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Corrosion Inhibitors for Reinforced Concrete: A Review

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Abstract

The objective of the topic is to review the recent trends in corrosion inhibitors for reinforced concrete and their application in the laboratory and field conditions. Inhibitors are chemical substances which when added to the concrete in small concentrations will inhibit or prolong the time to initiation of corrosion in concrete structures. This chapter focuses on the type of inhibitors used in concrete based upon their mode of action and the way of application. The section deals with anodic, cathodic, mixed inhibitors; performance of admixed inhibitor vs. migrating/surface applied inhibitor and their evaluation studies; and electrochemical injection of corrosion inhibitor (EICI) in concrete and electrochemical chloride extraction techniques has been reviewed.

Keywords: anodic inhibitors, cathodic inhibitors, mixed inhibitors, organic inhibitors, migrating inhibitors, electrochemical injection, reinforced concrete

1. Introduction

Corrosion of steel in concrete structures plays a significant role in affecting the service life of the concrete structures. Various methods have been developed with the intent of preventing the corrosion and to enhance the service life. The methods include the coating to the concrete surface, the coating to the reinforcement, cathodic protection, electrochemical methods, alternative reinforcement, and corrosion inhibitors. Among all the available techniques, the use of corrosion inhibitors is one of the most appropriate and efficient methods for corrosion protection of reinforced concrete structures due to the easy operation, low cost, and excellent corrosion resistance effect [1–8]. Inhibitors which are added to the concrete in small concentrations are intended to delay and slow the onset of corrosion in reinforced concrete. Most of the inhibitors act by stabilizing the steel surface by forming the protective film, and some

inhibitors react with concrete forming the complex thus reducing the permeability of the concrete. Corrosion inhibitors are generally used as admixtures in concrete for new construction, but they can also be utilized for repairs by admixed with concrete for patches, sprayed onto the surface of the concrete or applied by saturation treatment [9–13].

As per NACE international, “a corrosion inhibitor is a substance when added to an environment, either continuously or intermittently to prevent corrosion by forming a passive film on the metal.” In other processing industries, inhibitors are the first line of defense against corrosion [14].

Inhibitors slow down the corrosion process by:

- increasing the anodic or cathodic polarization behavior;
- reducing the movement of ions of the metallic surface;
- increasing the electrical resistance of the metallic surface.

1.1. Classification of corrosion inhibitors

Corrosion inhibitors for concrete are classified based on [15–18] (**Figure 1**):

- Electrochemical mechanism of action (anodic or cathodic, or both).
- Type of chemicals used (organic and inorganic).
- The way of application; either mixed with concrete or applied on hardened concrete (migrating inhibitors).

1.2. Anodic (passivating) inhibitors

This type of inhibitors forms an insoluble protective film on anodic surfaces to passivate the steel. An anodic inhibitor shifts the potential to the passivation zone causing the formation of a thin passive film on the anodic sites, which increases the potential of the anode and decrease the corrosion in rate. There are two types of passivating inhibitors.

- Oxidizing anions, such as chromates, nitrates, and nitrites, passivate the steel in the absence of oxygen.
- Nonoxidizing ions, such as phosphate, tungstate, and molybdates, require the presence of oxygen to passivate the steel.

Anodic inhibitors are effective only when present in sufficiently high concentrations [15]. Typically, the concentration required is determined by the level of chloride present in the environment in which the steel is exposed. The most commonly used anodic inhibitor for concrete is calcium nitrite [18]. Calcium nitrates show similar inhibiting properties in concrete. Some anodic inhibitors, such as nitrites, cause accelerated corrosion and pitting if the

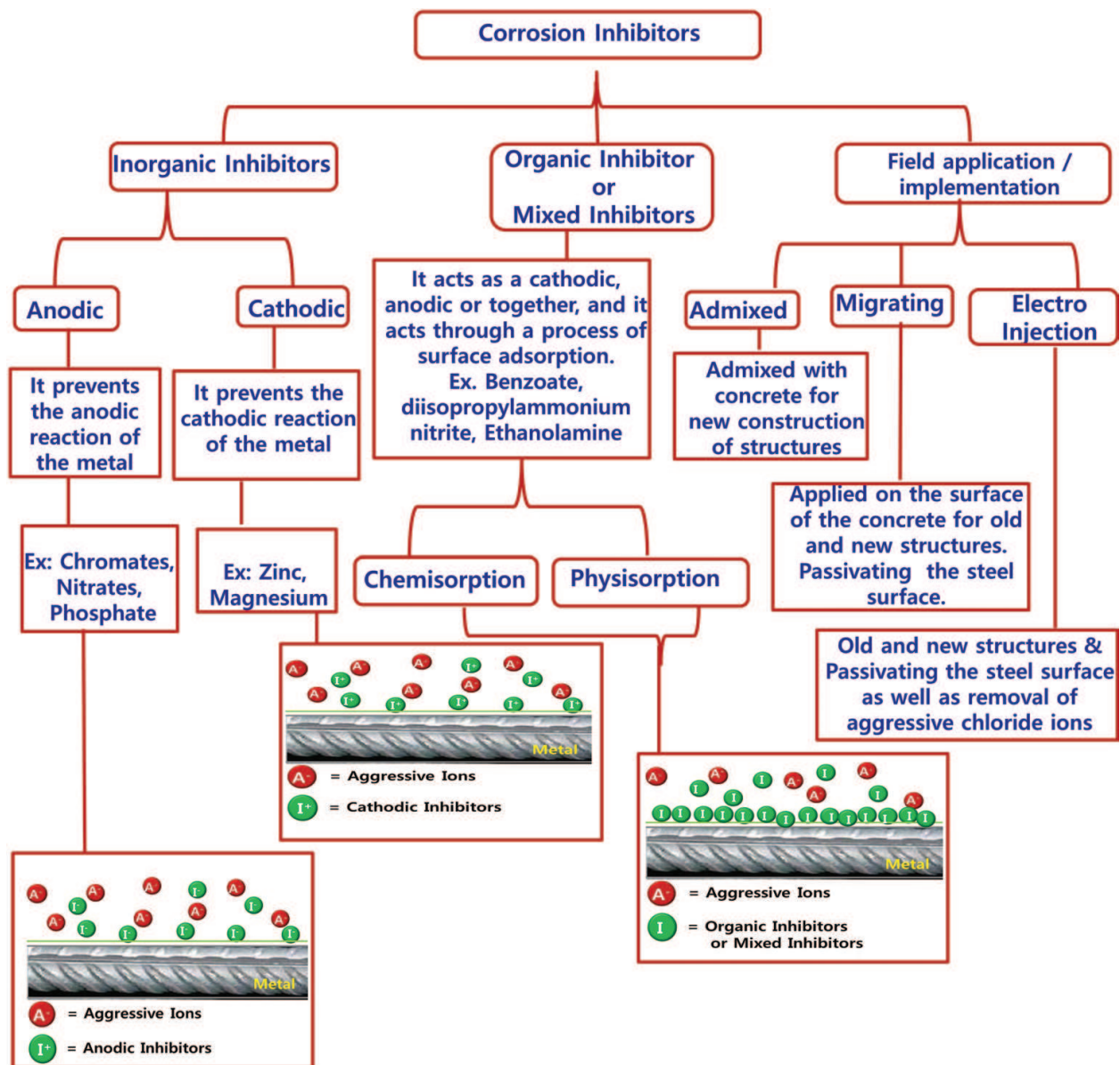


Figure 1. Classification of corrosion inhibitors.

concentration drops below the threshold/critical level [19]. Nitrates, benzoates, chromates, molybdates, and orthophosphates are used as anodic inhibitors.

