Chapter 6

Sustainable Corrosion Inhibitors for Concrete

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Abstract

Green chemistry and sustainability encourages the significance of preserving the nature and individual's wellbeing in cost effective way that intends to avoid toxicity and reduction of wastes. Therefore, the implication of green corrosion inhibitors in the field of concrete protection has also received immense attention these days. Indeed, the usage of such inhibitors is a well-known strategy for producing high performance concrete. In view of this, the present chapter discusses the research in the area of sustainable corrosion inhibitors for concrete assurance used commercially in various industries. It also highlights the concrete corrosion mechanisms and its protective measures, recent advances in this field.

Keywords

Concrete, Inhibitors, Reinforcement, SEM, Sustainable, EIS

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1. Introduction

Concrete is a mixture which usually consists of cement, water and aggregates that has been utilised in the major amount as structural material in past years. Cement is one of the primary segment of concrete which produces a paste when dissolved in water that settles and stiffens because of hydration phenomenon. Generally, concrete is relatively feeble in tension, thus changes must be done for the improvement in the tensile strength of the framework which could be by shifting to the different component that is strong in tension. In view of this, concrete frameworks are frequently toughened by embedding steel ribs, usually called as reinforcement in concrete. But, the primary obstacle in reinforcement in concrete is corrosion. Corrosion is a process which brings about the deterioration or decay of a material when exposed to severe environmental conditions [1]. Usually, concrete results in exquisite corrosion shielding. The immense alkaline condition in concrete leads to the development of a firmly adhering film, that passivates the steel, thereby safeguarding it from corrosion [2]. As per the literature, it is expected that the alkalinity of the concrete with pH values ranging from 12 to 14 promotes the production of a passive layer that helps in the shielding of the steel reinforced corrosion [3,4]. Passivation implies the inability of metals to lose electrons in the anodic process that makes metal inert in any corrosive condition. But, the assurance given by the concrete is not adequate because of the porosity of the material and inbuilt crevices which subsequently permits the penetration of aggressive substances like chloride ions and carbon dioxide (CO₂) that results in the reinforcement of steel corrosion by eliminating the protective adhering film over the surface [5]. Rapid degradation could be brought about via chloride ions in the marine region [6] or because of the usage of defrost salts or

via carbonation in urban regions [7]. Steel corrosion in concrete could be diminished by implication of numerous recognized strategies [8]; choice of steel that is corrosion-resistant, utilisation of coatings, incorporation of concrete sealers, usage of massive concrete covering, inclusion of corrosion inhibitors or cathodic protection. So as to give extra protection and enhance the life expectancy of reinforced concrete frameworks, various substances recognized as corrosion inhibitors have been employed in current years. Inhibitors can be termed as chemical molecules which eliminates the corrosion and increments the life expectancy of the reinforced concrete arrangement without essentially modifying the amount of added corrosive agent [9]. The utilization of inhibitors is a promising method contrasted to any alternative traditional strategies for safety and rehabilitation, because of their low expense and easy application [10].

Green chemistry has been drawing attention significantly in several areas by scheming chemicals, chemical techniques, and industrial substances with the intention to evade contaminants as well as decrease wastage. One of the branches in which green chemistry is providing development by encouraging the reduction of the ecological effect and the wastes is the field of metallic corrosion. Corrosion of metallic components is significant that is broadly considered an industrial issue, thus it has been discovered as a fruitful analysis area in sustainability. Green inhibitors are drawing considerable focus in the field of corrosion because of their immunity, biodegradability and sustainability [11]. Sustainability in the construction industry could be attained by means of various approaches, with decrease in consumption of gross energy, polluting discharge, and non-renewable natural resources. Considering all these, the following chapter talks about several sustainable corrosion inhibitors established for the concrete, their mechanisms of action and the requirement for green/sustainable corrosion inhibitors for the future with enhanced improvements.

2. Classification of corrosion inhibitors

Corrosion inhibitor portrays a prominent function in the corrosion phenomenon. Concrete corrosion inhibitors may be distinguished as organic, inorganic and natural inhibitors on the basis of the chemical composition. It is well represented in the schematic flow chart illustrated in Fig.1.

Figure 1. Schematic flow chart for illustrating the classification of concrete corrosion.

2.1 Organic inhibitors

Amines and alkanolamines have been extensively employed as an organic inhibitors due to their good solubility in water as well as they do not affect the behaviour of concrete [12]. Alkanol amine derived inhibitors might be used to reduce chloride as well as carbonation induced corrosion. Amines and alkanolamines possess unsatisfactory corrosion inhibitory effect as compared to the carboxylates especially polycarboxylates [13]. Carboxylate derived inhibitors will in general reduce the extent of hydration that occurs in concrete, expanding the setting duration [14].

