

REVIEW ARTICLE

Properties of corrosion inhibitors on reinforced concrete

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Abstract

Corrosion of reinforced concrete steel is one of the main reasons for the deterioration of reinforced concrete structures all around the world and the biggest problem that civil engineers are facing today. Various methods have been developed to protect the steel reinforcement in reinforced concrete against corrosion. According to recent statistics, the global cost of corrosion is determined to be \$2.5 trillion or 3.4 percent of world gross domestic product. New technologies and materials have been developed to delay, decrease or control the corrosion of concrete reinforcement and increase the durability. The most common corrosion prevention technique is the use of inhibitors. Inhibitors are chemicals that added to the concrete in small concentrations that prevent the onset of corrosion in reinforced concrete structures or extend the corrosion start time. The aim of this article is to review the recent developments in corrosion inhibitors used in reinforced concrete structures and their applications in field and laboratory conditions. This research is based on the types of inhibitors, their mechanism of action and their type of application. The main topics are; cathodic, anodic, mixed type inhibitors and their type of field applications. This research also includes: comparison the performance of admixed inhibitors, surface applied (migrating) inhibitors, electrochemical injection of corrosion inhibitors (EICI) and electrochemical chloride ion extraction (ECE) methods of corrosion inhibitors. The use of green (ecological) corrosion inhibitors (non-toxic and non-carcinogenic chemicals) becoming more popular nowadays. Studies with green inhibitors have been widely discussed in this review and we should increase their use in the next few years.

Keywords

Organic inhibitors; Inorganic inhibitors; Reinforced concrete; Corrosion; Green inhibitors.

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1. Introduction

The performance of metals/alloys is seriously affected by corrosion, especially when exposed in the aggressive media. Corrosion undoubtedly constitutes a serious burden on the industrial productivity and safety on a frequent basis. Sometimes, the catastrophe of corrosion deterioration is so severe that it can be equated to natural calamities (earthquakes, floods etc.). Therefore, corrosion may cause a considerable

liability to economy all over the world. According to recent statistics by NACE International, the global cost of corrosion is determined to be in the vicinity of \$2.5 trillion or 3.4 percent of world gross domestic product [1]. On the other hand, appropriate corrosion protection strategies may save billions of dollars in the long run.

Most of the soluble anions that detriment to structural materials while simultaneously existing in abundance is chloride, whether natural or industrial media are concerned [2]. The widespread

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investigative thus far, chloride ion dynamic role in the corrosion of metals is persisting as a focal point of renewed interest [3]. First, the chlorine ion, which comes with water, travels through the concrete pores and cracks and reaches the reinforced concrete steel. This event initiates corrosion [4]. The developed corrosion products create a volume increase around the reinforced concrete steel, which creates a higher-pressure potential in the concrete. This situation initiates the additional cracks so weakening the structure and reducing its durability [5].

In today's technology, many works have been done on concrete and many negative features of concrete have been eliminated. With the use of chemical and mineral admixtures, it is now easier to maintain the protection of concrete in all conditions.

The most important performance expected from a reinforced concrete structure is that it serves smoothly until the end of its service life. However, when we look at the earthquakes in our country, the structures have not been able to complete their expected service life due to the low values of structural standards and poor quality of the concrete components.

Reinforcement corrosion in reinforced concrete structures significantly affects the service life of the structure. The researches have revealed the destruction of the corroded reinforcement to concrete [6]. The main reason for this is that the corroded reinforcement results in a volume increase of 2 to 6 times. This causes an internal stress and results the cracking of concrete [7].

As a result, the bearing cross-sectional area of the reinforced steel is decreased, the integrity of the reinforced concrete structure is broken thus the fragmentation occurs. In order to minimize such damage, it is very important that the concrete is impermeable. So that the thickness of the concrete cover should be sufficient and continuous.

On the other hand, depending on the production conditions in the concrete (e.g. in a not well-compacted concrete), various air voids are formed and then the permeability increases. Consequently, it is easier for the compounds (oxygen, water and

chloride) that penetrate into the concrete (which are caused by defects in materials and workmanship) from the environment and reach to the reinforcement.

It is expected from reinforced steel is to serve for many years without the corrosion. However, with the increase in permeability, the high alkali level begins to decrease, the concrete cannot protect the reinforcement (passive film layer disappears) and formation of corrosion is starts [8]. Corrosion leads to volume increase, it creating cracks parallel to the reinforcement. Once the concrete has been cracked, it is completely vulnerable to atmospheric effects and the structural element will fill the service life rapidly [9].

The corrosion resistance of the steels which used as reinforcement is very low, but they still last long without being corroded in the concrete. The reason for that is the concrete has a high alkaline level. The alkaline environment in the concrete forms a passive film on the metal, which reduces the corrosion rate [10].

However, even good quality concrete cannot provide adequate protection and the steel may start to corrosion in poor environments. The passive film (which is surrounding the steel) must be destroyed for the corrosion of the steel is initiate. This can happen in several ways. The presence of chlorides ions (comes from dissolved salts and waterside environment) on the reinforcement surface at a higher concentration than the critical limit (which is considered to be 0.4-1.0% by weight of cement) can be given as an example [11].

The steel reinforcement in concrete is normally passivated due to the high alkalinity of the concrete (a passive film layer around the reinforcement). However, this passive film can be destroyed by two specific conditions: concrete carbonation and presence of chloride on the steel surface. The first condition is to reduce the pH of the concrete by activating the steel from the passive state; The second condition causes local disruption on the passive film, forming pits on the metal surface [12].

Various methods have been developed to prevent corrosion and increase service life. These methods include covering the concrete surface,

covering the reinforcement, electrochemical injection methods, anodic protection, alternative reinforcement steel and corrosion inhibitors [13,14]. Among all these techniques, advances of corrosion inhibitors in reinforced concrete structures, is one of the most suitable and efficient methods for the protection of reinforcement against corrosion by easy application, excellent corrosion resistance effect and low cost.