1.3. Cathodic inhibitors

Cathodic inhibitors slow down corrosion by reducing the rate of cathodic reactions in the corrosion environment. A cathodic inhibitor causes the formation of insoluble compounds precipitating on the cathodic sites in the form of a barrier film. These inhibitors are called precipitation inhibitors [20]. Zinc and magnesium salts are cathodic inhibitors that form precipitates of zinc hydroxide and magnesium hydroxide at the cathode [21, 22]. Phosphates precipitate as ferrous and ferric phosphates on the steel substrate [23]. Cathodic inhibitors are not as effective as anodic inhibitors, but they are not likely to cause pitting [24].

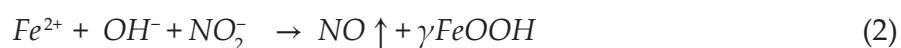
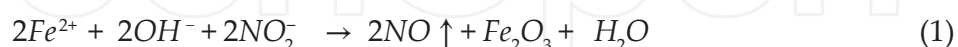
1.4. Mixed inhibitors

Mixed inhibitors quash both the anodic and cathodic reactions, and they reduce the corrosion rate by forming a thin protective hydrophobic film on entire surface of the metal through adsorption mechanism [25]. The material with the hydrophobic group that has polar groups, such as N, S, and OH, is effective. These inhibitors are called adsorption or film-forming inhibitors [26–28]. The effectiveness of the film depends on the chemical composition, molecular structure, and their affinities for the metal surface. Cationic inhibitors, such as amines, and anionic inhibitors, such as sulfonates, get adsorbed on the metal surface, whether it is charged positively or negatively. The strength of the bond is the dominant factor for organic inhibitors. Organic inhibitors can also act as pore blockers, reducing the permeability of the concrete. Amines and amino alcohols are the commonly used mixed inhibitors, which displace the chloride ion and form a durable passivating film [29].

Organic inhibitors are further classified into two categories, based upon their application: inhibitor admixed concrete and migrating corrosion inhibitors that are applied on the hardened surface of the concrete [10, 19]. Corrosion inhibitors may be a good alternative for repair concrete due to their lower cost and ease of application. The main application methods for corrosion inhibitors are: added to fresh concrete as an admixture, applied on the hardened concrete and damaged structures migrating corrosion inhibitors (MCI), added to repair mortars, used as a surface treatment to rebars before concreting [10].

1.5. Effect of anodic, cathodic, and mixed inhibitors in concrete

Corrosion of steel in concrete structures is the primary concern when the structures are exposed to the coastal marine environment. The use of corrosion inhibitors can delay the onset of chloride-induced corrosion, prolong the time to initiation of corrosion, and thereby reduce the corrosion rate [30, 31]. Calcium nitrite is the most commonly used anodic corrosion inhibitor for reinforced concrete. This inhibitor is a passivating inhibitor, which forms a passive film on the surface of steel and significantly reduces the corrosion rate of steel in chloride-contaminated concrete [1, 32]. The inhibitive action of steel with calcium nitrite is as follows [1, 10]:



Different authors have reported different threshold value threshold $[Cl^{-}]/[NO_2^{-}]$ ratio depends on the environment. It was reported that the re-passivation of the corroded steel was observed at the $[Cl^{-}]/[NO_2^{-}]$ ratio from 0.5 to 1 [32]. For chloride-contaminated concrete or mortar, the $[Cl^{-}]/[NO_2^{-}]$ ratio ranges from 1 to 3, and for simulated alkaline solutions and chloride-contaminated concrete, the $[Cl^{-}]/[NO_2^{-}]$ ratio ranges from 1 to 4 [3, 31]. Several laboratory studies have established the

System	E_{corr} (mV vs. SCE)	Tafel slopes		Corrosion rate (mmpy)	Efficiency (%)
		(mV dec ⁻¹)			
		ba	bc		
Plain	-544	53	84	0.0010	—
Plain +1% Cl ⁻	-566	58	88	0.0042	—
Plain +2% Cl ⁻	-576	50	87	0.0062	—
Plain +3% Cl ⁻	-580	58	85	0.0091	—
Plain +0.5% NO ₂	-538	50	87	0.0001	92
Plain +0.5% NO ₂ + 1% Cl ⁻	-547	53	87	0.0004	91
Plain +0.5% NO ₂ + 2% Cl ⁻	-556	51	85	0.0007	89
Plain +0.5% NO ₂ + 3% Cl ⁻	-566	51	81	0.0017	81

Table 1. Potentiodynamic polarization parameters for steel in ternary cement extract [45].

performance of calcium nitrite as an efficient corrosion inhibitor [1, 10, 15, 27, 33]. But, at the same time, possible increase of corrosion rate in case of low dosage or the presence of cracks [16]. Also, increase in dosage resulted in a decrease of the setting time and lowers the compressive strength of concrete and corrosion process may get accelerated [10, 32]. However, their application in corrosion protection is limited due to its toxicity and carcinogenicity [6, 34]. Chromates are carcinogenic, and hence its use is also prohibited [35, 36]. Haleem et al. [37] investigated the pitting corrosion behavior of phosphates, tungstate, and molybdates in chloride-contaminated Ca(OH)₂ solution and found that pitting corrosion current reaches steady state values, which depend on the way of introducing the inhibiting anions in the solution. Studies revealed that sodium phosphate forms a protective layer on the surface of the steel in chloride-contaminated synthetic concrete pore solution. Besides pretreatment of

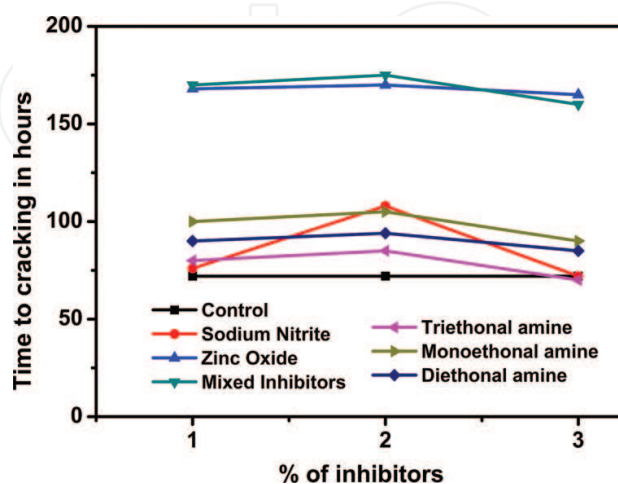


Figure 2. Impressed voltage test [1].

