Corrosion Inhibitors Behaviour on Reinforced Concrete—A Review

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Abstract Corrosion is one of the major deterioration problems in the reinforced concrete industry. Approximately, more than 18 billion dollars per year is incurred on the repair and rehabilitation of corroded structures throughout the world. The occurrence of corrosion is because of chloride particles present in the atmosphere and carbonation process in concrete. Reinforcement corrosion is an electrochemical process that defines the concentrations between variations of dissolved ions in the concrete. This paper focuses on the corrosion inhibitors which are used as migration corrosion inhibitors (applied on the surface) of the concrete specimen and admixed into the concretes. An in-depth study on the mechanism of corrosion and the effect of migrated, cathodic and anodic on reinforced concrete has been performed. A critical review of the causes of the corrosion as well as preventions by using organic, inorganic and natural inhibitors is carried out.

Keywords Electrochemical process · Corrosion inhibitors · Reinforced concrete Anodic · Cathodic

1 Introduction

Concrete is a construction material; it is a combination of binding material (cement) and aggregates such as fine and coarse aggregates. Concrete is weak in tension but strong in compression. To balance the tensile stresses in concrete, reinforcement bar is embedded in the concrete. Corrosion is the key setback of reinforcement in the concrete. Concrete acts as a physical barrier to steel because of its high alkalinity material property and protects the steel against the corrosion. Concrete is a porous material. Because of the porous nature of the concrete, the aggressive agents like chloride ions penetrate and destabilize the passivity film of steel, which leads to

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corrosion. Some of the inhibitors are identified to counteract the corrosion. Inhibitors are chemical substances which reduce the corrosion formation and increase the lifespan of the reinforced concrete structures. Based on the protection mechanism and chemical composition, inhibitors are classified into organic, inorganic and natural inhibitors. Corrosion inhibitors are reducing the rate of corrosion process by escalating the cathodic and anodic polarization behaviour [1]. However, the corrosion inhibitors are admixed and applied on the surface on the reinforced concrete. In the new constructions, corrosion inhibitors are used as admixtures and for existing structures they are used as migrating inhibitors.

2 Mechanism of Corrosion in Reinforced Concrete

2.1 Corrosion

Corrosion of reinforcement is an electrochemical process. Due to variation between the insoluble ions present in the reinforced concrete, susceptible corrosion occurs. The anodic and cathodic reactions are explained in Eqs. (1) and (2). Figure 1 shows the reactions of the corrosion process.

$$\text{Anodic reaction : Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^{-}(\text{oxidation reaction}) \tag{1}$$

$$\text{Cathodic reaction : O}_2 + 2\text{H}_2\text{O} + 4\text{e}^{-} \rightarrow 4\text{OH}(\text{redox reaction}) \tag{2}$$

Carbonation. Carbonation is the chemical process which causes corrosion of reinforcement. The percentage of CO_2 goes on increasing due to the emission of gases from industrial buildings presented mostly in urban areas. The CO_2 reacts with calcium oxide present in the concrete forms as calcium carbonate $CaCo_3$ explained in Eq. (3), and decreases the pH value of the concrete. The decrease in pH value destabilizes the passivity film of reinforcement surface which leads to corrosion [2].

$$\text{Ca(OH)}_2 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CaCO}_3 + 2\text{H}_2\text{O} \tag{3}$$

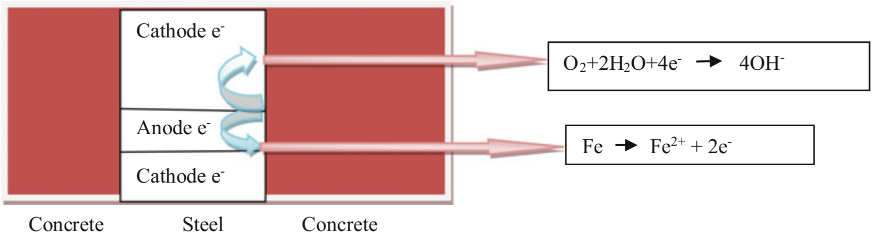

Fig. 1 Representation of corrosion process

Chloride attack. The durability of concrete structures decreases due to the corrosion of reinforcement bar when exposed to aggressive environmental agents like deicing salts and chloride ions. The presence of chlorides destabilizes the surface passivity film even when the pH value is more than 11.5. The preservation of the passivity layer is based on the balance between the amount of OH^- ions (alkalinity) and the quantity of Cl^- ions (acidity) which are explained in Eqs. (4) and (5). The correlation between the chloride ions and hydroxyl ions resists the pitting corrosion pitting rate. The corrosion can be minimized by a decrease in the water/binding ratio, the use of corrosion inhibitors, increasing concrete cover thickness [2].