Corrosion inhibitors which added at low concentrations to concrete are intended to slow or delay the onset time of corrosion in the reinforced concrete structure. Most of the inhibitors stabilize the steel by forming a protective film on the steel surface, some inhibitors react with the concrete complex to reduce the permeability of the concrete. Use of corrosion inhibitors in new constructions is usually added to the fresh concrete paste, but can also be used by spraying on the concrete surface in repair operations [15]. The main application technique for inhibitors are added as an additive to fresh concrete, applied on surface to the hardened concrete, added to the maintenance mortars or applied to the rebar surface before the concrete is poured [16].

The process of corrosion inhibitors as follows:

- Reduce the movement of ions towards the metallic surface,
- Increase the electrical resistance of reinforced concrete reinforcement,
- Increase anodic and cathodic polarization behaviour.

2. Reinforced concrete corrosion and corrosion mechanism

Corrosion inhibitors can divide into groups, depending on their mechanism of protection against corrosion, type of structure and composition or their physicochemical properties. Total inhibition of corrosion is almost impossible; however, the use of inhibitors enables to limit the process, speed and aggressiveness.

Corrosion is based mostly on the electrochemical mechanism which metal dissolves into the solution through the electrons flow. The site of metal dissolution acts as an anode and electrons

flows to the metal which acts as a cathode. Anodic and cathodic reactions taking place during corrosion are named half-cell reactions. Steel under corrosion works as connected electrodes: the anode and the cathode. Water presented in concrete works as an electrolyte solution in pores [17].

The covering layer on the concrete surface provides physical protection in order to prevent from reaching the gases (such as O_2 and CO_2 , as well as harmful ions such as SO_3 and Cl^-) to the reinforcement steel. The effectiveness of this physical protection depends on the thickness of the concrete cover and impermeability. However, the permeability of the concrete and the insufficiency of concrete cover leaves the concrete vulnerable to physical and chemical effects.

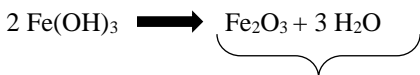
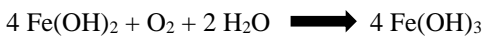
Concrete is protecting itself against chemical effects due to the $Ca(OH)_2$ and $NaOH$ components which released during the hydration of the cement. These components form an alkaline environment in concrete.

In reinforced concrete, the surface of steel is covered by a passive oxide film, which prevents the reinforced bars from corrosion. That passive layer is stable when the pH is greater than 11. When the pH of the concrete begins to decrease, it destroys the alkaline environment around the reinforcement. This high alkaline environment may be destroyed (depassivated) due to following reasons: sea water, chlorine from the salts and the decrease of pH by the carbonation [18]. During carbonation process carbon dioxide penetrates to the concrete, where it reacts with hydroxides. That carbonates are decreasing pH of the concrete and it disrupt the passivation layer on the steel.

The corrosion of the reinforcement steel is an electrochemical event. Corrosion always occurs by two complementary electrochemical reactions. These are oxidation and reduction reactions. Oxidation is the conversion of atomic metal to ion by losing electrons. Reduction is, spending the electrons in another environment that separated from the atom. Oxidation is called anode; reduction is called cathode reaction. The prevention of any of these reactions stops the corrosion process.

As shown in Figure 1, Fe^{+2} ions enter the electrolyte solution that coming from the anodic reaction. The electrons move along the steel bar and they acquired by the cathodic zone. $(\text{OH})^-$ ions (which come from the reaction in the cathode) come through the electrolyte to the anode. When the arrival of the $(\text{OH})^-$ ions ends, the electrical circuit of the whole cell closes. After that, $(\text{OH})^-$ and Fe^{+2} ions in the electrolyte solution, make a reaction with each other so that ferric hydroxide is formed. $\text{Fe}(\text{OH})_2$ (ferrous hydroxide) is an unstable and soluble hydroxide, it combined with the water and oxygen (present in the solution) to become stable $\text{Fe}(\text{OH})_3$ (ferric hydroxide) rust.

This rust is hydroxide of Fe_2O_3 (ferric oxide) and it precipitates as yellow rust in cavities around the anode. The resulting reactions are given below:



Hydrated Ferric Oxide (Rust)

2.1. Effect of cement dosage and oxygen diffusion

Increasing the dosage of cement in reinforced concrete will also increase the impermeability, so penetration of CO_2 and Cl^- ions to the concrete will

decrease. This gives a positive effect on corrosion prevention. In addition, cements with different properties can be produced by adding different amounts of pozzolan into the cement. These pozzolans also provide corrosion resistance to the reinforced concrete.

Calcium sulphate penetrates into concrete due to the lack of sufficient cement dosage in the concrete. Thus, calcium sulfate causes an expansion in hardened concrete. These expansions create deep cracks on the outer surface of the concrete, it damages the concrete cover so cause the corrosion of reinforcement [8].

Oxygen has the most detrimental effect on steel rebars. Without oxygen, steel rebars in alkaline environment do not cause corrosion even in the presence of aggressive species like chloride ions. Resistance against corrosion decreases with higher permeability of chloride ions [19].

Corrosion of the steel in the concrete occurs from the oxygen reduction reaction in the cathode. Therefore, the rate of corrosion depends on the rate of oxygen diffused into the concrete. Corrosion can be prevented if oxygen can be prevented from entering the concrete. In this case, the reinforcing steel takes a different amount of air, the regions with low airspace become anode, and the areas with much air are cathodes. Oxygen diffusion into concrete is faster in dry concrete.

