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Corrosion Inhibitors for Reinforced Concrete

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Abstract

Reinforced concrete has been widely used in the last century, however, due to aggressive agents such as carbonic gas and chloride ions, it suffers premature deterioration. The concrete is a physical barrier that protects steel from corrosion, and the alkalinity of concrete leads to the formation of a passive layer around the reinforcement, which increases protection against corrosive processes. However, concrete is a porous material and has cracks that allow the entrance of aggressive agents, destabilizing the passive layer and corroding steel. The corrosion is the major cause of deterioration of concrete structures and several methods of protection and repair have been developed to increase the durability of such structures. Corrosion inhibitors, chemical substances that reduce the corrosion rate, have been widely used, both for prevention and correction. Inhibitors are classified according to their method of application, their mechanism of protection and chemical composition. In this chapter, through a literature review the main inhibitors used in reinforced concrete structures and their acting mechanisms are presented, as well as their efficiency and some side effects on concrete. It is very important to know the different types of inhibitors for correct use, thus increasing the life span of reinforced concrete structures.

Keywords: reinforced concrete, deterioration, corrosion inhibitors

1. Introduction

Reinforced concrete is a successful steel and concrete combination that has been widely used for over 100 years [1]. Steel provides tensile strength to the set, while concrete, as a high alkalinity material and in the role of a physical barrier, protects the steel from corrosion. The alkalinity of the concrete, which, according to Abdulrahman et al. [2], with pH values of about

12 to 14, provides the conditions for the formation of a passive film protecting the steel reinforcement from corrosion [3].

However, the protection provided by the concrete is not sufficient because the material is porous and has fissures, thus allowing the penetration of aggressive agents, such as chloride ions that lead to the corrosion of the reinforcement. Also of note is the action of carbon dioxide (CO_2) that reacts with the cement hydration products, a process known as carbonation, resulting in the formation of calcium carbonate and consequently, a pH decrease, thus destabilizing the reinforcement passivating film and making it susceptible to corrosion [4].

The corrosion of steel reinforcement is one of the main causes of premature deterioration of reinforced concrete, leading to significant economic losses [5, 6]. Rapid deterioration can be caused by chloride ions in a marine zone or due to the use of thaw salts [7] or by carbonation in urban zones [8].

In order to provide additional protection and increase the life span of reinforced concrete structures, several products identified as corrosion inhibitors have been used in recent years [2]. Due the advantages that they offer, corrosion inhibitors have been receiving more attention in recent years. The use of inhibitors is a promising method to increase the durability of concrete structures exposed to chloride ions [9] and carbonation.

Inhibitors are chemicals which, when present at in certain concentrations, reduce the corrosion rate without significantly altering the concentration of any other corrosion agent [10]. Corrosion inhibitors may be a good alternative compared to other conventional methods of protection and repair, due to their lower cost and ease of application [11]. In addition, inhibitors can be applied preventively or as a corrective action [2].

Corrosion inhibitors can be classified according to their application methods, protection mechanism, or composition [12], which can be organic and inorganic, inhibiting the corrosive process through the formation of a passivating film (anodic inhibitors) or by increasing the polarity and decreasing the corrosion potential (cathodic inhibitors). There are also inhibitors that act both ways. These products can be applied directly to the reinforcement, by a pretreatment through the immersion of the reinforcement in an inhibitor solution, added in the kneading water during the concrete mixing, or applied to the surface of the reinforced concrete structure, with the inhibiting solution penetrating the concrete by capillarity.

Known corrosion inhibitors used in reinforced concrete structures are sodium nitrite (NaNO_2), calcium nitrite [$\text{Ca}(\text{NO}_2)_2$], sodium monofluorophosphate ($\text{Na}_2\text{PO}_3\text{F}$), amine-based inhibitors, sodium and potassium chromate, sodium phosphate, and bauxite residue (red mud) [13]. In parallel, surface protection systems are adopted, such as painting, applying varnishes, epoxy resins, chlorinated rubber resins, and water-repellant silicones. **Figure 1** shows the main inhibitors used for reinforced concrete, and **Table 1** shows some recent studies that used these inhibitors.

In this chapter, the main inhibitors used in reinforced concrete structures and their acting mechanisms are presented through a literature review, as well as their efficiency and some side effects on the concrete. Knowing the different types of inhibitors is essential for the correct use of them, thus increasing the life span of reinforced concrete structures.

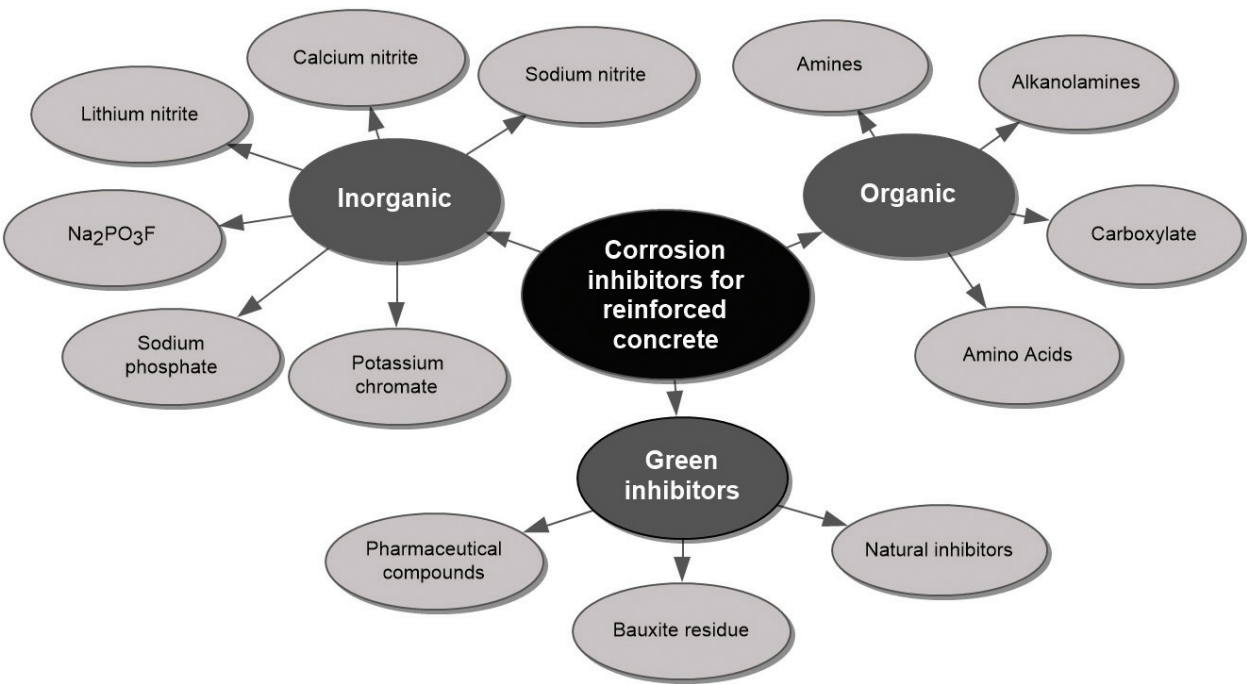


Figure 1. Corrosion inhibitors usually used for reinforced concrete.