$$Fe + 3Cl^- \rightarrow FeCl_3^- + 2e^- \quad (4)$$

$$FeCl_3^- + 2OH^- \rightarrow Fe(OH)_2 + 3Cl^- \quad (5)$$

3 Corrosion Inhibitors

Corrosion inhibitor plays an active role in the corrosion process. The rate of corrosion decreases by strengthening the passivity film [3]. Based on the chemical composition, corrosion inhibitors are divided into organic, inorganic and natural inhibitors. Based on the application, they are classified as admixed and migrated inhibitors. According to the protection mechanism, they are divided as anodic, cathodic and both. In the new constructions, corrosion inhibitors used as an admixture and for existing structures they can be used as migrating inhibitors.

3.1 *Organic Inhibitors*

Nowadays, organic corrosion inhibitors become very popular in the construction industry due to their security competence and lesser cost. Organic inhibitors are utilized as both admixed and migrating corrosion inhibitors. Amines and alkanolamines are broadly utilized as natural inhibitors because of their high dissolvability in water and little impact on the properties of concrete in its hardened and fresh state [2]. Alkanol amine-based inhibitors could ready to diminish both chloride- and carbonation-induced corrosions. Furthermore, organic inhibitors can capable to control the corrosion rate of less than 0.1 $\mu A/cm^2$. Organic inhibitors can take up by physisorption or chemisorptions. Physisorption causes the formation of mechanical barrier. In case of chemisorptions, organic inhibitors frame the thin covering film hindering the metal surface from the destructive spices by strapping chemical bonds [4]. Amines and alkanolamines have a poor corrosion inhibition impact contrasted with the carboxylates particularly polycarboxylates [5]. Carboxylate-based inhibitors tend to diminish the rate of hydration in concrete, increasing the setting time [3].

3.2 Inorganic Inhibitors

Inorganic inhibitors are very popular to mitigate the corrosion of reinforced concrete. Calcium nitrite is the most used inorganic inhibitor. 4% Ca $(NO_2)_2$ inhibitor mitigates the corrosion of reinforced concrete, which has no any side effect on strength of the concrete after longer span of structure is exposed to the chloride environment [6]. Calcium nitrite enhances the conversion of unstable ferrous oxides/hydroxides into stable ferric oxides/hydroxides which acts as a burly oxidizing agent on the surface of the reinforcement bar [7, 8]. In case of calcium nitrite-based inhibitors, an utmost concern is required for calculating the essential quantity; as the amount is lesser than essential, it will show the negative effect on both steel and concrete [9]. Some of the European countries like Germany and Switzerland have banned calcium nitrite due to its carcinogenic and toxic reactions [11]. Because of this reason, substitute inhibitors are being contemplated. The other inorganic inhibitor is sodium monoflurophosphate (Na_2PO_3F). Sodium monoflurophosphate (Na_2PO_3F) has the capability to postpone the corrosion beginning and diminish the rate of corrosion, still in the carbonated concrete. The Na_2PO_3F in aqueous and natural environmental experiences hydrolysis, framing orthophosphate and fluoride, which reacts with the corrosion products, warming Fe_3O_4, γ-Fe2O3, and FePO4.H2O passive layers [2]. Red mud is also an inorganic inhibitor, residuum from the bauxite preparing to produce of aluminium. It has that capability to enhance the corrosion resistance in reinforced concrete structures. The fundamental corrosion inhibitors utilized for reinforced concrete structures are listed in Table 1.