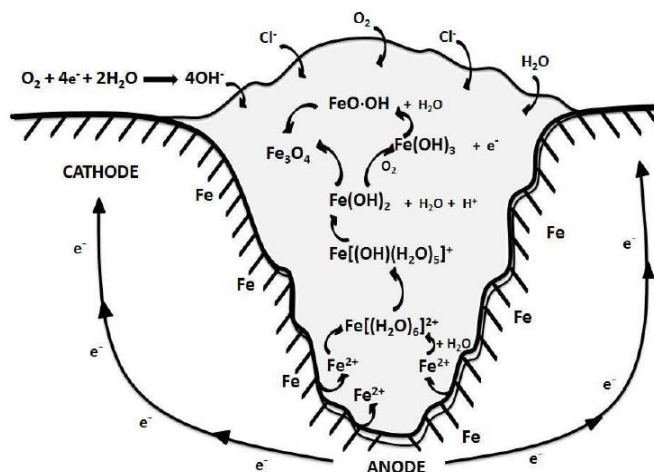


Fig. 1. Schematic representation of corrosion process under water, oxygen and chlorides attack.

Oxygen in the water (especially around the steel), consumes electrons and transforms into the OH^- ions. OH^- ions forms the iron hydroxide. That compound is a relatively soluble in aqueous media and may form oxides or different hydroxides, dependently on the pH of the environment. Concrete has high pH, which results in the formation of a passive layer of Fe_2O_3 around the steel [17].

3. Type of Corrosion inhibitors

Corrosion inhibitors used in reinforced concrete structure are shown as follows: [20,21] (Fig. 2)

- Mechanism of electrochemical action (cathodic, anodic, both)
- Class of chemicals used (inorganic or organic)
- Application (added to the concrete paste as an admixture or applied to hardened concrete surface).

4. Inorganic inhibitors

Inhibitors are separated into three electrochemical classes depending on their effects: (a) anodic, (b) cathodic and (c) mixed.

4.1. Anodic (Passivating) Inhibitors

In order to passivate the steel, anodic inhibitor forms an insoluble protective film on steel surfaces.

Anodic inhibitors oxidize ferrous ions, resulting in the creation of a dense passive film on the surface of the steel so anodic part of the corrosion reaction is repressed [22]. Anodic inhibitors increase the potential capacity of the anode and decrease the corrosion in rate by rotating the potential to the passivation zone.

Anodic reactions (oxidation of steel) are given below:



In general, inhibitors are divided into two groups:

- Oxidizing anions, such as nitrates and chromates, can deactivate the steel without oxygen.
- Non-oxidizing ions such as molybdate and phosphate needs oxygen to passivate steel.

High concentration is required for anodic inhibitors to be effective. The required concentration is determined by the chloride level present in the concrete. Calcium nitrite is one of the most widely used anodic inhibitors in concrete [21]. Some anodic inhibitors cause accelerated and pitting corrosion if their concentration in the concrete is not sufficiently high [24]. Also; benzoates, molybdates, chromates and orthophosphates are used as an anodic inhibitor. This type of inhibitors is included in the inorganic inhibitor class.

4.2. Cathodic inhibitors

Cathodic inhibitors precipitate the salts in the water and stop the reduction of the steel in the concrete. In cathodic inhibitors, the steel surface is covered by a barrier of precipitated salts, thereby reducing oxygen transfer to the cathodic zone [25]. If the amount of oxygen reacted during corrosion formation is reduced, both the corrosion potential and the corrosion rate will decrease.

The inorganics used as cathodic inhibitors are phosphates, carbonates, polyphosphates and silicates. The dosage of cathodic inhibitors should be high because the corrosion reduction effects are lesser than the anodic corrosion inhibitor [26].

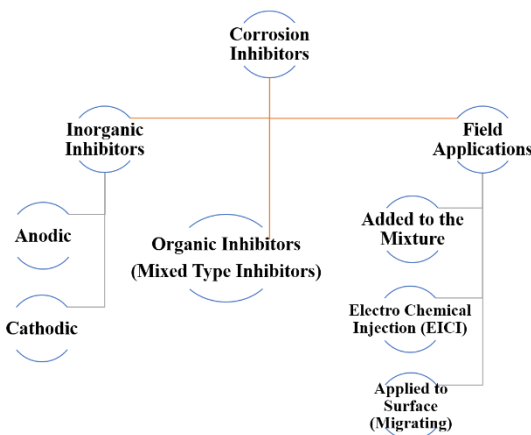
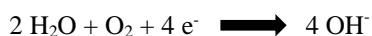


Fig. 2. Types of corrosion inhibitors used in reinforced concrete structure

Cathodic reactions (reduction of oxygen) are given below:



Hydroxyl ions (OH^-) consumed by oxygen in water are composed of free electrons in dissolved iron. $\text{Fe}(\text{OH})_2$ (ferrous hydroxide), a slightly soluble compound, can undergo additional oxidation reactions to form different oxides. The ferric species precipitate to form a thin and dense layer on the steel surface. This surface oxide layer (is often called the oxide film, or the passive film), is a physical barrier separating the steel from the electrolyte (pore solution).

Cathodic inhibitors reduce corrosion by decreasing the proportion of cathodic reactions in the corrosion process. Cathodic inhibitor forms compounds that are precipitated and insoluble in the cathodic regions which form a barrier film in those sites. Cathodic inhibitors are also called precipitation inhibitors [27].

Magnesium and zinc salts are the most well-known cathodic inhibitors [28,29]. Cathodic inhibitors are not as efficient as anodic inhibitors, but unlike anodic inhibitors, they are much less likely to cause pitting corrosion [30]. Cathodic inhibitors are inorganic inhibitors like anodic inhibitors.