Inhibitor	Type	Ref.	Inhibitor	Type	Ref.
Sodium nitrite	Inorganic	[14–16]	Amine	Organic	[15, 27–29]
Calcium nitrite	Inorganic	[15, 17–20]	Carboxylates	Organic	[27, 28]
Lithium nitrate	Inorganic	[7, 21, 22]	Amino acids	Organic	[27, 28]
Sodium monofluorophosphate	Inorganic	[23–25]	Pharmaceutical compounds	Green inhibitors	[30, 31]
Sodium phosphate	Inorganic	[25]	Red mud	Inorganic	[32]
Potassium chromate	Inorganic	[16, 26]	Natural inhibitors	Green inhibitors	[12, 33–35]

Table 1. Recent studies about the main corrosion inhibitors used for reinforced concrete structures.

2. Corrosion mechanisms in reinforced concretes

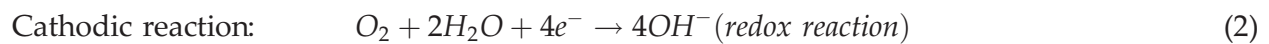
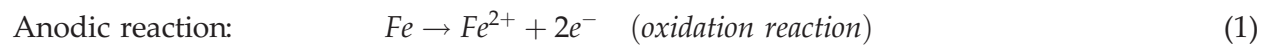
2.1. Corrosion

For the correct understanding of the mechanisms of action of the inhibitors, it is first necessary to understand the phenomena involved in the corrosion process in reinforced concrete because the mode of action of the inhibitors is closely related to the corrosion cell [36]. Corrosion can be defined as a process of deterioration of the material due to the chemical or electrochemical action of the environment, resulting in loss of material mass. The corrosion of the steel reinforcement of a reinforced concrete structure is an electrochemical process and occurs when there is difference in the concentration of dissolved ions inside the concrete, creating electrochemical potential cells or corrosion cells, characterized by a flow of electrons and ions between the cathodic and anodic regions [37]. The cathode and the anode are different regions of the same reinforcement, the

region with section loss being the anodic region where corrosion of the steel occurs. The iron turns into ferrous ions and electrons, which migrate from the anode to the cathode. The reinforcement areas that have a more positive electrochemical potential act like cathodes, reducing oxygen and consuming the electrons coming from the anodic areas, in the presence of water, to form hydroxyl ion. In the electrochemical cell formed, the steel bars act as electrical conductors, and the interstitial fluid of the concrete is the electrolytic environment in which the ions move [38]. The schematic representation of the electrochemical corrosion process is shown in **Figure 2**.

According to Souza [37], the presence of different electrochemical potentials that form the corrosion cells is a consequence of physical and/or chemical heterogeneities on the metal surface. In steel reinforcement, these heterogeneities are mainly caused by differences in the concentration of ions in the surroundings of steel, such as alkalis, chlorides, and oxygen. Causes of potential difference between the points of the rebar include the difference in humidity, aeration, and stress in concrete and steel. As a result, in the presence of the electrolyte, part of the metal becomes anodic and another part cathodic, thus forming an electrochemical cell.

Eqs (1)–(3) represent the reactions that occur at the anode and at the cathode.



According to Baroghel-Bouny et al. [38], ferrous hydroxide $[2Fe(OH)_2]$ may undergo new oxidation reactions, forming various hydroxides and oxides, depending on the pH, temperature, amount of oxygen, and water availability. Souza [37] states that generally $Fe(OH)_2$ is oxidized to insoluble ferric hydroxide $[2Fe(OH)_3]$, also represented by $Fe_2O_3 \cdot H_2O$, commonly known as rust. The formed oxides and hydroxides have a higher volume than steel, as shown in **Figure 3**. The volume of the corrosion products is compared to the initial volume of iron (Fe).

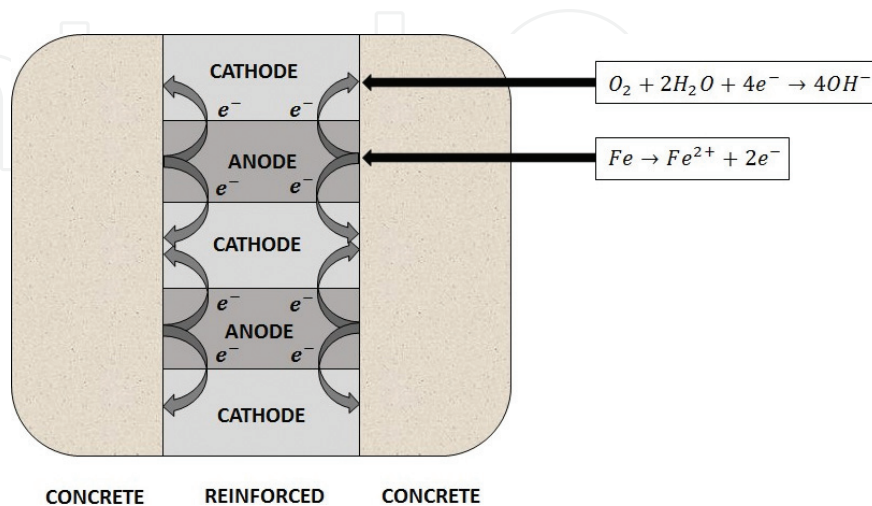


Figure 2. Representation of the corrosion process [37].

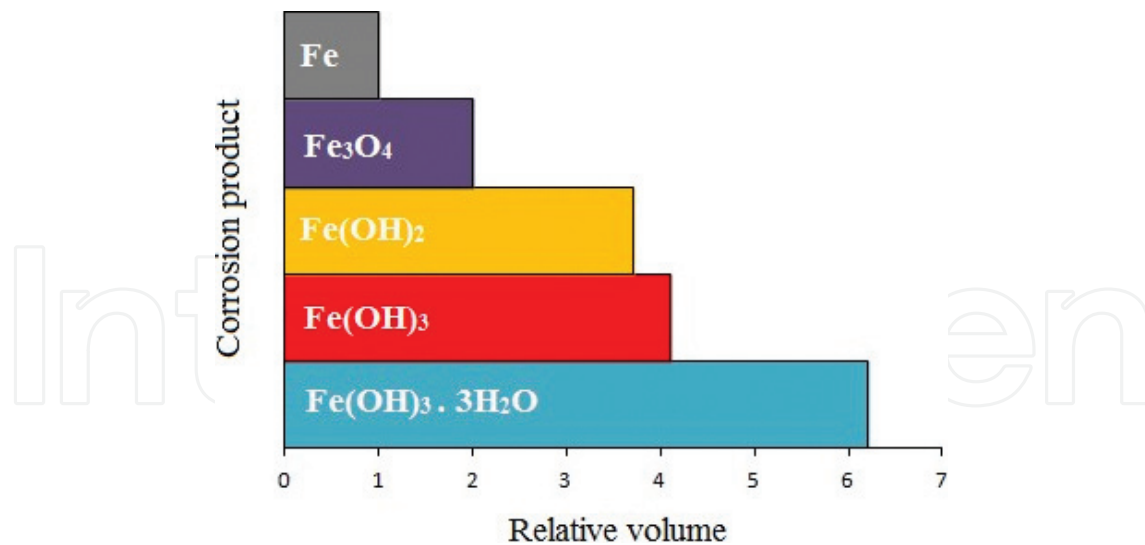


Figure 3. Corrosion product relative volume [38].