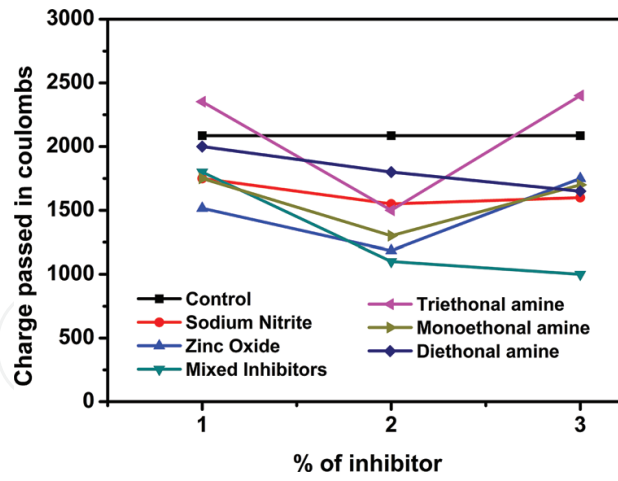


Figure 3. Rapid chloride penetration test [1].

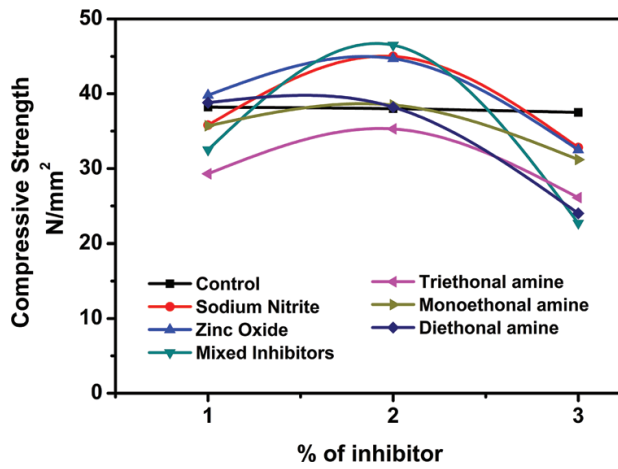


Figure 4. Compressive strength vs. percentage of inhibitors.

Systems	Corrosion rate (mmpy)		
	1%	2%	3%
Control	0.0093	—	—
NaNO ₂	0.0023	0.0093	0.0250
ZnO	0.0022	0.0023	0.0024
Mixed	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

Table 2. Corrosion rate of rebar exposed to various types of inhibitors admixed with chloride [1].

Systems	E _{corr} (mV)	Tafel slopes		I _{corr} (μAcm^{-2})	Corrosion rate (mmpy)
		(mV dec ⁻¹)			
		bc	ba		
OPC - Control	-580	80	350	20.5	0.240
NaNO ₂ 1%	-440	110	260	2.51	0.029
2%	-450	120	230	2.72	0.031
3%	-480	140	240	2.94	0.034
ZnO 1%	-440	115	300	1.35	0.015
2%	-490	140	280	1.29	0.014
3%	-480	150	260	1.79	0.020
Mixed 1%	-420	180	225	0.90	0.010
2%	-485	120	200	1.20	0.013
3%	-490	135	220	1.30	0.015
Triethanolamine 1%	-470	110	292	4.52	0.052
2%	-530	90	284	7.81	0.090
3%	-545	75	248	9.73	0.112
Monoethanolamine 1%	-510	83	306	10.5	0.121
2%	-560	87	300	10.2	0.118
3%	-550	82	301	12.7	0.147
Diethanolamine 1%	-500	90	400	13.4	0.155
2%	-570	85	356	14.8	0.172
3%	-565	80	345	12.6	0.146

Table 3. Potentiodynamic polarization parameters for mild steel in concrete containing different inhibitors [15].

steel with 0.5 M inhibitor solution for 72 h forms a protective layer which further enhanced the protection efficiency [38–41]. Nahali et al. [42] studied the effect of Na₃PO₄ addition in chloride-contaminated mortar and concluded that the addition of phosphate inhibitor in concrete decreases the chloride ions effect on localized corrosion.

Yohai et al. [43, 44] reported that the phosphate ions behaved as a mixed type inhibitor. Soluble phosphate compounds, such as disodium phosphate or mono fluoro phosphate, can be mixed with mortar or applied on concrete [42] by immersion or by surface application [45]. Song et al. [46] evaluated the role of alkaline nitrites on the inhibition of corrosion of steel in binary (OPC + PPC) and ternary cement (OPC + PPC + PSC) and reported that ternary system provides 81% protection efficiency (**Table 1**) for steel in concrete in the presence of 3% chloride concentration. Muralidharan et al. [47] evaluated the effect of various inhibitive ions (hydroxide, citrate, and stannate) in chloride-contaminated (OPC + FA) extract and mortar and found that the addition of inhibitive ions decreased the corrosion rate of the steel rebar in simulated concrete environments.

Furthermore, the effectiveness of corrosion inhibitors was enhanced by using hybrid corrosion inhibitors; these inhibitors had good corrosion resistance and low toxicity, but the mechanism of protection is not clear [48]. The combined effect of pitting and uniform corrosion on the surface of the rebar was studied by using sodium molybdate (Na_2MoO_4), cerium nitrate hexahydrate, 2,5-Dimercapto-1,3,4-thiadiazole (DT), 2-Mercaptobenzothiazole (MBT), and 1H-benzotriazole (BTA). All the inhibitors except DT and Na_2MoO_4 are toxic. From the study, they concluded that Na_2MoO_4 is the non-toxic inhibitor, which re-passivates the pits formed on the surface of the steel rebar by forming an insoluble FeMoO_4 compound [36]. Saraswathy et al. [1] and Song et al. [15] studied the effect of anodic, cathodic, and mixed inhibitors in concrete by conducting various short- and long-term accelerated techniques. They concluded that the mixed inhibitor had shown higher time to cracking (**Figure 2**), lower coulomb values (**Figure 3**), higher compressive strength (**Figure 4**), and lesser corrosion rate (**Tables 2 and 3**).