5. Organic inhibitors

Recently, inhibitors have further improved the protection efficiency of the reinforced concrete structure and have started to attract more attention in the construction areas due to its up-and-coming applications and contribution to its low cost [17]. Molecules composed by functional groups of carboxylates, amines and also their salts are used as organic inhibitors in concrete structures [31,32].

In general, organic inhibitors change the potential between steel and water in concrete pores to form a mechanical barrier to aggressive ions. Organic inhibitors may contain single or multiple functional groups, however many of them only delay the corrosion of steel from chloride and carbonate environment. Therefore, more researches

are needed about the application of organic inhibitors in the building industry.

Among many available methods of efficient protection of rebars in concrete against corrosion, the application of organic inhibitors is attractive because of their low cost and availability in the market. Organic inhibitors can be used as an admixture (ACI) in concrete constructions [15,21]. The effectiveness of the corrosion inhibitors lays in their chemical structure. Both, migrated corrosion inhibitors and admixtures corrosion inhibitors are able to create the passive layer on the embedded steel and preventing it against corrosion; however, the mechanism of the corrosion inhibition is mainly influenced by the chemical structure of the compound used. It was found that chemical structure is a significant factor with organic inhibition [12]. The organic inhibitor can able to cut both the anodic and cathodic reactions, thus reducing the corrosion rate of reinforcing steel [33].

Various reports and paper describe many different organic inhibitors of corrosion, however among all of them, amines and alkanolamines are the most used. Such compounds have been considered as efficient inhibitors, due to their structural properties.

Organic corrosion inhibitors are admixtures which can do more than just inhibit corrosion of the steel [35]. Table 1 shows other side effects on the fresh and hardened concrete properties

5.1. Mixed type inhibitors

In recent years, the research on the inhibiting effect of amines and alkanol amines in corrosion media has been intensified. Also, carboxylate groups have the potential of forming an organic layer on the entire surface and acting as a mixed inhibitor [23]. These mixed-type inhibitors cut both anodic and cathodic reactions.

Mixed inhibitors reduce the corrosion by forming a thin protective hydrophobic film on the entire surface of the steel [36]. The efficiency of the passive film depends on the molecular structure and suitability with the steel surface. Anodic and cationic inhibitors are adsorbed by the steel surface (whether they positively or negatively charged).

Table 1. The side effects of the organic inhibitors.

Properties	Effects
Setting and early-strength development of concrete	Can accelerate or retard, it depends on type and concentration of organic inhibitor [34]
Air content	No significant effect
Viscosity	Organic corrosion inhibitors reduce viscosity of self-compacting concrete
Permeability	It depends on type of organic inhibitor (for instance, organic acids react with cement components or hydration products)
Workability	It depends on functional groups, inhibitors with groups like -OH and -COOH causes an increase of workability; another inhibitor sometimes required additional superplasticizer to achieve the desired slump
Steel-concrete bond	Possible reduction of adhesion between steel and concrete

However, the dominant factor in organic inhibitors, such as mixed type, is the strength of the bond. Organic inhibitors (mixed type) also act as pore occlusion by reducing the permeability of concrete. Amino alcohols are commonly mixed-type inhibitors that replace the chloride ion and form a durable passive film on the steel surface [37].

Ormellese et al. [18] reported that alkanol amines have a weak corrosion inhibiting effect in the alkali solution of steel under chlorine. In this study, the comparison of carboxylates with alkanol amines and amino acids was investigated. Polycarboxylates have been observed to be more efficient against pitting corrosion than alkanol amines and amino acids.

6. Field applications of anodic, cathodic and mixed inhibitors in concrete

The most important reason for the corrosion of steel in reinforced concrete is the presence of chloride ions in concrete. Cl⁻ ions are the most important factor causing depassivation of the preventive layer on the steel surface in concrete environment. In chlorine and carbon dioxide environments, good concrete cover and good quality concrete protect the reinforcement against corrosion. However, when this layer is damaged, the process of entering chloride ions into concrete becomes easier [38]. Both the fresh concrete inhibitors and migrated corrosion inhibitors prevent steel corrosion by forming a passive film layer on the rebar surface through the adsorption mechanism [40].

Chloride and inhibitor ions in concrete work with 3 different mechanisms: electrical migration (electro-migration), natural diffusion and the movement of the pore solution due to capillarity. Commercially available admixture inhibitors penetrate the pores of concrete quickly, form a hydrophobic layer through physical or chemical adsorption and protect the steel reinforcement. Surface applied inhibitors are called migrating inhibitors. Surface applied inhibitor fills the pores of concrete and forms an insoluble compound [46]. This type of inhibitors is a suitable strategy for the repair of reinforced concrete structures due to their easy application and low cost [47,48].

The use of corrosion inhibitors in reinforced concrete structures delays the onset time of chloride-induced corrosion thereby the corrosion rate is reduced [39]. Calcium nitrite is a passivating inhibitor which creates a passive film on the steel surface and significantly decreases the corrosion rate of rebar in the concrete with chloride environment [41]. Many laboratory studies have shown that calcium nitrite has an effective performance as an anti-corrosion agent [16,20,32]. However, it is also possible to increase the rate of corrosion in the case of the presence of cracks on the concrete [42]. In addition, increase in dosage may result in delay in setting time, decrease in compressive strength and acceleration of corrosion process. Due to their toxicity and carcinogenicity, the use of corrosion inhibitors is not an environmentally friendly solution for civil

engineering. For example, chromates are carcinogenic and therefore they prohibited from use [43].

Carbonation is the most important event that causes the decrease of pH in concrete. Carbonation is caused by the reaction of carbon dioxide (or other acid gases such as SO_x , NO_x) entering the concrete from the surrounding atmosphere and reaction with free lime into the concrete. When the carbonation reaches the reinforcement, the steel corrosion is beginning. Research has shown that alkanolamine-based inhibitors (only for chloride-induced reinforcement corrosion) reduce the impact of carbonation-induced reinforcement corrosion [44].