These higher volume corrosion products lead to pressure, generating cracks and thus reducing the adhesion between the steel bars and the concrete and also the chipping and detachment of concrete [38]. The formation of these expansive products causes the deterioration of concrete structures and, therefore, reduces their life span.

However, not all corrosion products are harmful to concrete structures. The formation of Fe₃O₄, one of the products of reinforcement corrosion, generates a compact and adherent passive film (passivating film) on rebar, acting as a physical barrier between the corrosive environment and the steel surface, protecting it from the corrosion process in the absence of chloride ions [37]. The formation of this compound occurs only at high pH values when the concrete is alkaline. This is the passive state, while the concrete is alkaline and free from aggressive ions such as chloride. However, the passive protective film can be destroyed in a phenomenon called depassivation, by decreasing the pH of the concrete to values between 8 and 9 (carbonation) and/or by the existence of chloride ions dissolved in the pore solution [36]. After the reinforcement has been depassivated, it will become susceptible to corrosion.

The main causes of corrosion in reinforced concrete structures are the penetration of chloride ions in marine regions and the carbonation process in urban environments. Thus, to better understand the mechanisms of inhibition of corrosion, these two processes must be understood.

2.1.1. Carbonation

In the absence of chloride ions, the steel passivating film is considered stable because the pH of the solution in the concrete pores is greater than 11.5. As Portland cement has high alkali contents and solid calcium hydroxide (about 20%) in the solution, the pH of the environment under normal conditions exceeds 12 [39]. However, reinforced concrete structures over time can undergo a decline in pH due to a process known as carbonation, which destabilizes the passivating layer and therefore leads to the beginning of the corrosion process. Carbonation occurs

mainly in urban areas where there are large amounts of CO_2 emitted by vehicles and industrial parks [40]. **Figure 4** shows an example of corrosion on a viaduct caused by carbonation [41].

Carbonation is a process in which carbon dioxide (CO_2) penetrates the concrete by diffusion, reacting with the water present in the pores and forming carbonic acid. Carbonic acid reacts with the portlandite [$\text{Ca}(\text{OH})_2$] formed during the cement hydration, resulting in the formation of calcium carbonate (CaCO_3) (Eq. (4)). This reaction causes a reduction in the environment pH to around 8 as the formed product (CaCO_3) is less alkaline than portlandite [42]. From the Pourbaix diagram (**Figure 5**), which shows the regions of immunity, passivation, and corrosion in an iron-water system at 25°C , the pH reduction to 8 with the same corrosion potential leads



Figure 4. Corrosion on the reinforced concrete of a viaduct [41].

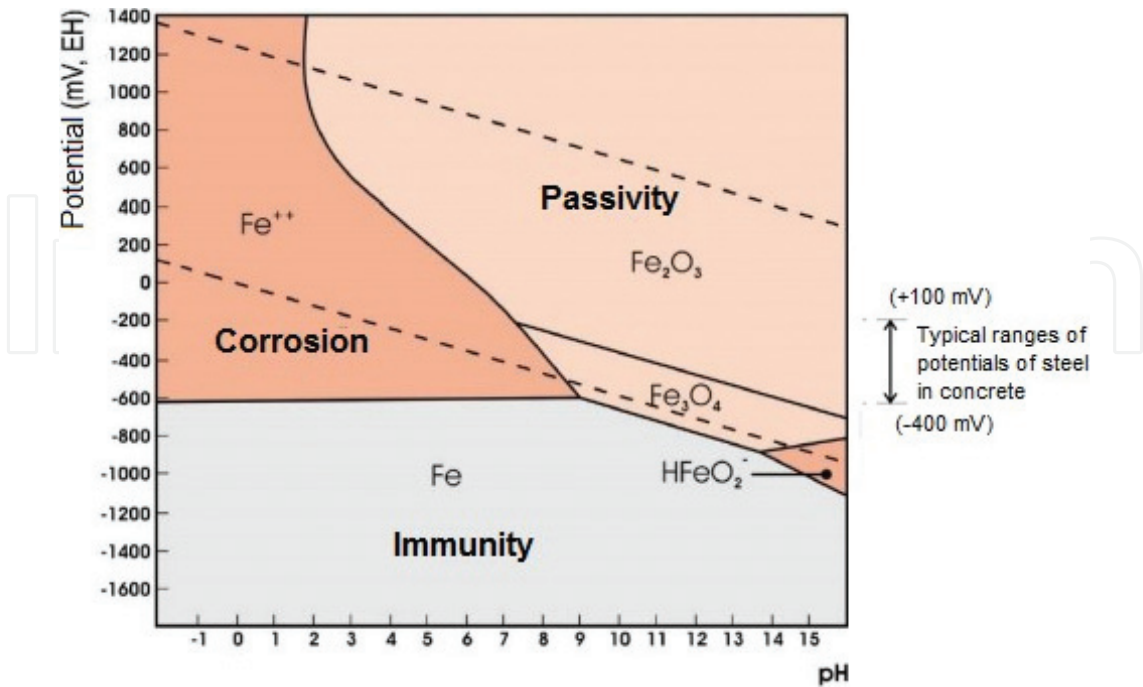
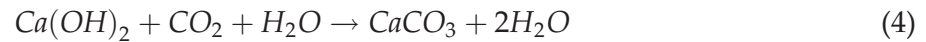


Figure 5. Iron-water system, without chloride, at 25°C Pourbaix diagram [43].

the system from the passivation region to the region of corrosion. This pH reduction is responsible for the destabilization of the passivating film, thus initiating the corrosive process. The summarized carbonation reaction is presented in Eq. (4):



2.1.2. Chloride attack

The presence of chlorides in concrete, arising from seawater, marine atmosphere, setting time accelerator additives containing CaCl_2 , water or contaminated aggregates from industrial pollutants, is one of the main causes of corrosion of reinforced concrete reinforcements [44]. **Figure 6** shows an example of corrosion caused by the action of chloride ions on Qeshm Port, Iran [45].