2.2 Inorganic inhibitors

Inorganic inhibitors are incredibly pervasive for providing protection to reinforcement steel corrosion. Calcium nitrite is one of the widely utilised inorganic inhibitor. 4% $\text{Ca}(\text{NO}_2)_2$ prevents reinforced steel corrosion, that may impart negligible adverse consequence on the quality of the concrete even if the structure is treated in the chloride environment for a longer duration [6]. Although for calcium nitrite derived inhibitors, a prime attention is needed for ascertaining the requisite amount; as if the concentration is lower than the requisite, it would reflect the bad effect together on steel as well as concrete [9]. Many European countries such as Germany and Switzerland have forbidden calcium nitrite as a result of its harmful and lethal reactions [15]. Because of this reason, alternative inhibitors have been considered. Another inorganic inhibitor that has been

used is sodium monofluorophosphate ($\text{Na}_2\text{PO}_3\text{F}$). $\text{Na}_2\text{PO}_3\text{F}$ in aqueous and natural condition is susceptible to hydrolysis, producing orthophosphate in addition to fluoride that interacts with the corrosive substances like Fe_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$, or $\text{FePO}_4\cdot\text{H}_2\text{O}$. Red mud, residuum from the bauxite is additionally used as an inorganic inhibitor, which possess the ability to improve the corrosion protection in reinforced concrete frameworks [12].

2.3 Natural inhibitors

For the corrosion phenomenon, natural inhibitors can be considered as most effective as well as exceptionally beneficial for the surroundings as compared to other corrosion inhibitors [16]. Researchers nowadays are focusing in the direction of establishing natural strategies for corrosion issues. Their main objective is to develop cost effective, less hazardous, environmental friendly and biocompatible corrosion inhibitors. Few plant extracts have been utilised as natural inhibitors such as polyphenolics, terpenes, alkaloids, flavonoids, and so on which fulfil entire characteristics of natural inhibitors [17]. Sugar portions of vegetable extracts has been tested for providing good inhibition naturally to reinforced steel corrosion [18]. In order to improve the mechanical behaviour of reinforced concrete, Magrabe banana's stem juice has been employed as concrete admixture [19]. To enhance the durability of reinforced concrete deteriorated via sulphate or chloride ions, *Bambusa arundinacea* extract has been used as a green corrosion inhibitor [18].

3. Mechanism of corrosion in reinforced concrete

For an appropriate comprehension about the mechanisms of the inhibitor's action, it is primarily important to comprehend the process associated with the corrosion of reinforced steel [14]. The corrosion phenomenon of the reinforced concrete framework is an electrochemical procedure that usually happens with the change in the amount of soluble ions in the interior of concrete, building electrochemical potential cells or corrosion cells, outlined with the movement of electrons or ions among the cathodic and anodic zones. Various anodic as well as cathodic reactions are elucidated in equations described below (Eq. 1-5). The schematic representation of the overall reaction mechanism in order to provide the better picture of electrochemical corrosion phenomenon is also represented in Fig. 2.

Anodic reactions

Cathodic reaction

Figure 2. Model for electrochemical phenomenon for corrosion of steel in concrete.

3.1 Carbonation

Carbonation is a procedure where carbon dioxide gets through the concrete via diffusion reacts with the water existing in the pores, subsequently produces carbonic acid. Carbonic acid further associates to the calcium hydroxide formed at the time of the cement hydration, bringing about the development of calcium carbonate. Such process results in the declination of the surrounding pH to about 8 because the produced CaCO_3 is less basic as compared to the calcium hydroxide [20]. Such pH decrease is accountable for the destabilization of the passivation layer, thereby commencing the corrosion phenomenon. The overall carbonation process could be reflected from Eq. 6 and 7:

3.2 Chloride attack

Chloride attack is primarily the main reason behind the reinforced steel corrosion. The existence of chlorides ions (Cl^-) in concrete usually originates from seawater, coastal

areas, setting time accelerator additives having CaCl_2 , water or pollutants from industrial contaminants and they may be attributed as the main causes of reinforced concrete corrosion [21]. Chloride ions penetrate to the concrete through the pore network and micro cracks, producing the oxide film over the reinforcing steel and therefore speeds up the reaction of corrosion and concrete deterioration [22]. Appearance of chloride ions in the solution encompassing iron, which binds to Fe^{2+} of passive layer onto the metallic surface and develops an iron–chloride complex (Eq. 8). Further hydrolysis of such complex leads to ferrous hydroxide in addition to chloride ions that are available for additional attack above the steel surface (Eq. 9).