Heren et al. [45] showed that the strength of concrete is decreasing when the concentration of corrosion inhibitor increase. Also, this effect is further increased as the dosage of inhibitor increases in the cement paste.

Nahali et al. [49] examined the effect of the addition of Na_3PO_4 to the concrete mortar in the chloride environment and concluded the effect of chloride ions on local corrosion is reduced when they added phosphate to the concrete. Yohai et al. [50,51] reported that phosphate ions acted as mixed-type inhibitors. Phosphate compounds (such as disodium phosphate or monofluoro phosphate)

can be mixed into the concrete mortar or it can be applied to the concrete surface.

Nguyen et al. [53], using two 0.1 M NaOH and 0.1 M Na_3BO_3 electrolytes for one to four weeks, carried out the electrochemical injection method with a tetrabutylammonium bromide salt at a current density of 5 A/m^2 . The results show that the electrochemical injection method using 0.1 M Na_3BO_3 is more effective in improving the compressive strength of mortar compared to 0.1 M NaOH.

Thangavel et al. [54] investigated the migrating and mixed type corrosion inhibitors, (with Portland ordinary cement, Portland pozzolan cement and Portland slag cement paste) that effect to steel under the conditions of macro-structure. They were monitored the (over 1 year) macrocell corrosion parameters such as anode potential, macrocell current, and the total integrated current.

Corrosion rate of rebar in different types of cement were evaluated by gravimetric weight loss method (the method based on measuring the weight differences of the substance and calculating the amount of material) [52,54]. In all cement types, the admixed type inhibitor has the best effect and Portland slag cement showed the lowest corrosion rate from others (see Table 2).

Table 2. Corrosion rates of steels effected by normal cement, slag cement and pozzolanic cement [55]

System	Alkalinity (pH)	Free Chloride Contents (ppm)	Corrosion Rate (mmpy)
Ordinary Portland Cement			
Control	11.45	4667	0.2044
Migrating	12.16	3750	0.1878
Admixed	12.08	3813	0.1892
Portland Pozzolan Cement			
Control	11.46	3257	0.1810
Migrating	12.40	2862	0.1621
Admixed	12.33	3229	0.1751
Portland Slag Cement			
Control	11.46	2019	0.1396
Migrating	12.40	1813	0.1027
Admixed	12.31	2017	0.1188

Muralidharan et al. [56] found that the addition of various inhibitory ions (hydroxide, citrate and stannate) into the mortar prepared with Portland cement and fly ash, is reduced the corrosion rate of the steel in the concrete samples with chlorinated environment.

Topcu and Boga [38] has investigated the effect of reinforcement with fly ash concrete samples under the influence of corrosion. As a result of their experiments, adherence have no relationship with concrete quality and cement type. It has been observed that adherence strength decreases at very high rates in the samples that are damaged due to corrosion.

Song and Saraswathy [20] investigated the effects of 3 different type of inhibitors on concrete in order to apply long and short term accelerated corrosion techniques. Mixed type inhibitor; shows higher cracking time (Fig. 3), lower permeability (Fig. 4), higher compressive strength (Fig. 5) and lower corrosion rate (Table 3).

Impressed voltage test technique is an accelerated corrosion test technique that provides indirect information about the permeability properties of concrete.

Cabrini et al. [57] compared the effects on critical chloride concentration of lactic acid salts and nitrite ions used as inhibitors. The tests were performed in a pH between 12.6 to 13.8. This system has been prepared to estimate the critical chloride concentration of passive reinforcement in non-carbonated reinforced concrete structures.

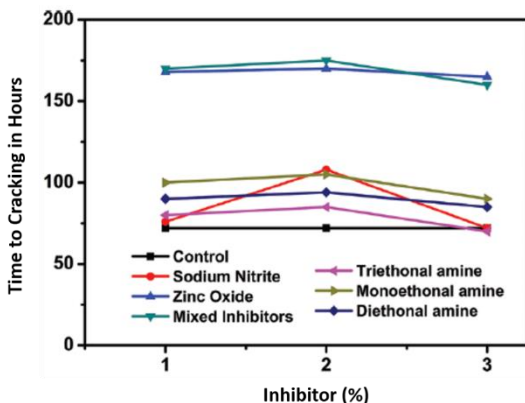


Fig. 3. Impressed Voltage Test [13]

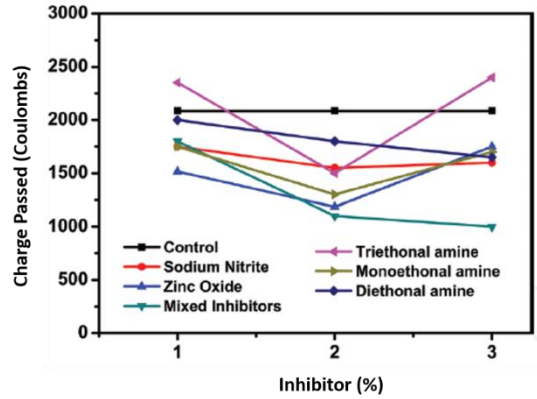


Fig. 4. Rapid Chloride Penetration Test [13]

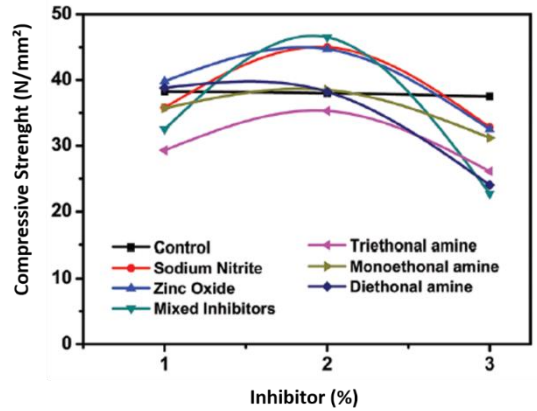


Fig. 5. Compressive Strength and Percentage of Inhibitors [13]