In the presence of chlorides, the passivating film can be destroyed even at pH values greater than 11.5. Small amounts can do this as this phenomenon is related to the amount of hydroxides available in the solutions present in the concrete pores. The maintenance of the passivating film depends on the balance between the alkalinity (verified by the amount of OH^- ions) and the acidity (verified by the quantity of Cl^- ions). Thus, the relationship between chloride ions and hydroxyl ions controls the rate of pitting corrosion [39, 46]. According to studies carried out by Hausmann [46], for Cl^-/OH^- molar ratios higher than 0.6, the passivating film becomes permeable or unstable, thus leaving the steel reinforcement unprotected against corrosion.

The corrosion process due to chloride ions is different from the corrosion process caused by carbonation because corrosion does not occur in a generalized way, but rather by pitting. In corrosion due to the action of chlorides, there is the formation of micro piles, in which the pitches constitute the anodic zones and the passivating film the cathodic surface [38].

The complete mechanism of corrosion due to the action of chloride ions is not yet fully understood. The most accepted theory suggests that the presence of ions causes a destabilization of the passivating layer, reacting with iron to form iron hydroxide (Eqs. (5) and (6)). In this process, the chloride ions are not consumed and are thus available to continue to react.



Figure 6. Corrosion of reinforced concrete in Qeshm port, Iran [45].

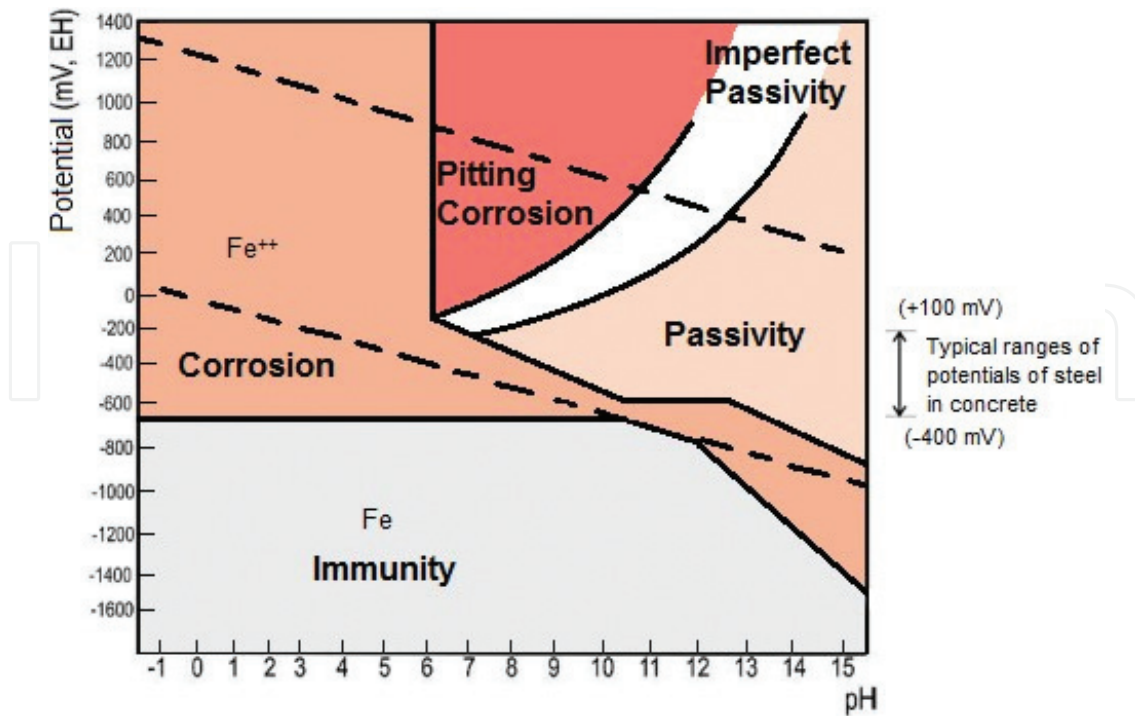


Figure 7. Iron-water system with the presence of chloride, at 25°C Pourbaix diagram [43].



Several aspects influence the probability of occurrence of corrosion due to chlorine ions. The decrease in the concrete water/cement ratio and concrete relative humidity, resistivity and increasing concrete cover thickness, the use of mineral additions, and the use of inhibitors tend to hinder the occurrence of corrosion.

The influence of the chloride ions on the depassivation of reinforcement can be observed by the alteration in the Pourbaix diagram for the iron-water system in the presence of chlorides (Figure 7). In this diagram, a decrease in the passivity region is observed in comparison to the Pourbaix diagram without the presence of chlorides (Figure 5). This reduction is due to the presence of pitting corrosion and imperfect passivity regions occurring due to the presence of these ions. From this diagram, it is possible to observe that corrosion can occur for all pH values, including values between 8.5 and 14, the zone of passivity or immunity for the iron-water system without chloride ions.

3. Corrosion inhibitors

Corrosion inhibitors are chemicals that when present in suitable quantities are capable of promoting a reduction in corrosion rate without significantly altering the concentration of any corrosive agent [10]. Thus, this concept excludes other corrosion protection methods that

alter the concentration of aggressive agents, such as some mineral additives and other surface protection mechanisms such as coatings and pore blockers.

Corrosion inhibitors can act in the corrosive process in two ways: delaying the reinforcement depassivation, strengthening the passivating film, or reducing the corrosion rate after depassivation [36]. Thus, the use of corrosion inhibitors, when in adequate concentrations, delays the corrosive process and therefore prolongs the life span of reinforced concrete structures [13]. Nowadays, with increasing concern about the durability of reinforced concrete structures, the use of corrosion inhibitor additives has been gradually increasing so as to prolong the life span of the structures [15].

For reinforced concrete structures, different products are used to protect new and settled structures. For new structures, the inhibitors can be added to the fresh concrete mix, in a preventive way, to avoid or delay the onset of the corrosive process. In the preexisting structures, inhibitors can be added to repair mortars or repair concrete, applied to the concrete surface, or introduced through holes or grooves on the surface in order to accelerate the diffusion through the covering [13].

Among the inhibitors applied in existing concrete structures are the liquid products, usually phosphate substances such as monofluorophosphate [13]. For this category of inhibitors, it is essential that these substances have absorptive capacity so that they can penetrate the concrete structure through the interstitial pores to reach the reinforcement.

Inhibitors, especially those mixed with concrete, can alter the concrete properties both in the fresh and hardened state and may influence the setting time, the strength gain rate, and other properties. Thus, it is fundamental to understand its mechanism of action and its possible side effects in order to avoid unforeseen damage.

3.1. Classification of inhibitors

Corrosion inhibitors used in reinforced concrete structures can be classified according to their chemical composition (organic and inorganic), their protection mechanism (anodic, cathodic and both), or their method of application (mixed into the concrete and applied to the surface) and may also be grouped into another class known as green inhibitors.

3.1.1. Chemical composition

The action mechanisms and use of inhibitors are derived from their base (chemical composition). According to Ryu et al. [22], different types of inhibitors are used, traditionally divided into inorganic chemical compounds (basically nitrites) and organic (alkanolamine and carboxylates).