3.3 Natural Inhibitors

In the corrosion process, natural inhibitors are more efficient and highly advantageous to the environment than other corrosion inhibitors [10]. Some of the plant sources are used as natural inhibitors like polyphenolics, terpenes, alkaloids, flavonoids, etc. Those have fulfilled all the requirements of natural inhibitors characteristics [11, 12]. Sugar portions of vegetable concentrates were tried as a natural inhibitor in the reinforced concrete [13]. To enhance the mechanical and

Table 1 The ongoing investigation of the fundamental corrosion inhibitors utilized for reinforced concrete structures [2]

Inhibitors	Type	Inhibitors	Type
Sodium nitrite	Inorganic	Amine	Organic
Lithium nitrite	Inorganic	Amino acids	Organic
Potassium chromate	Inorganic	Carboxylates	Organic
Calcium nitrite	Inorganic	Red Mud	Inorganic
Sodium monoflurophosphate	Inorganic	Pharmaceutical compounds	Green
Sodium phosphate	Inorganic	Natural inhibitors	Green

physiochemical properties of reinforced concrete, Magrabe bannan's stem juice is used as concrete admixture [14]. To improve the strength of reinforced concrete contaminated by sulphate and chloride, Bambusa arundinacea extract is utilized as a natural corrosion inhibitor [13]. Red mud is used as a green inhibitor; it is a composite based on ferric oxide, alumina and a residuum originated from bauxite refining for aluminium protection. Red mud demonstrates a critical diminishing in the rate of corrosion, as the percentage of red mud content is increased in the reinforced concrete [2]. Few recommendations are agricultural by-products such as sugar cane bagasse, coconut shell, palm oil fruit bunch, rice husk ash, etc., which can able to reduce the corrosion initiation.

3.4 Anodic Inhibitors

Anodic inhibitors form the insoluble passivity layer on the surface of steel bar and stop the corrosion process. Passivating inhibitors such as nitrites represented as a special type of anodic inhibitors if they are present in sufficient concentration [3]. They are two types of passivating inhibitors, i.e. non-oxidizing ions and oxidizing anions. In case of oxidizing anions, passivating of steel happens in the absence of oxygen. The non-oxidizing ions require the presence of oxygen for the passivity of the steel [1]. Reinforced concretes rely on the utilization of calcium nitrite [Ca (NO_2O_2] and calcium nitrate [Ca $(NO_3)_2$] as an anodic inhibitor, as they introduce comparable inhibiting properties [5]. Molybdates, nitrates, chromates, orthophosphates, and benzoates are used as anodic inhibitors.

3.5 Cathodic Inhibitors

Cathodic inhibitors resisting corrosion by slow down the cathodic reactions rate. Carbonates, phosphates, silicates, zinc oxide and polyphosphates are examples of cathodic inhibitors [15]. These inhibitors have metal ions; they have the ability to generate a cathodic reaction of the metal due to alkalinity, thus producing insoluble compounds that precipitate selectively on the cathodic site. Cathodic inhibitors do not depend on the metal composition; it only depends on the chemistry of water; because of this, they are applicable to all metals [16]. Cathodic inhibitors are less efficient than anodic inhibitors; these inhibitors will not create any pitting [17].

3.6 Admixed Inhibitors

Corrosion inhibiting concrete admixtures is providing protection to reinforcement against corrosion. Organic inhibitors are very popular to use as admixed in the concrete. Amines and alkanol mines and their salts are utilized as organic inhibitors in the concrete [18]. These inhibitors are mixed into the concrete in the plastic state. At that moment, the mixing water is in contact with the steel surface. At the time of concreting, they are considered as corrosion inhibitors since they connect synthetically or electrochemically with the surface of the steel [5]. These inhibitors prevent the reinforcement bar against the corrosion by shaping a thin layer of defensive obstruction film on the surface of the rebar through adsorption component [1]. Pozzolanic materials (Fly ash, silica fume) are also used as admixed inhibitor in the reinforced concrete because of having glassy siliceous materials which contain aluminous compounds [19].

Admixed corrosion inhibitors can persuade the rate of cement hydration process and enhance the mechanical conflict and other properties [20]. Sodium nitrite or potassium nitrites cause a reduction in the compressive strength and raise the danger of alkali–aggregate reaction. Then again, the calcium nitrite quickens the cement hydration, which requires the expansion of a water reducer and a setting retarder in the solid blend [2].

3.7 Migrating Corrosion Inhibitors (MCI)

An MCI is applied to the outside surface of the hardened concrete, and furthermore, the inhibitors ought to infiltrate into the concrete cover and achieve the steel support in an adequately high focus to ensure the steel against the corrosion. This MCI focuses more on the way of application and focuses less on the electrochemical interaction between the steel and inhibitor [3]. In the case of MCIs, organic inhibitor compounds like amine, alkanolamines and carboxylic are very popular. Organic inhibitors stifle the both cathodic and anodic responses by shaping a monolayer film at the concrete–steel interface [21]. In the event of inorganic inhibitors, sodium monoflurophosphate can be generally utilized as a part of the field to save the beginning of consumption or to decrease the rate of erosion [22]. Monoflurophosphate is applied at the concrete surface in the form of an aqueous solution with a mass rate run between 10 and 20% [23].