2. Effect of organic inhibitors in concrete

2.1. Admixed vs. migrating corrosion inhibitors (MCI)

Recently, organic inhibitors gained more attraction in the construction industry due to their promising application as admixtures in reinforced concrete with improved protection efficiency and low cost [49]. Organic inhibitors are used as an admixed corrosion inhibitor [13, 18] or migrating corrosion inhibitors (MCI) [18, 50–52]. Migrating inhibitors are also called as surface applied inhibitors. Both admixed and migrating corrosion inhibitors prevent steel corrosion by forming a thin layer of protective barrier film on the surface of the rebar through adsorption mechanism. Amines and alkanol amines [1, 52–54] and their salts are used as organic inhibitors in concrete. It has been reported that the alkanol amine-based inhibitors could be able to decrease the corrosion rate of the carbonation induced corrosion effect only for the chloride-induced corrosion of reinforcement [55]. Furthermore, the results indicated that penetrating corrosion inhibitors when applied to the surface of existing or new structures can be able to reduce the corrosion rate below $0.1 \mu\text{A}/\text{cm}^2$. Organic inhibitors can adsorb by chemisorption or physisorption. Chemisorption leads to the chemical reaction between active centers of corrosion onto metal and organic inhibitor, where charges from the polar group of inhibitor and charges from metal and metal oxides formed in concrete are shared. Then, organic inhibitor forms the thin coating film blocking the metal surface from the aggressive species by strong chemical bonds. Physisorption leads to the formation of a mechanical barrier, made by organic inhibitors [56]. This inhibitor can halt both the anodic and cathodic reactions, thus reducing the corrosion rate of the reinforcing steel [57]. It has been reported that carboxylate and amino alcohol-based corrosion inhibitors show dual actions in concrete as the amines and alkanol amines adsorb on the metal surface and form a protective film against chloride [58, 59], whereas the carboxylate ester compound reacts with calcium hydroxide, precipitates and blocks the pores of the concrete. This pore blocking property is said to be a secondary protection mechanism against reinforcement corrosion [16, 18, 44, 58]. Furthermore, another study reported that some organic inhibitors adsorb better on the iron surface in the active state than in the passive state [60]. Ormellese et al. [61] reported that amines and alkanol amines (**Table 4**) had poor corrosion inhibition effect on steel in chloride

Amines [61]		Carboxylic acids [66]
Methylamine	$\text{CH}_3\text{-NH}_2$	Sodium gluconate
Dimethylamine	$(\text{CH}_3)_2\text{-NH}$	D-Saccharic acid, monopotassium salt
Ethylamine	$\text{CH}_3\text{CH}_2\text{-NH}_2$	Calcium α -D Eptagluconate
Propylamine	$\text{CH}_3\text{CH}_2\text{CH}_2\text{-NH}_2$	Phthalic acid, monopotassium salt
Cyclohexylamine	$\text{C}_6\text{H}_{11}\text{-NH}_2$	Lactic acid
Triethyltetramine	$\text{NH}_2\text{-CH}_2\text{CH}_2\text{-(NHCH}_2\text{CH}_2)_2\text{-NH}_2$	Maleic acid
Hexamethylenetetramine	$\text{C}_6\text{H}_{12}\text{N}_4$	Suberic acid
Alkanolamines		Adipic acid
Monoethanolamine	$(\text{OHCH}_2\text{CH}_2)\text{-NH}_2$	Sodium benzoate
Dimethylethanolamine	$(\text{CH}_3)_2(\text{OHCH}_2\text{CH}_2)\text{-N}$	
Triethanolamine	$(\text{OHCH}_2\text{CH}_2)_3\text{-N}$	
Methyldiethanolamine	$(\text{CH}_3)(\text{OHCH}_2\text{CH}_2)_2\text{-N}$	

Table 4. Various amines and alkanolamines investigated by Ormellese et al. [61] and Monticelli et al. [66].

containing alkaline solutions. They further observed that polycarboxylates are more efficient against pitting corrosion. Comparison of carboxylates with amines/alkanol amines and amino acids were investigated in the same study, and the results are summarized in Predeferri's diagram showing pitting potential vs. chloride concentration (**Figure 5**). From the figure, it is evident that amines/alkanol amines had only moderate effectiveness, while carboxylates showed the best behavior at low and medium chloride levels. It was reported that amines were reported to reduce the compressive strength of cement paste and the reducing effect increased with increasing dosage [62]. Heren et al. [63] showed that the decline in concrete strength was enhanced by an increase in corrosion inhibitor concentration.

Surface-applied migrating corrosion inhibitors (MCI) are suitable for repairing the chloride-contaminated concrete. In concrete, chloride and inhibitor ions work on three mechanisms: natural

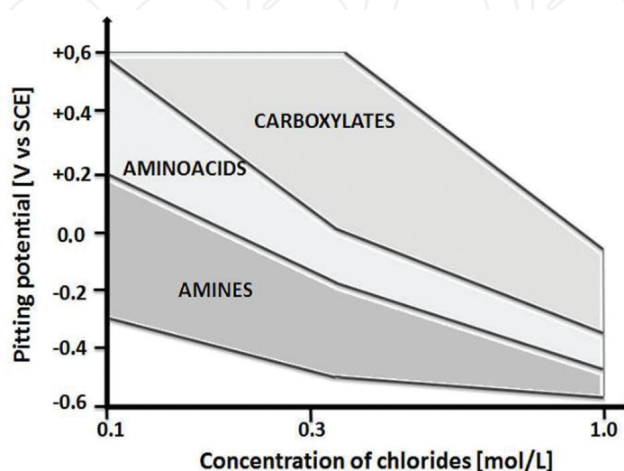


Figure 5. Pedferri type diagram showing pitting potential vs. chloride ions and the range of corrosion organic inhibitors [61].

diffusion, electrical migration, and transport by movement of pore solution due to the capillary suction or pressure gradient. MCIs are typically based on commercial organic compounds. Aminoalcohols rapidly penetrates through the pores of the concrete, and it protects the steel rebar by forming a hydrophobic layer by physical or chemical adsorption. Another function of this inhibitor is, it reacts with the cement particles and forms an insoluble compound blocking the pores of the concrete [58]. This type of inhibitors is an appropriate strategy to rehabilitate reinforced concrete structures because of its ease of operation, low cost, and safety. MCIs are topically applied to the chloride-contaminated concrete surfaces before placement of the patches and overlays [64]. Zheng et al. [7] studied the durability of the surface applied inhibitor in concrete by conducting various accelerated tests and concluded that the durability of the concrete is improved. Criado et al. [65] examined the surface applied corrosion inhibitors in mortars with fly-ash additives. Another study has shown that amino alcohol-based inhibitors are most effective on the reference mortar specimens than on the specimens with ladle furnace slag. Further, it was noted that the corrosion rate was lowered in the samples with lesser chloride percentage, but was not effective with higher chloride ion containing mortar specimens [66].