3.1.1.1. Inorganic inhibitors

Regarding inorganic inhibitors, nitrites stand out as the most used. These inhibitors, mainly added to the blend of fresh concrete as a preventive action, began to be tested in the 1950s. Initially sodium nitrite was studied. However, due to side effects, such as poorer of concrete

strength and increased occurrence of the probability of alkali-silica reaction (RAS), which have negative effects on the concrete, it was replaced by calcium nitrite, the first to be widely commercialized on a large scale [13].

According to Ryu et al. [20], greater care is needed in estimating the quantity of calcium nitrite-based inhibitors to be used, because if the amount is less than necessary, it will have a negative impact on both the concrete and steel. Thus, it is of utmost importance to define the optimal amount to be added for the inhibitor work properly.

According to Abdulrahman et al. [2], the main advantage of using calcium nitrite is the possibility of using rational methods, based on the quality of the concrete, the exposure conditions, and the amount of calcium nitrite, to design it for a long life span with a certain chloride/nitrite expected ratio. In addition, nitrites are effective in inhibiting the corrosion process caused by both chloride ions by carbonation and the action of sulfate ions [47]. Among the side effects in concrete, nitrites accelerate the setting of fresh concrete and increase its strength gain rate [36].

Despite their efficiency in reducing the corrosion rate of concrete structure reinforcement, nitrites are carcinogenic and toxic [48] and banned in several European countries, such as Germany and Switzerland [5]. Because of this, alternative inhibitors are being studied. Among other inorganic inhibitors are sodium monofluorophosphate ($\text{Na}_2\text{PO}_3\text{F}$) and red mud.

Sodium monofluorophosphate ($\text{Na}_2\text{PO}_3\text{F}$) has the ability of both delaying the corrosion onset and reducing the corrosion rate, even in carbonate concretes. The $\text{Na}_2\text{PO}_3\text{F}$ in aqueous and neutral environment undergoes hydrolysis, forming orthophosphate and fluoride, which reacts with the corrosion products, forming Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$, and $\text{FePO}_4\cdot\text{H}_2\text{O}$ passive films.

Red mud is a residue from the bauxite processing in the manufacture of aluminum. It has the capacity to increase reinforced concrete structures resistance to corrosion. Its performance as corrosion inhibitor is discussed in Section 3.1.4. of this chapter.

3.1.1.2. Organic inhibitors

Like inorganic, organic inhibitors have been widely used in recent years, with several studies on their mechanisms of action and efficiency [27, 49–51]. Organic compounds can donate electrons to or receive electrons from the surface of the metal, forming covalent bonds and are therefore excellent corrosion inhibitors [51]. According to Zhi-Yong et al. [49], organic inhibitors applied on the concrete surface are considered one of the simplest and most effective methods to control the corrosion in existing reinforced concrete structures. Ryu et al. [52] argue that organic inhibitors are popular and frequently used to control corrosion in reinforcement concrete, including in the presence of chloride ions.

Those inhibitors are developed based on organic compounds which have nitrogen (N), oxygen (O), and sulfur (S) atoms and multiple bonds within molecules which aid the adsorption of these on the metallic surface because its efficiency is related to the adsorption properties. Additionally, adsorption depends on the nature and state of the metallic surface, the corrosive

environment type, and the chemical structure of the inhibitor [2]. According to Hmamou et al. [53] and Singh et al. [54], the adsorption on the steel surface depends on various factors. These are mainly on the physical-chemical properties of the inhibitor group, as with the functional group, the donated atom's electronic density and the character p of the orbital.

Thus, the inhibition efficiency depends on the molecular electronic structure containing active centers of adsorption (S, N, O), the molecular size, the method of absorption, the formation of metallic compounds, and the rate of inhibitor cover on the metallic surface [51].

Within the corrosion inhibitors, the amines and alkanolamines are widely used due to their high solubility in water and small influence on the properties of concrete in its fresh and hardened state [27]. These inhibitors have a high capacity to spread themselves through the concrete. They are called volatile inhibitors or migration inhibitors as they can be mixed on the concrete, repair mortar, or be applied on the concrete surface during service [13].

The amines are organic compounds which possess a nitrogen atom with a lone pair that provides the material with the capacity to adhere to the metal surface, protecting it from corrosion [27]. According to Lourenço and Souza [13], the amine can be adsorbed on the metal surface, preventing contact between the metal and the corrosive environment, forming a protective steel barrier. Additionally, the amine is capable of removing corrosion products from the metallic surface, granting direct contact of the metallic surface with the protection layer [13].

Another group used as organic inhibitors is substances such as carboxylate, characterized by the presence of a carboxylic acid group ($-\text{COOH}$) [27]. As amines, these substances have the ability of adhere to the surface of the metal, thus forming an organic layer, protecting the steel from corrosion [36]. Among the effects generated in the concrete, carboxylate-based inhibitors tend to decrease the cement hydration rate, increasing the setting time and slowing the increase in resistance rate [36].

Amino acids, molecules composed by functional groups of amine and carboxylate (**Figure 8**), are also used as organic inhibitors [27].

In a study comparing 80 organic inhibitors, Ormellese et al. [27] conclude that amines have a low effect of inhibition, amino acids presented an inhibiting effect, but not enough for industrial

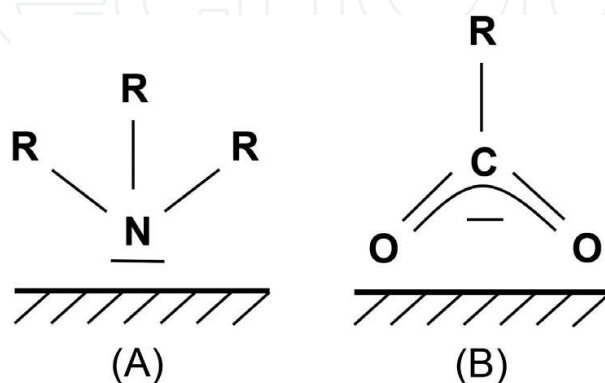


Figure 8. Functional groups of amines (A) and carboxylates (B) [27].

application. The authors also concluded that the substances with carboxylate, particularly polycarboxylates, present high efficiency in corrosion rate reduction. These are the most promising among the tested inhibitors.

3.1.2. Protection mechanisms

The inhibitors are classified as anodic, cathodic, or mixed [13] according to the electrochemical protection mechanism.

3.1.2.1. Anodic mechanism of protection

Anodic inhibitors, also known as passivation inhibitors, act as oxidizing agents, gaining electrons [36]. Such inhibitors act by promoting the oxidation of the ferrous ions on ferritic ions, which precipitate, forming a passive dense film on the steel surface and ceasing the corrosion process anodic reaction [13, 36]. The cohesive and insoluble film formed on the metallic surface is a result of the reaction between the inhibitors and the product of corrosion [55]. According to Myrdal [36], the effects of these inhibitors on the cathodic reaction are negligible.