Table 3. Reinforcement Corrosion of Various Inhibitor Types in Chlorine Environment [13]

Inhibitors	Corrosion Rate (mm/y)		
	% 1	% 2	% 3
Control	0.0093	--	--
Sodium Nitrite	0.0023	0.0093	0.0250
Zinc Oxide	0.0022	0.0023	0.0024
Mixed Type	0.0009	0.0012	0.0037
Triethanolamine	0.0117	0.0038	0.0071
Monoethanolamine	0.0171	0.0042	0.0096
Diethanolamine	0.0203	0.0034	0.0083

The presence of organic inhibitors in passive film was determined by IR spectroscopy. The results confirm that 0.1 M aspartate shows an inhibitory

effect. Also, calcium lactate is reducing the corrosion propagation and does not increase the concentration of critical chloride.

Surface applied inhibitors, are applied locally to the chloride containing environment before the concrete repair is starts (patches and coatings) [58]. Criado et al. [60] studied surface-applied (migrated) corrosion inhibitors in mortars containing fly ash. Zheng et al. [59], by applying various accelerated tests, examined the durability of the inhibitor applied to the surface in concrete and found that the durability of the concrete was increased.

7. Electrochemical Injection of Corrosion Inhibitors (EICI)

Electrochemical injection of corrosion inhibitors (EICI) is an effective corrosion reduction technique to increase the durability of reinforced concrete structures in carbonate and chloride environments.

In the electrochemical injection method, a current density of 1-5 A/m² is applied for several weeks between the cathode and an anode (showed in the Fig. 6) placed externally on the concrete surface [61].

During the application, the cationic contents in the corrosion inhibitor are shifted from the concrete cover to the cathode, while the chloride ions in the

concrete migrate from the concrete to the outer anode [55,61].

Mangayarkarasi and Muralidharan [62] investigated the efficiency of electrochemical injection of inhibitors in chloride-containing concrete using normal Portland cement (OPC), Portland pozzolanic cement (PPC) and Portland slag cement (PSC). Inhibitor contains of 0.1 M guanidine, 0.1 M thiosemicarbazide, 2 M triethanolamine and 2 M ethyl acetate. They concluded that the injection of the multicomponent inhibitor has an activity of 88% in terms of the reduction in corrosion rate while current density is 0.5 A/m², regardless of the chloride levels and different concretes.

Karthick et al. [63] investigated the EICI technique on an old concrete plate containing chloride at a current density of 0.5 A/m² using the same type of inhibitor. The effect of inhibition and inhibition mechanism was evaluated by various electrochemical tests such as SEM, FTIR, EDAX and MIP. MIP studies showed that after the EICI technique, a decrease in porosity rate of concrete samples was observed by about 50% SEM analysis showed that the hybrid inhibitor formulation acted as an agent filling the pores.

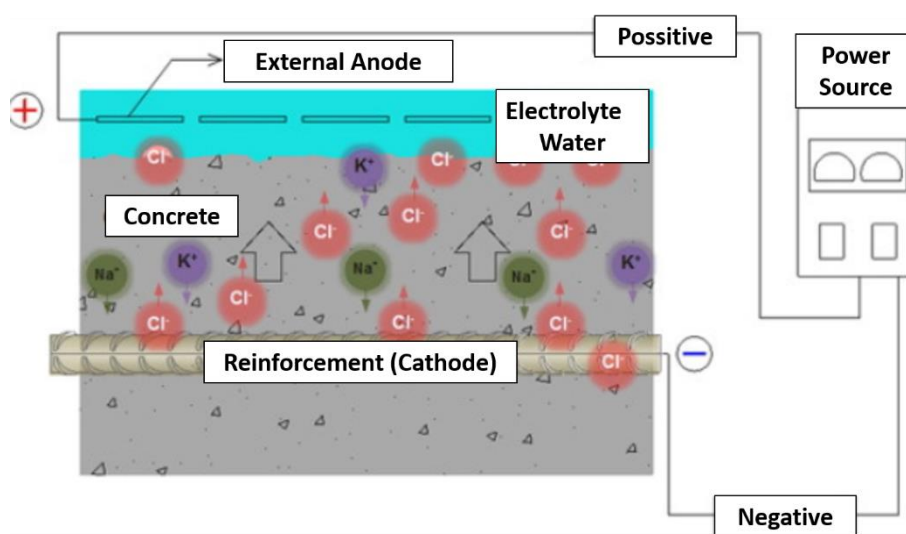


Fig. 6. Schematic Representation of Electrochemical Injection (EICI) method

Xu et al. [32] tried a new method of bi-directional electron-transfer maintenance [BIEM] to inject corrosion inhibitor (triethylenetetramine) into concrete samples with chloride environment. In this process, an electric field was applied between the embedded reinforcement (cathode) and the outer anode to pass the inhibitor from the outer electrolyte to the concrete sample and remove the chloride ions from the concrete. After the treatment, the samples were pierced with a drill to determine the concentrations of corrosion inhibitors, chloride and hydroxyl ions in the concrete.

Among the current electrochemical repair techniques, electrochemical chlorine ion extraction (ECE) is the most commonly used technique for the repair of chloride-containing structures. Furthermore, chloride ions tend to return after stopping the repair process, so this approach cannot completely eliminate the chlorides in the structure and is only a temporary solution.