Organic MCIs are mostly mixed inhibitors. It creates a hydrophobic layer that helps to repel moisture away from the steel rebar [67]. Monticelli et al. [68] investigated the different type of inhibitors based on amine/alkanol amine and carboxylate (dicarboxylic and hydrocarboxylic acids) on steel corrosion behavior in saturated calcium hydroxide solution containing 0.1 M chloride and chloride admixed mortar. They concluded that among the inhibitors studied, dicyclohexylammonium nitrite seems to be a better inhibitor than dicyclohexylamine. Further, they found that maleic acid was efficient in increasing the pitting potential of the steel in chloride-contaminated alkaline solutions. Of all the acids tested, maleic acid failed to hinder the corrosion process during longer exposure in mortars as like sodium nitrite. However, there is some controversy regarding their use. Elsener et al. [69] reported that amines/alkanol amines are not effective against chloride-induced corrosion. Most of the problems related to low effectiveness have been associated with leaching and evaporation of AMAs volatile components [70, 71] leading to decrease the inhibitor effective concentration in concrete.

Thangavel et al. [72] studied the effect of migrating vs. admixed corrosion inhibitors for steel in Portland, pozzolana, and slag cement concretes under macrocell condition. Macrocell corrosion parameters such as anode potential, macrocell current, and the total integrated current were monitored over a period of 1 year. The corrosion rate of the steel rebar embedded in different types of cement concretes was assessed by gravimetric weight loss method. The admixed inhibitor consists of 0.5% sodium citrate +0.5% sodium stannate and migrating inhibitor consisted of 0.5% amino alcohol, 0.5% amines and 0.5% nitrites. **Table 4** shows the various types of inhibitor combinations studied. The authors have concluded that MCI performed better than the admixed system in all the three types of cement used. Among the three types of cement, PSC showed lowest corrosion rate (**Table 5**). MCI showed 60% reduction in macrocell current (**Figures 6–8**) and admixed system showed 40% reduction in macrocell current in PSC concrete.

2.2. Electrochemical injection of corrosion inhibitors (EICI)

Several methods of repair treatments are adopted in the rehabilitation of concrete structures. They are a partial replacement of concrete cover, electrochemical re-alkalization, electrochemical chloride extraction, cathodic protection, and surface application of corrosion inhibitors [73–75].

Systems	Alkalinity (pH)	Free chloride contents (ppm)	Corrosion rate (mmpy)
OPC			
Control	11.45	4667	0.2044
Migrating	12.16	3750	0.1878
Admixed	12.08	3813	0.1892
PPC			
Control	11.46	3257	0.1810
Migrating	12.40	2862	0.1621
Admixed	12.33	3229	0.1751
PSC			
Control	11.46	2019	0.1396
Migrating	12.40	1813	0.1027
Admixed	12.31	2017	0.1188

Table 5. Corrosion rate of steel in OPC, PPC and PSC concretes [73].

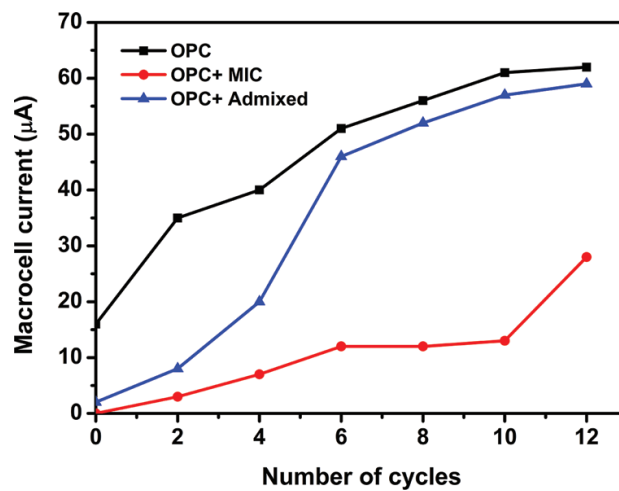


Figure 6. Macrocell current vs. number of cycles of exposure for steel in OPC concrete under macrocell condition [72].

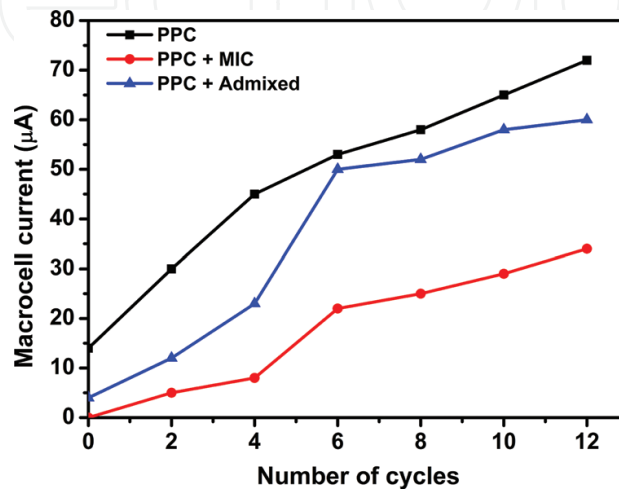


Figure 7. Macrocell current vs. number of cycles of exposure for steel in PPC concrete under macrocell condition [72].

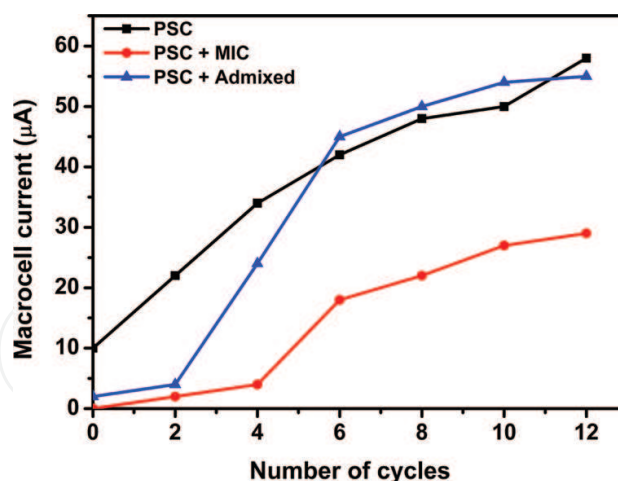


Figure 8. Macrocell current vs. number of cycles of exposure for steel in PSC concrete under macrocell condition [72].

Electrochemical injection of corrosion inhibitors (EICI) was found to be an efficient corrosion mitigation technique for carbonated and chloride-contaminated reinforced concrete structures to improve the durability. In EICI, a current density of $1\text{--}5\text{ A m}^{-2}$ is usually applied between the embedded steel cathode and an externally placed anode on the concrete surface in an aqueous solution containing inhibitors for a few weeks [76]. During the application of current, the cationic species of the corrosion inhibitor migrate into the concrete cover to the cathode, whereas the chloride ions in the concrete migrate out of the concrete towards the external anode [73, 76]. EICI was found to be an effective method of preventing corrosion in existing structures; and this method serves as a rehabilitative measure to retard or reduce corrosion. Kubo et al. [77] applied the EICI technique in a 40-year-old carbonated reinforced concrete railway viaduct in Tokyo. They tried the electrochemical injection of the organic base corrosion inhibitor, ethanolamine into an existing aged carbonated concrete and it was found to allow penetration of an adequate concentration of the inhibitor near the steel. It was found that pH near the steel was changed due to the buffering action of the inhibitor. It was also found that due to the variation in the concrete cover (as is usually the case in real concrete structures) the current density distribution was affected resulting in an uneven injection treatment. Further, it was reported that detailed information on the distribution of concrete cover within the structure is therefore needed to establish a reasonable treatment plan for successful inhibitor injection.