4. Recent developments on sustainable corrosion inhibitors for concrete

Usually, corrosion inhibitors for reinforced steel in concrete are incorporated single time in the structure and an efficient inhibitor for reinforced concrete must possess following characteristics:

- efficient even at very less concentrations
- long term endurance in the interior of the solid
- homogeneous distribution
- They may be easily detachable from concrete and should not affect the characteristics of the concrete.

Ecological issues are expanding globally and may probably going to impact the selection criteria for corrosion inhibitors in the next generation. Eco-friendly and cost effective inhibitors which may overcome the requirement for synthesis [23] were demonstrated to be productive and exceptionally advantageous for the surroundings and are proven to be sustainable contrasted to few organic as well as inorganic inhibitors [23]. Plant sources fulfil all basic necessities as their derivatives specifically alkaloids, flavonoids, terpenes or polyphenolics are highly enriched with electron donating hetero groups (S, N, O and conjugated π electrons). These plants are rich source of naturally produced chemical substances, which may be removed via easier and low-cost processes, besides being biodegradable. Therefore, plant sources can be utilized to produce natural and sustainable corrosion inhibitors, hence its current advancements has been investigated in several papers [24,25]. In view of this, biomass or renewable raw substances can be employed for several industrial applications to promote green chemistry and sustainability. One of the areas where green chemistry, usually related to biomass-derived substance, is

establishing advancements, by decreasing the ecological impact and the wastes, is linked to the safeguarding metals. Fig. 3 illustrates the use of natural sources and biomass wastes extracts as sustainable corrosion inhibitors for steel reinforced corrosion. The significance of developing bio-wastes is important in the field of corrosion. Few works that studied the extracts from natural residues or bio-wastes, that are usually scrapped in the surroundings otherwise, are employed as corrosion inhibitors by many researchers.

Figure 3. Extracts used as sustainable corrosion inhibitors for steel reinforced corrosion.

Quraishi et al. [26] explored the effects of calcium palmitate solely and in aggregation with calcium nitrite on the corrosion of steel in concrete. The results of the study proved calcium palmitate as a proficient and promising inhibitor; providing 91 to 92% efficiency after 90 days of treatment in 3.5% NaCl environment. It was also shown that the inhibitor do not have any effect on the mechanical durability of cement as well as concrete. Petro graphic study revealed that calcium palmitate blocks the pores, subsequently reducing the extent of corrosion. Further investigation suggested that calcium palmitate inhibited corrosion through adsorption mechanism. Inhibitor created the film over the steel surface by means of polar carboxylate group obstructing the pores and thus producing insoluble hydrophobic ferric stearate salt.

Palanisamy et al. [27] analysed the activity of another plant extract i.e. *Prosopis juliflora* on the corrosion of reinforced steel in 3.5 % NaCl. Corrosion tests were conducted for 30 days immersion time of rebar without and with the inhibitor. From corrosion tests, it was revealed that the corrosion inhibitor reached the efficiency of 91% at 120 ppm concentration of inhibitor.

Zhang and his co-authors [28] examined the corrosion inhibitory behaviour of maize gluten meal extracts for steel in simulated concrete pore solution having 3.0 wt% NaCl. The outcomes of EIS and polarization measurements have been found to be in good correlation with each other that suggested an increment in the corrosion inhibition of steel after addition of extract relatively to the solution. Adsorption of inhibitor on the metallic surface obeyed Langmuir adsorption isotherm which may be primarily due to physisorption. Moreover, the amide moieties in the primary components of extract were additionally helpful to provide adherence to the surface of steel. The sustainable extract is obtained as a by-product from starch manufacturer that is proven to be an efficient and natural inhibitor for combating concrete corrosion having efficiency of 62.71–88.10%.

Pradipta and co-workers [29] showed that at same volume, green tea extract (GT) displayed an elevated inhibition efficiency (I.E.) as compared to widely used calcium nitrite inhibitor for the corrosion of reinforced steel inserted in mortar. GT acted as a mixed type corrosion inhibitor that enhanced rebar polarization resistance (R_p); reflecting the generation of a protective covering on steel surface. After the development of such layer, rebar corrosion was diminished. Surface studies indicated that the film was rich in calcium, particularly the calcium carbonate polymorphs.