During the application of the ECE process, the removal of the chloride from the concrete and the passivation of the concrete using the nitrite (migrating) inhibitor were tested simultaneously. After ECE process; the migration of nitrite ions is passivating the metal surface, as well as the efficiency of removal the chloride ions are increases [63].

8. Eco-friendly corrosion inhibitors (Green inhibitors)

Many synthetic or natural chemicals are used as inhibitors to protect metals and alloys against corrosion [64,65]. However, inhibitors have high toxicity, as well as chromate, phosphate and arsenic-containing compounds cause environmental and health problems [66].

In order to eliminate these concerns, studies are made on alternative environmentally friendly inhibitors. These inhibitors called 'Green Corrosion Inhibitors' it is mostly composed of plants or organic compounds whose toxicity is known [67]. Nowadays boron is used for various purposes in almost every area. Although the cationic form of boron is known, not so many studies have been done.

Gerengi et al. [69] compared the results of boron cation ionic liquids EMITFB (1-ethyl-3-methylimidazolium tetrafluoroborate) and BMPTFB (1-butyl-1-methylpiperidinium tetrafluoroborate) inhibitory activity in 0.1M HCl environment with using Electrochemical Impedance Spectroscopy (EIS) and Potentiometric Polarization (TP) methods. They discussed the morphological changes on the metal surface by electrochemical measurements.

As can be seen from Fig. 7, only the traces of the polishing device are seen on the metal surface before the experiment. It is seen that metal surface is disrupted by the action of HCl when St37 metal is exposed to 0.1 M HCl environment. When the inhibitors are added to the working environment, it is observed that the film is formed on the metal surface and the formed film protects the metal against corrosion [68].

As a result of this study, it was determined that EMITFB and BMPTFB molecules behave as mixed type inhibitors by TP method. It was observed that the percentages of inhibition obtained for both ionic liquids were close to each other but the values obtained for BMPTFB were higher than those of EMITFB, thus, the metal was less corroded by the addition of BMPTFB [68]. With this study, it is clear that boron element, which is easily soluble in water and also abundant in our country, has been opened in an alternative area with high value.

Hossain et al. [70] investigates the impact of cinnamaldehyde as an eco-friendly inhibitor in mitigating corrosion detriment on mild steel in aerated NaCl (3% w/w) using weight loss and potentio-dynamic polarization methods. The results indicate moderate inhibition efficiency of cinnamaldehyde reaching around 70% at an optimum level of 0.5 g/L or 500 ppm by establishing an adsorption film on metal surface. Adsorption of the cinnamaldehyde seemed to adhere to the Langmuir isotherm. The corrosion rate decreased with cinnamaldehyde dose up to the optimum level while increased slowly with the medium temperature. The calculated inhibition efficiencies using both corrosion monitoring techniques were found to be in good agreement.

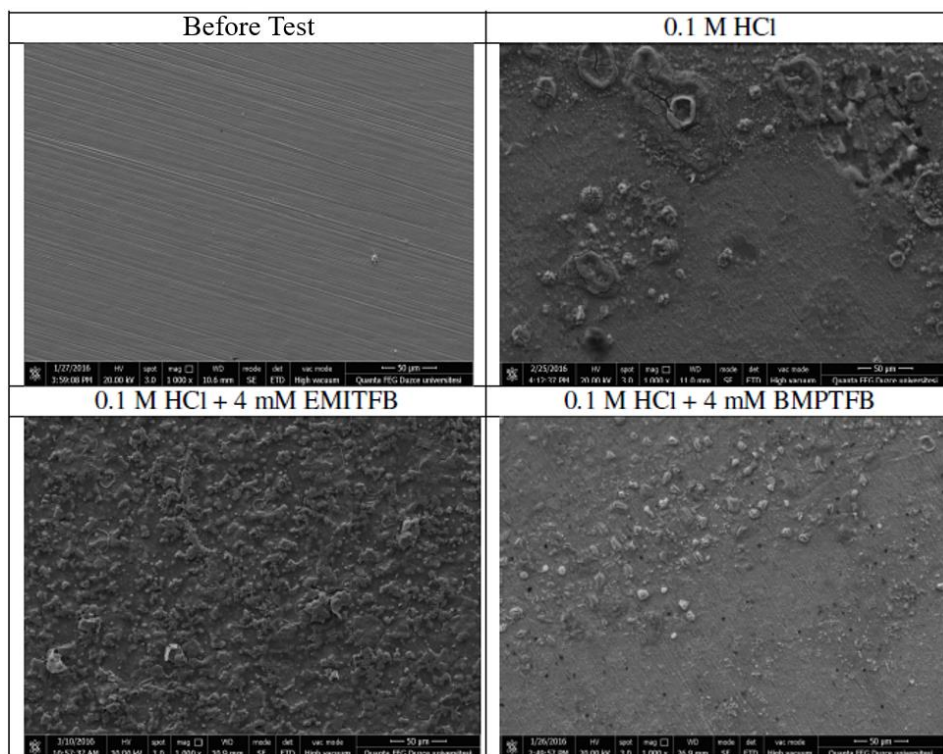


Fig. 7. St37 metal before the experiment; SEM Images showing the corrosion mechanism prepared by the addition of 4 M EMITFB and 4 M BMPTFB in to the 0.1 M HCl environment [68]

Okeniyi et al. [71] as a result of their physico-chemical analyzes on *Phyllanthus muellerianus*, *P.muellerianus* has non-toxic, environmentally friendly potentials and protects metal from corrosion. They concluded that the components obtained from the leaves of *P.muellerianus* reduced the total corrosion of reinforcement in reinforced concrete when used as additives in reinforced concrete samples immersed in 0.5 M H_2SO_4 environment.

Fig. 8 shows that as the total number of days increases, also the amount of corrosion increases. In addition, the total amount of corrosion decreases when increase of the concentration of *P. Muellerianus* used in the test samples. In order to test the errors or prejudices that may occur in the experiment, test copies are designed.