Mangayarkarasi et al. [78] studied the efficiency of the electrochemical injection of inhibitors in chloride admixed concrete with OPC, PPC, and PSC concrete by using electrochemical techniques. The inhibitor consists of 0.1 M guanidine, 0.1 M thiosemicarbazide, 2 M triethanolamine, and 2 M ethyl acetate. They concluded the multi-component inhibitor injection showed more than 95% efficiency (Table 6) in terms of reduction in corrosion rate irrespective of chloride levels in different concretes at a current density of 0.5 A/m^2 . Karthick et al. [2] investigated the EICI by using the same type of inhibitor in a chloride-contaminated old concrete slab (Figure 9) at a current density of 0.5 A/m^2 . The efficiency of the inhibitor formulation was evaluated through various electrochemical tests, and the mechanism of inhibition was established by FTIR, SEM, EDAX, and MIP studies. They found that FTIR studies (Figure 10) indicated that the functional group of the inhibitors namely -NH_2 , C-H , and $\text{C}\equiv\text{C}$ move towards the cathode of embedded rebar and adsorbed on the metal surface and thereby provided

System	Cement	E_{corr} (mV vs. SCE)	I_{corr} (mA.cm ⁻²) × 10 ⁻⁵	Corrosion rate (mmpy) × 10 ⁻³	Inhibitor efficiency (%)
Without electro injection	OPC	-591	91.910	10.650	—
	PPC	-567	82.080	9.512	—
	PSC	-478	30.690	3.556	—
With electro injection	OPC	-282	6.034	0.699	93.43
	PPC	-345	2.276	0.263	97.22
	PSC	-295	2.024	0.234	93.40

Table 6. Polarization parameters for the corrosion of rebar embedded in OPC, PPC, and PSC concretes with and without electro injection process [79].

inhibition. MIP studies (**Figure 11**) proved that nearly 50% reduction in porosity was observed for concrete samples after EICI. SEM analysis (**Figure 12**) indicated that the hybrid inhibitor formulation act as a pore blocking agent. They also found that the EICI treatment can shift the rebar potential (+300 mV) towards the passive region in the potentiodynamic polarization curve (**Figure 13**) with the result the corrosion rate of the rebar also reduced considerably.

Pan et al. [79] evaluated the inhibition efficiency of eight organic inhibitors by monitoring the corrosion rate steel in aggressive, simulated concrete pore solution through electrochemical injection method. The data showed that tetrabutylammonium bromide (TBA-B) and tetramethylammonium chloride (TMA-C) outperformed other chemicals as corrosion inhibitors in the simulated concrete pore solution, by reducing the corrosion rate of steel by 85 and 75%, respectively. Nguyen et al. [80] performed the EICI rehabilitation treatments in repair mortar with tetra butyl ammonium bromide salt at a current density of 5 A/m², by using two electrolytes of 0.1 M NaOH and Na₃BO₃ for 1 and 4 weeks, respectively. The results reveal that the EICI treatment with 0.1 M Na₃BO₃ was more efficient in improving the chloride penetration resistance and the compressive strength of the mortar, relative to 0.1 M NaOH as the electrolyte.

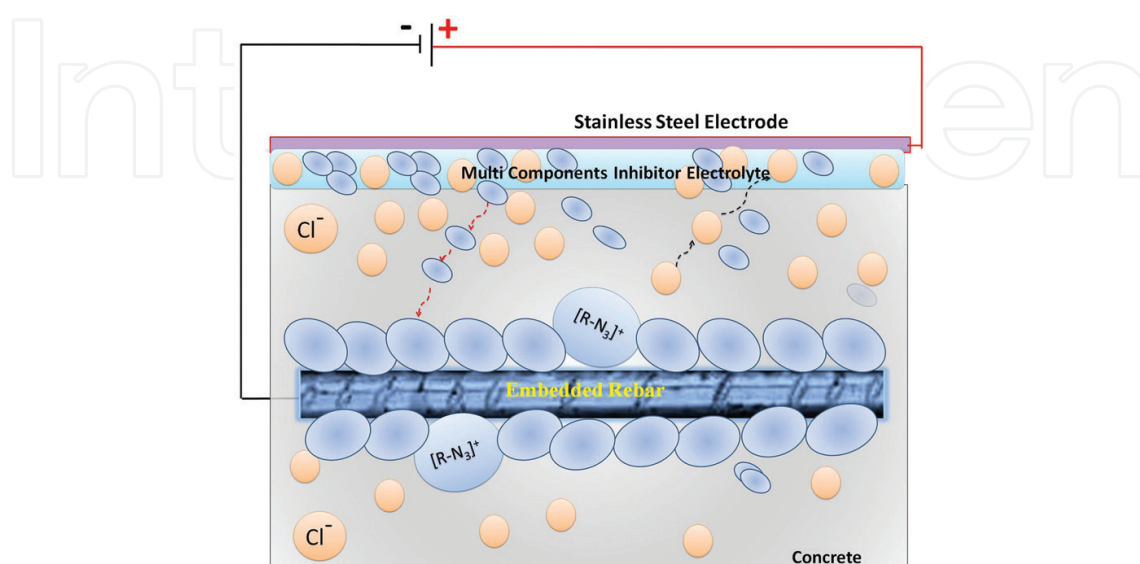


Figure 9. Schematic representation of electrochemical EICI process in concrete [2].

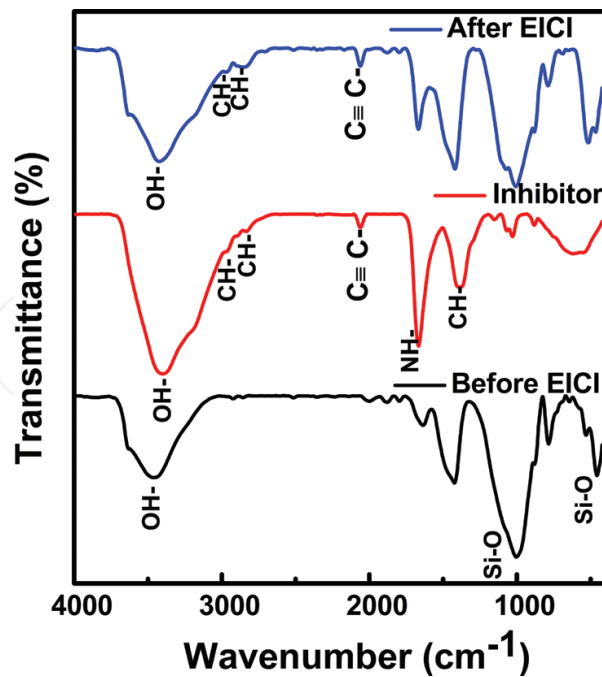


Figure 10. FTIR spectroscopy for concrete—before and after EI [2].

