pressure, and velocity as well as metal properties and corrosive environment chemistry. System corrosion failures are usually localized and attributed to micro conditions at the failure site. Adequate testing must include the most severe conditions that can occur in the system and not be limited to macro or average conditions. Examples of microenvironments are hot spots in heat exchangers and highly turbulent flow at weld beads.

The practice of corrosion inhibition requires that the inhibitive species should have easy access to the metal surface. Ideally, surfaces should therefore be clean and not contaminated by oil, grease, corrosion products, water hardness scales, and so forth. Furthermore, care should be taken to avoid the presence of deposited solid particles. This conditioning is often difficult to achieve, and there are many cases where less than adequate consideration has been given to the preparation of systems to receive inhibitive treatment.

It is also necessary to ensure that the inhibitor reaches all parts of the metal surfaces. Care should be taken, particularly when first filling a system, that all dead ends, pockets, and crevice regions are contacted by the inhibited fluid. This will be encouraged in many systems by movement of the fluid in service, but in nominally static systems it will be desirable to establish a flow regime at intervals to provide renewed supply of inhibitor.[13]

Inhibitors must be chosen after taking into account the nature and combinations of metals present, the nature of the corrosive environment, and the operating conditions in terms of flow, temperature, and heat transfer. Inhibitor concentrations should be checked on a regular basis and losses restored either by appropriate additions of inhibitor or by complete replacement of the whole fluid as recommended, for example, with engine coolants. Where possible, some form of continuous monitoring should be employed, although it must be remembered that the results from monitoring devices, probes, coupons, and so forth, refer to the behavior of that particular component at that particular part of the system. Nevertheless, despite this caution, it must be recognized that corrosion monitoring in an inhibited system is well established and widely used.

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