4 Conclusion

- This paper reviewed on the applications of different corrosion inhibitors in reinforced concrete in case of field and laboratory conditions.
- Corrosion inhibitors are an efficient method of preventing corrosion, economical and simple application method.
- Passivity film is developed around the steel bar as corrosion inhibitors are used in reinforced concrete.

- When the chloride ions concentration was less than the corrosion inhibitors concentration, then only reinforcement is protected by corrosion inhibitors.
- The optimum quantity of corrosion inhibitors only should be used in the concrete, and more than optimum quantity causes to leaching, pitting and retarding effect.
- Amines, alkanolamines and carboxylates are mostly used mixed inhibitors in reinforced concrete.
- Migrating corrosion inhibitors (MCI) play an important role in the strengthening of deteriorated structures due to chloride ions ingress into the concrete.
- MCI is more focused on the way of application and less focused on the electrochemical interaction between the steel bar and inhibitor.
- Most of the inhibitors demonstrate auxiliary impacts on the fresh and solidified concrete. Nitrites/nitrates quicken the setting of fresh concrete, where the same number of carboxylic acids tends to hinder the cement hydration rate [3].
- Sodium monoflurophosphate is mostly used MCI among all others.
- Natural inhibitors are more efficient and highly advantageous to resist corrosion and its environmentally friendly.
- Paddy ash and palm oil fruit bunch perform very effectively to resist the chloride and carbonation effects on reinforced concrete.

References

1. Lee, H. S., Saraswathy, V., Kwon, S. J., Karthick, S. (2018). Corrosion inhibitors for reinforced concrete: A review. In *Corrosion inhibitors, principles and recent applications*. https://doi.org/10.5772/intechopen.72572.
2. Rivetti, M. L. S., da Silva Andrade Neto, J. de Amorim Junior, N. S., Ribeiro, D. V. (2018). Corrosion inhibitors for reinforced concrete. In *Corrosion inhibitors, principles and recent applications*. https://doi.org/10.5772/intechopen.72772.
3. Myrdal, R. (2010). *Corrosion inhibitors—state of the art*.
4. Diamanti, M., Ormellese, M., & Perez-Rosales, E. V. (2016). An experimental and theoretical study of the inhibition mechanism of organic substances in concrete. *Une, 13*(10), 15.
5. Elsener, B., Angst, U. (2015). *Corrosion inhibitors for reinforced concrete*. Science and Technology of Concrete Admixtures, Elsevier Ltd. https://doi.org/10.1016/b978-0-08-100693-1.00014-x.
6. Batis, G., Siders, K. K., & Pantazopoulu, P. G. (2016). Anti-corrosion methods and materials influence of calcium nitrite inhibitor on the durability of mortars under contaminated chloride and sulphate environments. *Materials, 51*(23), 182–190. https://doi.org/10.1108/00035590410523201.
7. Ormellese, M., Berra, M., Bolzoni, F., & Pastore, T. (2006). Corrosion inhibitors for chlorides induced corrosion in reinforced concrete structures. *Cement and Concrete Research, 36*(3), 536–547. https://doi.org/10.1016/j.cemconres.2005.11.007.
8. Wieczorek G, Gust J (1995) Corrosion inhibitors. In *Proceedings of 8th European Symposium*, (pp. 599–608). University de ferrara, Italy.
9. Abudul Rahaman, A. S., Ismail, M., & Hussain, M. S. (2011). Corrosion inhibitors for steel reinforcement in concrete: A review. *Scientific Research and Essays, 6,* 4152–4162. https://doi.org/10.5897/SRE11.1051.