Liu and Shi [81] presented a state of the art report on electrochemical chloride extraction (ECE) and EICI, which covers the laboratory studies and computational models to predict the kinetics of ECE and EICI. Sawada et al. [76] evaluated ethanolamine and guanidine, the two organic inhibitors for steel, in aqueous media by immersing the carbonated and non-carbonated concrete and impressing a current density of 1–5 A/m² for 3–14 days. It was found that the efficiency was far higher in carbonated concrete than in non-carbonated concrete and that, in the carbonated specimens, the inhibitors became concentrated near the embedded steel. In non-carbonated concrete, guanidine penetration was accelerated, but the ethanolamine penetration was not significantly enhanced by the application of current density.

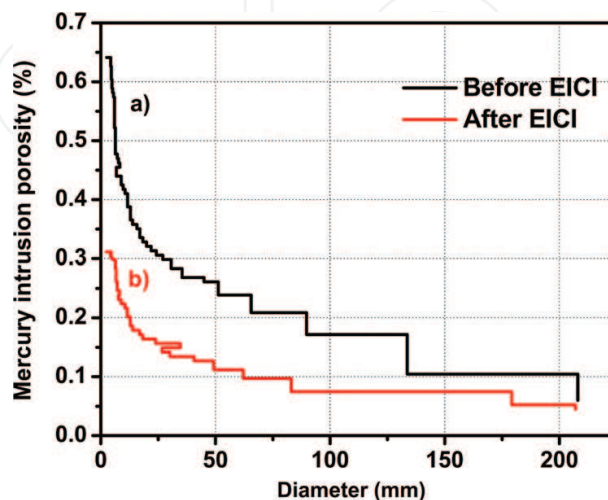


Figure 11. Mercury intrusion porosity for before and after EI process for concrete [2].

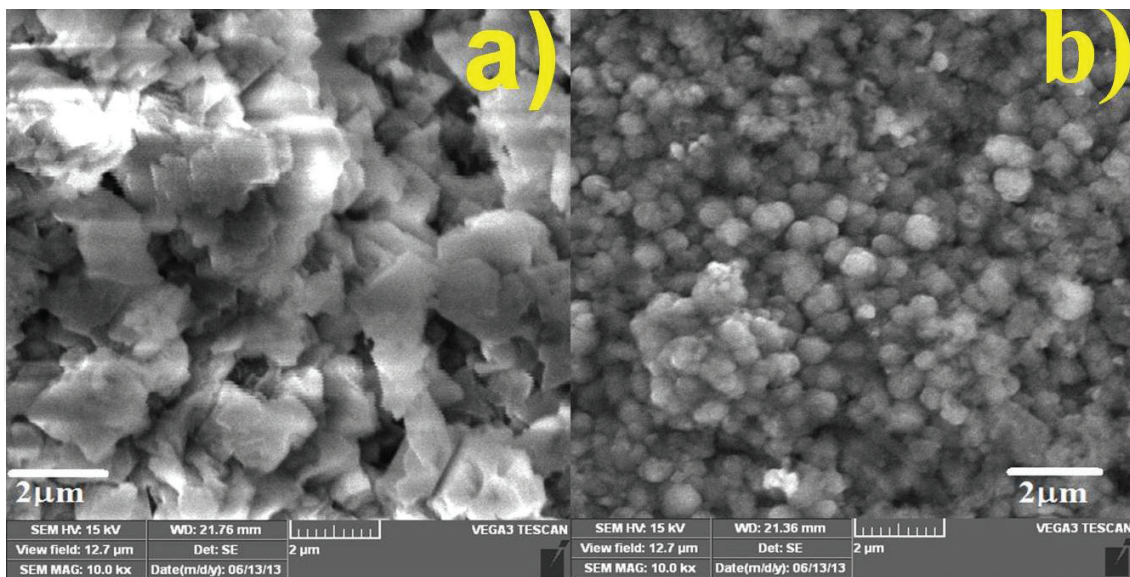


Figure 12. SEM images for concrete before and after EI [2].

Xu et al. [54] adopted a novel method called bi-directional electromigration rehabilitation [BIEM] for injecting the corrosion inhibitor (triethylenetetramine) into chloride-contaminated concrete specimens. In this process, an electric field was applied between the embedded steel cathode and external anode to inject the inhibitor from an external electrolyte to the concrete specimens and extract the chloride ions from the cover zone concrete. After the treatment, the specimens were drilled to determine the concentration profiles of the corrosion inhibitor, chloride, and hydroxyl ions within the concrete. ECE was compared with as a control experiment using saturated $\text{Ca}(\text{OH})_2$ solution as an external electrolyte. They found that the chloride content decreased, and alkalinity increased after treatment. The concentration of the inhibitor injected around the embedded steel bars was adequate to provide corrosion protection. Among

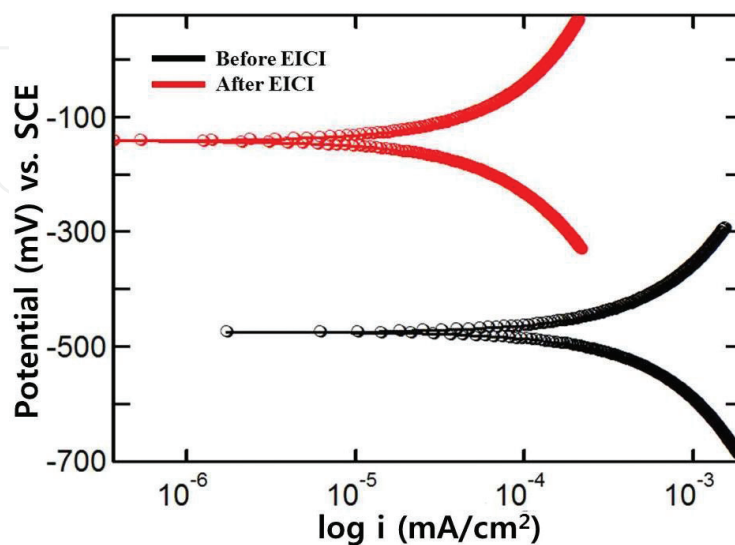


Figure 13. Potentiodynamic polarization curve for rebar in concrete before and after EI [2].

the electrochemical rehabilitation techniques available, ECE is the most widely used method of repairing chloride-contaminated structures. However, this approach cannot completely remove the chlorides in the structure and is only a temporary solution because chloride ions tend to come back after treatment is stopped [75]. Simultaneous effect of chloride removal and re-passivation of concrete by using nitrite (migrating) inhibitor was tried by the application of ECE treatment. The electrochemical response of the embedded rebar after the ECE treatment was found that the migration of nitrite ions re-passivated the steel surface and the chloride removal efficiency was also increased [82].