According to Myrdal [36], the action of the anodic inhibitors increases the electrochemical potential of the anodic region, and therefore the anodic and cathodic curves intercept with a lower corrosion current and higher corrosion potential, as illustrated in **Figure 9**.

The anodic inhibitors are effective if present in high concentrations, which is defined according to the level of chloride existing in the environment to which the steel will be exposed [56].

According to Elsener [57], reinforced concrete counts on the use of calcium nitrite $[\text{Ca}(\text{NO}_2)_2]$ and calcium nitrate $[\text{Ca}(\text{NO}_3)_2]$ as anodic inhibitor, as they present similar inhibiting properties [36]. Nitrite alkali salts, benzoate, and chromate are also used as anodic inhibitors [11].

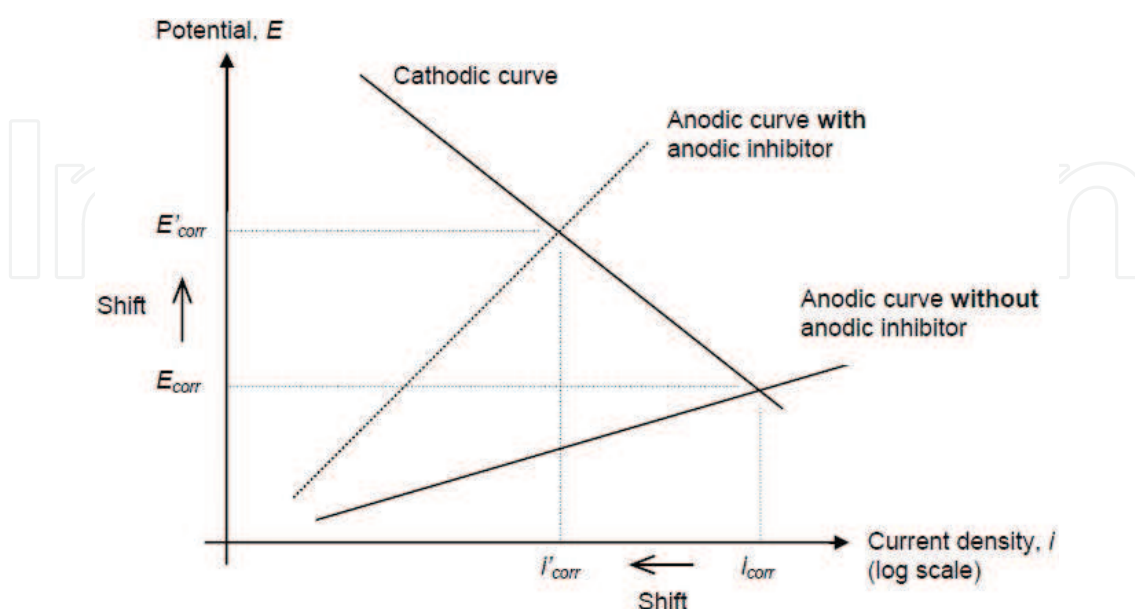


Figure 9. Corrosion potential with anodic inhibit effect (E_{corr} = corrosion potential and i_{corr} = corrosion rate) [36].

3.1.2.2. Cathodic mechanism of protection

The cathodic inhibitors act during the corrosion process on the cathodic region and prevent a cathodic reaction on the steel [55]. These inhibitors retard the oxygen reduction reaction that occurs on the steel surface, as they produce insoluble compounds that precipitate on the cathodic regions, forming a superficial barrier upon deposition on the metal, thus forming a compact and adherent film [36, 55]. This barrier restricts oxygen diffusion and the conduction electrons in this region [55].

The reduction in the oxygen supply in the corrosion process reduces the corrosion rate and the corrosion potential for lower negative values [36, 55]. By the time the corrosion potential is reduced, it is usual to consider that there is a smaller corrosion risk [36]. It can be observed in the Pourbaix diagrams (Figures 5 and 7), in which the lower the potential, the bigger the probability for the steel to be in an immunity zone. Figure 10 illustrates the cathodic inhibitor behavior on the corrosion process.

As observed in Figure 8, the cathodic inhibitor promotes a change in the corrosion potential and in the corrosion rate for the values E'_{corr} and i'_{corr} , respectively. As the corrosion potential is reduced to lower values, the corrosion rate diminishes [36], thus cathodic polarization occurs.

Examples of cathodic inhibitors include carbonates, phosphates, polyphosphates, and silicates [36]; zinc oxide was also reported by Rincón et al. [58] as a cathodic inhibitor. According to Söylev and Richardson [11], sodium hydroxide and sodium carbonate are among the most used cathodic inhibitors, which tend to increase the pH around encompassing the steel, in addition to reducing the oxygen transport and creating a film on the steel surface.

The contents of cathodic inhibitors tend to be higher than anodic inhibitors because the suppression effect of the corrosive process is inferior to the anodic inhibitors [59].

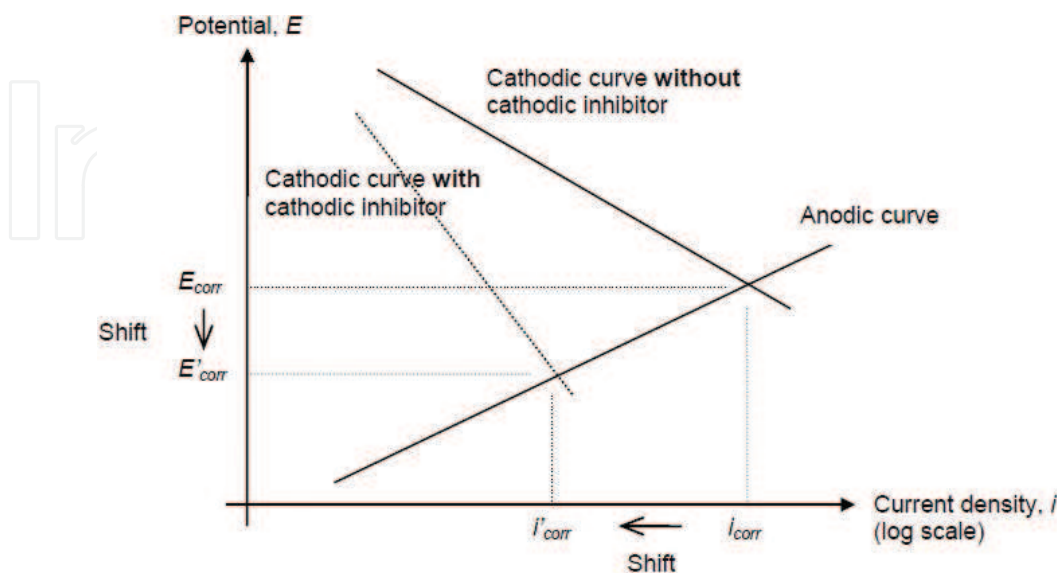


Figure 10. Corrosion potential with cathodic inhibitor effect (E_{corr} = corrosion potential and i_{corr} = corrosion rate) [36].