10. Salawu, A. A., Ismail, M., Majid, M. Z. A., Majid, Z. A., Abdullah, C., & Mirza, J. (2014). Green *Bambusa Arundinacea* leaves extract as a sustainable corrosion inhibitor in steel reinforced concrete. *Journal of Cleaner Production, 67,* 139–146. https://doi.org/10.1016/j.jclepro.2013.12.033.
11. Raja, P. B., & Sethuraman, M. G. (2008). Inhibitive effect of black pepper extract on the sulphuric acid corrosion of mild steel. *Materials Letters, 62*(17–18), 2977–2979. https://doi.org/10.1016/j.matlet.2008.01.087.
12. Kesavan, D., Gopiraman, M., & Sulochana, N. (2012). Green inhibitors for corrosion of metals: A review. *Chemical Science Review and Letters, 1*(1), 1–8.
13. Raja, P., Ghoreishiamiri, S., & Ismail, M. (2015). Natural corrosion inhibitors for steel reinforcement in concrete—a review. *Surface Review and Letters, 22*(03), 1550040. https://doi.org/10.1142/S0218625X15500407.
14. Berke, N. S., Rosenberg, A. (1989). Technical review of calcium nitrite corrosion inhibitor in concrete. *Transportation Research Record*, *1211*, 18–27. http://www.scopus.com/inward/record.url?eid=2-s2.00024775345&partnerID=40&md5=4cec0e2e96870184eb9ba388c6d59e7a.
15. de Rincón, T., Perez, O., Paredes, E., Caldera, Y., Urdaneta, C., & Sandoval, I. (2002). Long-term performance of ZnO as a rebar corrosion inhibitor. *Cement and Concrete Composites, 24*(1), 79–87. https://doi.org/10.1016/s0958-9465(01)00029-4.
16. Roberge, P. R. (1999). *Hand book of corrosion engineering*. New York: Mc Graw Hill Hand book.
17. Davis, J. R. (2000). *Corrosion: Understanding the basics*. Materials park, OH, USA: ASM international, p. 563. ISNB:978-0-871470-641-6.
18. Angst, U. M., Buchler, M., Schlumpf, J., & Marazzani, B. (2016). An organic corrosion-inhibiting admixture for reinforced concrete: 18 years of field experience. *Materials and Structures/Materiaux et Constructions, 49*(7), 2807–2818. https://doi.org/10.1617/s11527-015-0687-2.
19. Shi, X. X., Fortune, K. N., & Gong, J. (2012). Durability of steel reinforced concrete in chloride environments: An overview. *Construction and Building Materials, 30,* 125–138. https://doi.org/10.1016/j.conbuildmat.2011.12.038.
20. Gaidis, James M. (2004). Chemistry of corrosion inhibitors. *Cement and Concrete Composites, 26*(3), 181–189. https://doi.org/10.1016/S0958-9465(03)00037-4.
21. Holloway, L., Nairn, K., & Forsyth, M. (2004). Concentration monitoring and performance of a migratory corrosion inhibitor in steel-reinforced concrete. *Cement and Concrete Research, 34*(8), 1435–1440. https://doi.org/10.1016/j.cemconres.2004.01.019.
22. Monticelli, C., Fringnani, A., & Trabanelli, G. (2000). Study on corrosion inhibitors for concrete application. *Cement and Concrete Research, 30*(4), 635–642. https://doi.org/10.1016/S0008-8846(00)00221-0.
23. Chaussadent, T., Nobel-Pujol, V., Farcas, F., Isabelle, M., & Fiaud, C. (2006). Effectiveness conditions of sodium monoflurophosphate as a corrosion inhibitor for concrete reinforcements. *Cement and Concrete Research, 36*(3), 556–561. https://doi.org/10.1016/j.cemconres.2005.09.006.
24. Dariva, C. G., Galio, A. F. (2018). *Corrosion inhibitors-principals, mechanisms and applications*. http://dx.doi.org/10.5772/57255.intechopen.
25. Xu, C., Jin, W., & Wang, H. (2016). Organic corrosion inhibitor of triethylenetetramine into chloride contamination concrete by electro-injection method. *Construction and Building Materials, 115,* 602–617. https://doi.org/10.1016/j.conbuildmat.2016.04.076.
26. Bryan, N. S., Alexander, D. D., Coughlin, J. R., Mikowski, A. L., & Boffetta, P. (2012). Ingested nitrate and nitrite and stomach cancer risk: An updated review. *Food and Chemical Toxicology, 50*(10), 3646–3665. https://doi.org/10.1016/j.fct.2012.07.062.
27. Selim, L., & Tantawi, Z. S. H. (1996). Improvement of concrete properties and reinforcing steel inhibition using a natural product admixture. *Journal of Materials Science and Technology, 12*(2), 95–99.