Anitha et al. [30] assessed *Rosa damascena* leaves as a green corrosion inhibitor for reinforced steel corrosion (Fig. 4). The anticorrosion performance has been estimated using electrochemical impedance technique in addition to polarisation measurements in simulated pore solution. The adsorption phenomenon followed Langmuir adsorption isotherm indicating the physisorption mechanism. The highest inhibition efficiency was found to be 82% having 12 v/v % compositions. SEM representations described the chelating behaviour of phytochemical components comprising hetero atoms like Oxygen, Nitrogen or aromatic and pi electrons associating to iron ions and thereby promoting the protection for metallic corrosion.

Figure 4. Illustration of mechanism of *Rosa damascene* as sustainable/green corrosion inhibitor for reinforced steel corrosion. Reproduced with permission from [30]; Copyright 2019 @ Elsevier.

Replacement of cement powder with sustainable waste products is the primary attention of research in concrete field. Loto and his co-authors [31] investigated cow bone ash (CBA) for estimating anticorrosion behaviour on mild steel corrosion in artificial concrete pore solution using potentiodynamic polarization study and current–time displacement studies. Recorded data reflected that CBA extensively diminished the corrosion process with highest inhibition efficiency of 80.18% having 20% CBA showed anodic sort of inhibition. Also, the cathodic side of the polarization plot depicted eminent reduction in slope after 0% CBA.

Shubina et al. [32] reported biomolecules as potential environmental friendly inhibitor for steel reinforcement in concrete. Biomolecules employed in present investigation are one of the new categories of substances generated from bacterial cells. The inhibition behavior in simulated concrete pore solution has been illustrated utilizing classical electrochemical techniques and microscopic studies. The reduction in corrosion current density was found to be significant after including 1 gL^{-1} of inhibitor in the simulated concrete pore solution. Linear Polarization measurements as well as Electrochemical Impedance analysis reflected comparatively better inhibition performance ($\approx 58.6\%$).

Furthermore, XPS studies and SEM results depicted that such kind of biomolecules might be considered as film producing mixed type inhibitor.

Abbas et al. [33] investigated the performance of green inhibitor extracted from the waste of orange peels. They extracted dry orange peel using methanol extract at 6-hour immersion time in methanol with the pressure of 60 mbar and 40°C. From the experimental data like electrochemical polarisation measurements and weight-loss testing performed for 7 days immersion time of rebar, it was demonstrated that this inhibition showed a good performance in aqueous 3.5 wt% NaCl solutions. The steel rebar showed that the corrosion rates of rebar reduced to 0.02 mm/year at 3% composition of inhibitor.

Akshatha et al [34] performed studies on inhibitor with leaves of *ruta graveolens* and *azadirachta*. The extracted leaf of *Azadirachta indica* (neem) and *ruta graveolens* plants were used as organic inhibitors. Comparison with inorganic inhibitor like sodium nitrate and ethylene diamine tetra acetic (EDTA) disodium dehydrate was also done. The inhibitors were added during mixing of concrete and the reinforcing steel bar. The concrete was made of cement of OPC 43 grade with specific gravity 3.279. The rebar was dipped in hydrochloric acid (HCl), sodium chloride (NaCl) and magnesium sulphate (MgSO₄) solution for performing corrosion tests. From half-cell potential measurement, experiment in 5% HCl for 56 days, it can be seen that extracts of *Azadirachta Indica* have shown the most positive potential, followed by *ruta graveolens*, sodium nitrate and EDTA disodium dihydrate. The same trend was also observed when the experiments were conducted in 5% NaCl solutions which illustrated that *Azadirachta Indica* gave the most positive corrosion potential.

Shaymaa et al. [35] studied powdered rice husk for corrosion of steel in concrete. Extract of rice husk was included to the concrete with American mix design method (ACI 211) with the strength of 30 MPa in 28 days. The samples of rebar were treated with tap water for 30 days and immersed in 3.5% NaCl environment. Corrosion experiments were conducted for the solution of varied concentrations (1%, 2% and 3%) of inhibitor. The corrosion current was determined to be 41.3 $\mu\text{A}/\text{cm}^2$ for the solution without inhibitor which becomes 28.5 $\mu\text{A}/\text{cm}^2$ and 7.8 $\mu\text{A}/\text{cm}^2$ for the solution having 1% and 3% rice husk powder concentration, respectively. It signified that the reduction of corrosion rate was 30% and 81% respectively

Joshua et al. [36] characterized *phyllanthus muellerianus* as an inhibitor that promote sustainability for combating concrete steel-reinforcement corrosion in industrial condition. They used 0.5M H₂SO₄ media to simulate industrial/microbial condition. At the concentration of 6.67 g/L, this inhibitor reduced corrosion rate of rebar to 90%. While at the concentration of 1.67%, the reducing corrosion rate was found out to be 78%. From

investigation, leaves of *phyllanthus muellerianus* and *euphorbiaceae* contained tannins, phlobatanins, saponins, flavooids, terpenoids and alkanoids as major constituents.