3.1.2.3. Mixed mechanism of protection

The mixed inhibitors act both on the cathodic and the anodic regions, usually by the adsorption on the steel surface, forming a protecting layer [11], therefore being denominated adsorption inhibitors [60] or pellicle forming inhibitors [61]. The inhibitor reduces the corrosion rates, causing no significant changes to the corrosion potential. The corrosion potential is slightly changed for the anodic or cathodic side, so regardless of the most affected reaction, the total effect upon the corrosion potential is negligible [36]. This type of inhibitor is therefore just effective on the reduction of the corrosion rate (i_{corr}) as shown in **Figure 11**.

Several mixed inhibitors are organic compounds such as amines and alkanolamines [12], capable of application both as inhibitors mixed on the fresh concrete, as much as inhibitors applied on the concrete surface which migrate to its interior [36].

3.1.3. Application methods

Inhibitors can also be classified according to the application method. They can be either mixed with the concrete or applied to the surface of the structures.

3.1.3.1. Mixed into the concrete

Additives are mixed to concrete usually to improve its properties in the fresh or hardened states; however, corrosion inhibitors act mainly on the steel surface. Inhibitors are mixed into the concrete in the fresh state, at the moment the mixing water is in contact with the steel surface at the time of concreting. They are considered corrosion inhibitors because they interact chemically or electrochemically with the surface of the steel [61].

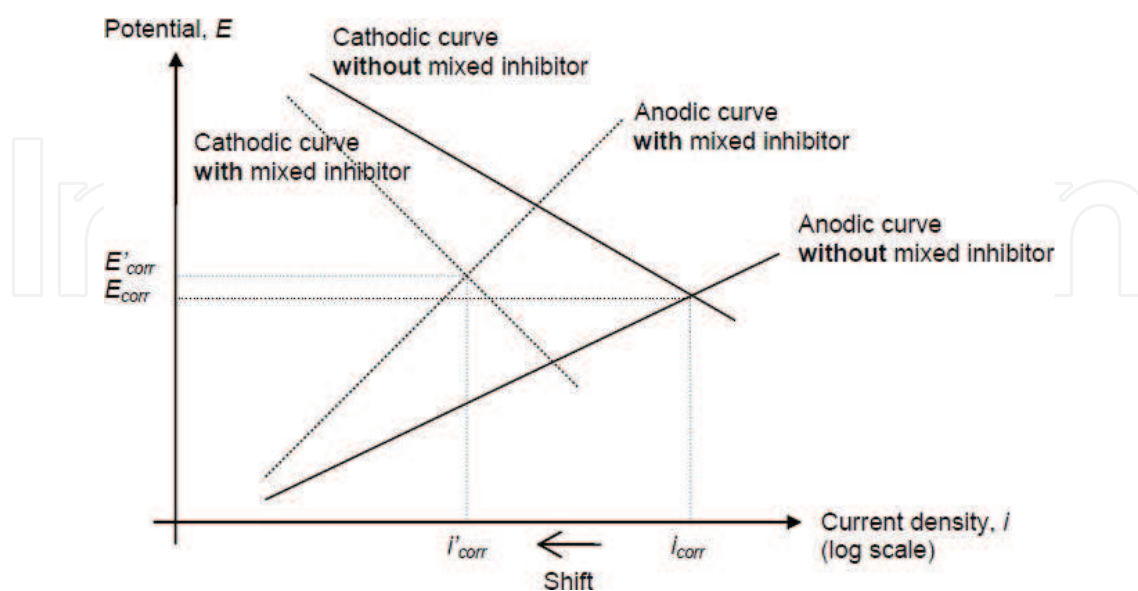


Figure 11. Corrosion potential with mixed inhibitor effect (E_{corr} = corrosion potential and i_{corr} = corrosion rate) [36].

These inhibitors should not impair the properties of the concrete, but as a result of being mixed in the fresh state, they usually give other characteristics to the concrete as well as inhibiting corrosion. Given this, some studies have been developed in order to verify the effects of corrosion inhibitors on the properties of the concrete. According to Gaidis [62], inhibitors can influence the concrete hydration process, the gain in mechanical resistance, and other properties.

According to Elsener and Angst [61], monofluorophosphate (MFP) cannot be used as a corrosion inhibitor mixed into the concrete due to its reaction with the fresh concrete, which removes the active substance from the concrete pore solution and retards its hydration; it is therefore recommended only for surface application. The sodium nitrite or potassium nitrites cause a fall in the concrete compressive strength and raise the risk of alkali-aggregate reaction (AAR). The calcium nitrite, on the other hand, acts by accelerating the cement hydration, which requires the addition of a water reducer and a setting retarder in the concrete mix.

3.1.3.2. Applied to the concrete surface (absorption and migration)

The corrosion inhibitors applied to the surface should be capable of migrating to the concrete interior until they reach the metal reinforcement through absorption by capillary pores [36] and become adsorbed on the metallic surface. These are also called migration corrosion inhibitors (MCI) and are considered an effective technique, able to inhibit and retard the reinforcement corrosive process and the concrete structure corrosive process [63]. Several studies have been developed [63, 64] in the use of this technique, and it is becoming one of the main methods used, mainly due to the ease of application.

These inhibitors act by forming an adsorbed film on the steel surface, preventing the depolarizing agents (O_2 and Cl^-) from getting into direct contact with the reinforcement surface, avoiding therefore the onset of the corrosive process [5]. Fei et al. [5] claim that this protective layer formed by the inhibitors and blocks the electrons flow on the concrete/metal interface, also creating a barrier to the aggressive ions, making the reinforcement less prone to corrosion. The efficiency of the inhibitor in protecting the steel from corrosion depends mainly on the interaction between the inhibitor and the metallic surface [51].

Among the corrosion inhibitors applied to concrete, there are the alkanolamines and amines, which are able to penetrate the capillary pores and micro pores of the concrete [63]. Lan et al. [64] found that inhibitors of amino alcohol and carboxylates applied on the high resistance concrete contaminated with chlorides are efficient at inhibiting the corrosive process in medium and low concentrations of chloride ions.

3.1.3.3. Commercial inhibitors

Several corrosion inhibitors for reinforced concrete structures are marketed worldwide. **Table 2** shows some of these inhibitors and their respective manufacturers, chemical basis, and method of

Manufacturer	Product	Chemical basis	Method of use
Sika	CNI	Calcium nitrite	Mixed into concrete
	FerroGard 901	Amino alcohols	Mixed into concrete
	FerroGard 903	Amino alcohols	Applied on concrete
BASF	MasterLife 222	Amines and esters	Mixed into concrete
	MasterLife CI30	Calcium nitrite	Mixed into concrete
W. R. Grace	DCI	Calcium nitrite	Mixed into concrete
Cortec Co.	MCI 2000	Amino alcohols	Mixed into concrete
	MCI 2005	Amine carboxylate	Mixed into concrete
	MCI 2007	Superplasticizer + amine carboxylate	Mixed into concrete
	MCI 2020	Amino alcohols + carboxylic acid salt	Applied on concrete
Euclid chemical	EUCON BCN	Calcium nitrite	Mixed into concrete
	EUCON CIA	Calcium nitrite	Mixed into concrete

Table 2. Examples of commercial inhibitors.

use. As can be seen in **Table 2**, most of the commercially available corrosion inhibitors are organic or calcium nitrite based.