These second series, called the copy (duplicate) series, has the same concentration and curing conditions as the first series. If there are significant differences in the two series of the same pouring

conditions (temperature, environmental conditions), this inequality must be investigated. If there is no significant difference between the series (which is desired), the experimental work is confirmed.

Effective reduction of reinforcement corrosion will certainly increase the strength of the reinforced concrete structure. Thus, the results of the total corrosion analysis and the non-toxic properties of *P.muellerianus* prove that this natural material can be used as an environmentally friendly, renewable and sustainable material to reduce steel reinforcement corrosion in concrete.

9. Conclusions

Corrosion is the most important factor that makes the structures vulnerable to earthquakes by causing cross section loss in the columns and beams that constitute the main frame of the buildings. It is clear that most of the damaged buildings after the earthquake are caused by corrosion.

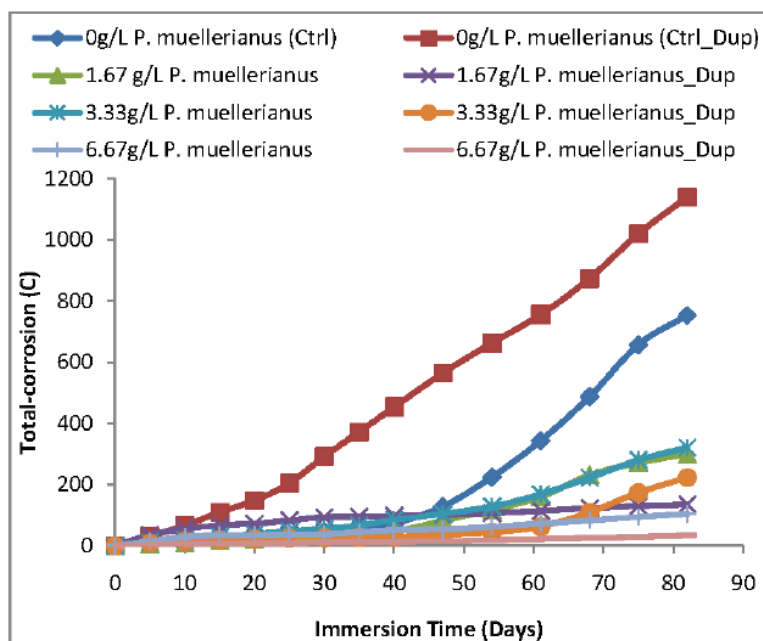


Fig. 8. Plots of total-corrosion effects of *P. muellerianus* leaf-extract on concrete steel-reinforcement in industrial/microbial simulating medium [71]

The use of inhibitors of low environmental impact is becoming more popular nowadays. Studies with green inhibitors have been widely discussed and we should increase their use 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.

The focus of this review is the recent developments of inhibitors in reinforced concrete structures; in order to examine various types of inhibitors based on their mechanisms of action, laboratory and field conditions.

As a result of researches and literature reviews, the following results have been obtained:

- The strength of concrete is decreasing when the concentration of corrosion inhibitor increase. It has been reported that this effect is further increased as the dosage of inhibitor increases in the cement paste.
- In all cement types, the admixed type inhibitor has the best effect and Portland slag cement showed the lowest corrosion rate from others.
- According to researches, the effects of 3 different types of inhibitors on concrete which applied long and short term accelerated corrosion techniques; Mixed type inhibitor, showed higher cracking time, lower permeability, higher compressive strength, and lower corrosion rate.
- Researchers concluded that the injection of the multicomponent inhibitor has an activity of 88% in terms of the reduction in corrosion rate while current density is 0.5 A/m^2 , regardless of the chloride levels and different concretes.
- Topcu and Boga [38] has investigated the effect of reinforcement with fly ash concrete samples under the influence of corrosion. As a result of their experiments, adherence have no relationship with concrete quality and cement type. It has been observed that adherence strength decreases at very high rates in the samples that are damaged due to corrosion.
- Mixed-type inhibitors (carboxylate and amine-based compounds) are generally used in

concrete. Due to their capillary effects, such inhibitors can penetrate into the concrete surface when they are applied [23].

- It has been found that inhibitors both migrated and surface applied are easy application and cost-effective for field implementation.
- Surface-applied inhibitors can reach the reinforcement through the concrete cover, however if the thickness of the concrete cover on the reinforcement is too high or the density of the concrete is too high, sufficient inhibitor concentration is required to protect the rebar against corrosion [72].
- Long-term applications are necessary to understand organic (mixed-type) inhibitors. Due to; chloride content, cement type, inhibitor type etc. there is a need for widely research in real reinforcement in various effects [73].
- Inhibitors have high toxicity, as well as chromate, phosphate and arsenic-containing compounds cause environmental and health problems. In order to eliminate these concerns, studies are made on alternative environmentally friendly inhibitors. These inhibitors called 'Green Corrosion Inhibitors' it is mostly composed of plants or organic compounds.
- *P.muellerianus* plant has non-toxic, environmentally friendly potentials and protects metal from corrosion. The components obtained from the leaves of *P.muellerianus* reduced the total corrosion of reinforcement in reinforced concrete when used as additives in reinforced concrete samples immersed in 0.5 M H_2SO_4 environment [71].
- Studies on the inhibitory activity of boron cationic ionic liquids in EMITFB (1-ethyl-3-methylimidazolium tetrafluoroborate) and BMPTFB (1-butyl-1-methylpiperidinium tetrafluoroborate) show that the elements in the composition of the synthesized product are adsorbed to the metal surface to protect the metal from corrosion. With this study, the use of boron element, which is easily soluble in water and also abundant in our country, is used in an alternative value-added area [69].

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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