Vernonia amygdalina extract has been examined as green corrosion inhibitor for mild steel rebar concrete in 3.5M NaCl solution by Loto et al. [37]. Corrosion resistance of *Vernonia amygdalina* was analysed using weight loss technique, potential & pH estimations and several concrete parameters were further discussed. The inclusion of *Vernonia amygdalina* extract into the solution significantly changed the potential, pH and compressive strength.

Okeniyi et al. [38] investigated *Rhizophora mangle* L extract which behaved as effective corrosion inhibitor admixture for reinforcing steel in 0.5M H₂SO₄. The electrochemical outcomes were analysed by using statistical distribution fitting models and subsequent inhibition efficiencies were further estimated. Inhibition efficiencies outcomes by experimental procedure and theoretical calculations has been plotted with respect to various amounts of extract; correlation and conflict among experimental data and theoretical assumed data has been also evaluated.

Eyu et al. [39] discussed the anticorrosion performance of *Vernonia amygdalina* extract for carbon steel in concrete in 3.5M NaCl solution. Corrosion study was performed using weight loss experiments, corrosion potential calculations, half-cell calculations, concrete resistivity measurement as well as visual analysis. The outcomes acquired were also correlated with commercially available inhibitors like sodium nitrite or calcium nitrites. Phytochemical constituents of *Vernonia amygdalina* extract were described to contain alkaloids, saponins and tannins. Corrosion tests may be illustrated by the plots against weight loss, inhibition efficiency as well as corrosion rate. Outcomes achieved evidently discussed that *Vernonia amygdalina* extract showed analogous corrosion resistance when compared to commercially available inhibitors (Sodium nitrate and Calcium Nitrite).

Abdulrahman et al. [40] has broadly discussed and illustrated the anticorrosion behaviour of *Bambusa arundinacea* (BA) extract for reinforced steel corrosion in concrete. It was investigated to enhance the strength of concrete polluted by chloride or sulphate environment. The obtained data was correlated with known Calcium nitrite and ethanolamine inhibitors. Effect of inclusion of MgCl₂ and MgSO₄ over concrete strength had been estimated and elucidated. Fundamental advantages of present analyses illustrate that inclusion of inhibitor shows negligible adverse effect on concrete durability. BA did not comprise any heavy metal that also eliminates the risk of production of dioxin on interacting with chloride contaminated water.

Lisha et al. [41] used *azadirachta indica* (neem) powder and dehydrated aloe vera as corrosion inhibitor for steel in concrete. M 25 grade concrete was used with coarse

aggregates of 20 mm size. The concrete was immersed in solution with salinity of about 3.5% (35 g/L). The concrete with green corrosion inhibitors has reduced corrosion rate of steel on concrete from 0.3 to 0.22 mm/y. Aloe vera inhibitor extract was able to diminish corrosion rate to 0.27 mm/y. The results of study showed that *azadirachta indica* (neem) reflects better corrosion inhibition efficiency when compared to the aloe vera inhibitor.

Conclusions and outlook

Usually, inorganic/chemical inhibitors have been employed in corrosion protection of steels in concretes. However, due to its hazardous nature for the environment, usages of such inhibitors are going to be confined. As a substitute, green/sustainable corrosion inhibitors have gained much interest in choosing inhibitors for reinforced steel. Such green inhibitors fulfil all the needed features of inhibitors employed for steel in concretes that includes lower cost, compatibility with concretes, non-toxicity, biodegradability and applicability for industrial constructions. Mechanism theories of inhibitors in combating corrosion phenomenon in steel rebar include formation of barrier film over the metallic surface via physical/chemical reactions among steel and concretes. Therefore, they don't allow the penetration of corrosive ions to the metallic surface by obstructing concrete pores. Additionally, inhibitors could interfere anodic or cathodic reactions which diminish the corrosion rates. Subsequently, the demand of eco-friendly inhibitors for steel rebar has enhanced significantly. From the literature, several evidences conclude that the plant or biomass waste extracts might be used as excellent corrosion inhibitors for steel reinforced corrosion. Moreover, competing with the higher inhibition efficiency obtained by ideal inorganic/chemical inhibitors should be considered in the future and may be a significant area of future research. But, from the studies, it can be confidently concluded that green inhibitors will continue to provide corrosion protection in the future with further modifications. Future improvements may include development of modified corrosion inhibitors possessing excellent adsorption ability to attain more attractive anticorrosion performance.

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