3. Summary of inhibitors used

Tables 7 and 8 show the review of the most commonly used corrosion inhibitor dosage in concrete. From the table, it is evident that recently organic inhibitors are mainly focused and most of the studies are carried out in simulated concrete pore solution containing chloride. Only a few studies are conducted in mortar and concrete. Very fewer field studies are undertaken.

Reference	Inhibitor used	Dosage	Environment
Jiang et al. [6]	Deoxyribonucleic acid as a biological corrosion inhibitor	0.0025%	Simulated concrete pore solution
Zheng et al. [7]	Organic inhibitors—surface applied		Concrete
Diamanti et al. [22]	Organic inhibitors	0.0001, 0.001, 0.01, and 0.1 M	Concrete pore solution
Xu et al. [33]	Anodic, cathodic, and mixed inhibitors	1, 2% by vol.	Simulated environment
Nahali et al. [41]	Na ₃ PO ₄		Mortar +Cl ⁻
Yohai et al. [42]	Na ₃ PO ₄		Mortar +Cl ⁻
Fei et al. [47]	Cathodic inhibitor		Pore solution
Verbuggen et al. [48]	Organic inhibitors	10 ⁻⁴ M	Concrete pore solution
Ormellese et al. [50]	Organic inhibitors/Migrating	0.3 mol/L	Concrete pore solution
Shi et al. [52]	Migrating corrosion inhibitor		Mortar
Xu et al. [54]	Organic inhibitors—electro-injection		
Criado et al. [66]	Organic inhibitors	0.05 M	Activated fly ash mortar
Prieto et al. [67]	Organic inhibitors—surface applied	0.500 kg/m ²	Mortar
Cabrini et al. [68]	Organic inhibitors	0.1 M	Pore solution
Kubo et al. [78]	Electrochemical injection (Amine based)	0.5–2.0 mol/l	Real concrete bridge (40-year-old railway viaduct)
Sanchez et al. [82]	Electrochemical removal and migration of inhibitor	Nitrite	Reinforced concrete

Table 7. Review of inhibitors in concrete (2010–2017).

Type of inhibitor	Exposure condition	Inhibitors	pH	Dosage	Efficiency (%)	References
Anodic inhibitors	Concrete admixed 1.96% NaCl	Ca(NO ₃) ₂	6.0–6.5	0.49	26.51	[32]
				0.98	60.54	[32]
				1.96	88.65	[32]
	Sat. Ca(OH) ₂ + 3% NaCl	Na ₃ PO ₄	10.5–11.8	1 mol/l	60.02	[38]
				2.5 mol/l	64.85	[38]
				5 mol/l	78.2	[38]
				7.5 mol/l	80.0	[38]
				10 mol/l	78.1	[38]
	Concrete immersed in 3% NaCl	NaNO ₂	7.5–8.5	1%	87.9	[15]
				2%	87.08	[15]
3%				85.83	[15]	
Cathodic Inhibitors	Concrete immersed in 3% NaCl	ZnO	6.95–7.8	1%	93.75	[15]
				2%	94.16	[15]
				3%	91.66	[15]
Mixed Inhibitors or organic inhibitors	Concrete immersed in 3% NaCl	NaNO ₂ + ZnO	7.2–8.5	1%	95.8	[15]
				2%	94.58	[15]
				3%	93.75	[15]
organic inhibitors	Concrete immersed in 3% NaCl	Triethanolamine	6.0–7.0	1%	77.04	[15]
				2%	62.5	[15]
				3%	53.33	[15]
	Concrete immersed in 3% NaCl	Monoethanolamine	11–11.8	1%	49.58	[15]
				2%	50.8	[15]
				3%	38.75	[15]
	Concrete immersed in 3% NaCl	Diethanolamine	9.8–10.2	1%	35.42	[15]
				2%	28.33	[15]
				3%	39.16	[15]
OPC Concrete immersed in 1% NaCl	Disodium β-glycerol phosphate Pentahydrate + sodium 3-aminobenzoate	Adjusted to 7.0	0.05 M + 0.05 M	63	[65]	
			0.05 M + saturated	81	[65]	
		Disodium β-glycerol phosphate pentahydrate + sodium N-phenylanthranilate	adjusted to 7.0			

Table 8. Different type of inhibitor dosage in concrete.

4. Conclusions

The following conclusions were drawn:

- The review focused only on the use of various types of inhibitors in concrete under laboratory and field condition.
- The corrosion inhibitors are effective in preventing reinforcement from corrosion within concrete structures.
- The corrosion inhibitor forms a protective film around the embedded steel bars.
- The inhibitors for concrete are classified as an anodic, cathodic, and mixed type of inhibitors based on the mode of action.
- Recently, mixed and organic types of inhibitors are the most commonly used inhibitors in concrete due to their synergistic effect.
- Organic corrosion inhibitors were ineffective in preventing steel corrosion when their concentrations were too low [19]. The corrosion inhibitors can provide adequate protection for reinforcement only when the concentration of the inhibitor is higher than that of the chloride ions in the pore solution [54].
- Some inhibitors get leached out over an extended period of exposure.
- Over dosage of inhibitors will cause pitting, leaching, and retarding effect.
- While under dosage of inhibitor may lead to inefficient protection of the steel rebars.
- The efficiency of the inhibitor strongly depends on the initial chloride ions concentration in concrete.
- The performance of the inhibitor strongly depends on the quality of concrete.
- Amines-, alkanol amines-, and carboxylate-based mixed inhibitors are mostly used in reinforced concrete.
- Amines and alkanol amines are capable of diffusing through concrete when applied on the surfaces of the structures by capillary action.
- Migrating inhibitors play a significant role in the repair and rehabilitation of damaged and chloride-contaminated concrete structures.
- Migrating or surface applied inhibitors are found to be the cost-effective treatment for field implementation due to the ease of application. For this type of application, penetrating type amine/carboxylic-based inhibitors are preferable.
- The surface-applied inhibitors can penetrate up to the depth of the embedded steel reinforcement; thus, adequate concentrations are necessary to provide corrosion protection when the concrete cover is too thick, or the concrete compaction is too high [83].
- Electrochemical injection of corrosion inhibitors (EICI) is found to be an effective corrosion mitigation technique for carbonated and chloride-contaminated reinforced concrete structures to improve the durability.

- In this type of repair method, continuous monitoring of the condition of steel is essential not only in the electrochemically treated area but also in its adjacent regions.
- Still, the mechanism of mixed/organic inhibitors is not very well understood in long-term applications. Hence, it needs more extensive investigation in real concrete structures by considering the various aspects, such as chloride content, types of cement, types of inhibitors, etc.

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