3.1.4. *Green inhibitors*

Inhibitors may be natural or synthetic [55]. Synthetic inhibitors are artificially produced and can lead to damage to both man and the environment, synthetic organic inhibitors in particular. Due to these problems, several studies have examined the versatility and feasibility of the use of environmentally sustainable inhibitors, known as green or natural inhibitors [33].

These natural and low-cost inhibitors that are capable to feed the need for synthetics [33–35] have been shown to be more effective and highly beneficial to the environment compared to organic and inorganic inhibitors produced by chemical and petrochemical industries [34].

Examples of green inhibitors are natural organic compounds obtained from several types of plants such as herbs, spices, and others [12, 34]. Such plants are an abundant source of naturally synthesized chemical compounds, which can be extracted through simple and low-cost practices, besides being biodegradable. Much research has been carried out into the extraction of natural stems, leaves, or plant seeds [12, 33–35].

Within the classification of green inhibitors is red mud, a compound based on ferric oxide and alumina and a residue generated in bauxite processing for aluminium production. Ribeiro et al. [43] evaluated the incorporation of red mud in the reinforced concrete, in contents of 10, 20, and 30% of the cement mass. The authors experimentally observed a significant decrease in the reinforcement corrosion rate as the amount of red mud increased. The corrosion reduction is probably due to the increase in the alkalinity near the region of the steel reinforcement, which favors the reestablishment of the passivating film, in addition to the high concentrations of aluminates, which hinder the diffusion of chlorides.

3.2. Factors influencing inhibitor choice

Given the variety of available inhibitors, choosing the appropriate inhibitor should be based on the physical-chemical properties of the inhibitor, as well as the nature and conditions of the metal surface and the aggressive environment in which the concrete structure is situated [51].

The efficiency of the corrosion inhibitors can be calculated by Eq. (7), which relates the decreasing corrosion rate with the use of the inhibitor:

$$E_f = \frac{R_o - R_i}{R_o} \times 100 \quad (7)$$

where E_f —efficiency factor (%)

R_o —corrosion rate on concrete without inhibitors ($\mu\text{A}/\text{cm}^2$)

R_i —corrosion rate on concrete with inhibitors ($\mu\text{A}/\text{cm}^2$)

Table 3 summarizes the results obtained in several studies with varied inhibitors.

Ref.	Inhibitor	Type	Efficiency (%)	Aggressive conditions
[15]	Calcium nitrite, 25 (g/L)	Inorganic	92.30	Carbonation
[15]	Calcium nitrite, 10 (g/L)	Inorganic	64.90	3.5% NaCl
[22]	Calcium nitrite, 8.94 (g/L)	Inorganic	85.75	0.99 NaCl (g/L)
[22]	Calcium nitrite, 71.55 (g/L)	Inorganic	83.26	7.91 NaCl (g/L)
[15]	Sodium nitrite, 25 (g/L)	Inorganic	95.00	Carbonation
[15]	Sodium nitrite, 10 (g/L)	Inorganic	82.60	3.5% NaCl
[14]	Sodium nitrite, 40 ppm	Inorganic	61.40	—
[20]	Lithium nitrate, 2.15 (g/L)	Inorganic	63.67	0.99 de NaCl (g/L)
[20]	Lithium nitrate, 17.21 (g/L)	Inorganic	31.71	7.91 de NaCl (g/L)
[15]	Sodium molybdate, 10 (g/L)	Inorganic	95.40	Carbonation
[15]	Sodium molybdate, 40 (g/L)	Inorganic	82.60	3.5% NaCl
[14]	Sodium molybdate, 1000 ppm	Inorganic	98.60	—
[15]	Tannin, 10 (g/L)	Organic	64.00	Carbonation
[15]	Tannin, 10 (g/L)	Organic	80.60	3.5% NaCl
[15]	Amine, 10 (g/L)	Organic	84.80	Carbonation
[15]	Amine, 10 (g/L)	Organic	61.80	3.5% NaCl
[14]	Sodium nitroethane, 20 ppm	Organic	87.40	—
[65]	DAESPN, 5×10^{-3} M	Organic	39.40	3.0 M NaCl
[65]	Bis-HSPN, 10^{-3} M	Organic	59.00	3.0 M NaCl
[51]	PT, 10^{-3} M	Organic	93.68	HCl 1 M
[66]	Amine-ether, 10 (g/L)	Organic	41.30	Carbonation

Table 3. Efficiency factors of various inhibitors studied by different authors.

Among the inhibitors shown in **Table 3**, sodium molybdate shows the highest efficiency (82.60–98.60%); however, despite its good performance, it is expensive which makes the use of this inhibitor unviable for some applications.

4. Future trends

The use of inhibitors of low environmental impact is becoming more popular nowadays mostly due to the major concerns about the use of these chemicals. Studies with green inhibitors have been widely discussed, and we should their use increase in the next few years.

There remain some gaps in our knowledge, and further work is needed, for example, the effect of inhibitors upon the properties of fresh concrete and the development of multifunctional blends, besides the use of inhibitor without undesired secondary effects starting from a combination of different types, such as a mixture of an inhibitor that has a setting retarder effect with an inhibitor that has a setting accelerator effect [36].

Lastly, Quraishi et al. [67] point out the importance of studies about association of the effects of chemical admixture (corrosion inhibitors) and minerals (pozzolans) so as to increase the life span of reinforced concrete structures.

5. Final considerations

Among the commercially available inhibitors, there is a wide variety classified according to their chemical composition, method of protection, and method of use. The use of inhibitors generally leads to side effects in the concrete; therefore an understanding of these substances is of fundamental importance in order to avoid damage to structures.

The environmental issue related to toxicity and carcinogenic inhibitors, such as calcium nitrite, which is widely used, has led to several studies reviewing the use of current inhibitors and developing natural inhibitors that do not harm the properties of concrete while being eco-friendly [33]. It is important to investigate any side effects the inhibitor may have on the properties of concrete, both in the fresh and hardened states [36].

The concrete composition and microstructure must be considered in the evaluation of the performance of corrosion inhibitors, as they may influence several aspects of the concrete in the corrosive process [5]. Therefore, when evaluating inhibitors, it is necessary to verify their composition, mechanism of action, and application, as well as the aspects related to concrete and also the influence of the inhibitors on the concrete (changes in the hydration process, porosity, resistance, others).

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