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Recent advances in the use of inhibitors to prevent chloride-induced corrosion in reinforced concrete --Manuscript Draft--

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Abstract:	<p>Rebars corrosion is one of the most important phenomena affecting durability of reinforced concrete structures. Corrosion inhibitors are considered as an effective preventative technique to delay the onset of corrosion and/reduce the corrosion rate. Substances can be both organic and inorganic in nature. Besides the well-known effectiveness of nitrite-based inhibitor, new organic and inorganic substances have been investigated as alternative to face safety and environmental issues related to nitrites. From the '90s, a wide number of organic substances were studied, including amines, alkanolamines, carboxylates and mixtures of esters. The present literature review is focused on the effectiveness of the most commonly used inhibitors as nitrites and amines. The use of alternative inhibitors, as nitrates, new organic and green compounds, i.e. natural substances typically extracted from plants, is investigated.</p>
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Dear Editor,

I am enclosing herewith a manuscript entitled:

“Recent advances in the use of inhibitors to prevent chloride-induced corrosion in reinforced concrete”

The manuscript has been prepared according to the “Cement and Concrete Research” guidelines.

The article is as state of art on the use of corrosion inhibitors in concrete to prevent chloride-induced corrosion. Both inorganic and organic substances have been considered. Among the first group, nitrite and nitrate efficiency has been investigated. To overcome the drawback of nitrites, in the last 20-30 years a wide number of organic substances were studied, including amines, alkanolamines, carboxylates and mixtures of esters. In the last decade, more attention has been given to the use of natural compounds, than a section has been dedicated to green inhibitors extracted from different kind of leaves.

All authors of this review paper have directly participated in this study; all authors have read and approved the final version submitted. The authors declare no competing financial interest. No specific funding source has supported this research. The paper is original and not considered for publication elsewhere. Please consider it for publishing in your Journal. Thank you for kind attention.

Best regards,

Marco Ormellese

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Highlight

- Corrosion inhibitors are a low cost and easy handling method
- Nitrites are the most efficient available inhibitor
- Nitrates seems to be promising alternative
- DMEA, TETA and benzoate are the most efficient organic compounds
- Green substances extracted from leaves shoed promising results

Recent advances in the use of inhibitors to prevent chloride-induced corrosion in reinforced concrete

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ABSTRACT

Rebars corrosion is one of the most important phenomena affecting durability of reinforced concrete structures. Corrosion inhibitors are considered as an effective preventative technique to delay the onset of corrosion and/reduce the corrosion rate. Substances can be both organic and inorganic in nature. Besides the well-known effectiveness of nitrite-based inhibitor, new organic and inorganic substances have been investigated as alternative to face safety and environmental issues related to nitrites. From the '90s, a wide number of organic substances were studied, including amines, alkanolamines, carboxylates and mixtures of esters. The present literature review is focused on the effectiveness of the most commonly used inhibitors as nitrites and amines. The use of alternative inhibitors, as nitrates, new organic and green compounds, i.e. natural substances typically extracted from plants, is investigated.

Keywords: corrosion, chloride, concrete, durability, inhibitors, nitrite, nitrate, organic, green.

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1. INTRODUCTION

Reinforced concrete is a versatile, economical and successful construction material: “the combination of high compression strength of concrete and high tensile properties of reinforcing steel gives an ideal composite material which offers, compared to other materials, a wide range of applications in structural engineering” [1]. The highly alkaline pore solution (pH around 13), formed during cement hydration, allow to protect the carbon steel reinforcements embedded inside concrete, promoting their passivation. Nevertheless, the passivity condition can decay (i.e. depassivation) with consequent breakdown of the protecting oxide layer on the rebars surface. The two main reasons are attributed to the presence of chlorides at the carbon steel surface, in a content higher than a critical threshold, and to the concrete pore solution pH reduction, generated by the reaction with atmospheric carbon dioxide [1]. Once corrosion has initiated, the reduction of reinforcements cross section and the concrete cover cracking and spalling arise, leading to structural complications. To avoid or reduce corrosion, high quality concrete (low W/C ratio and use of blended cement), proper curing times and adequate concrete cover are mandatory. Additional prevention methods, as corrosion inhibitors, external coatings, corrosion resistant rebars and cathodic prevention or protection, may be considered in severe working condition or when very long service life are requested [1].

Among these methods, corrosion inhibitors have been successfully applied for preventing corrosion in many fields for many years, due to their low costs and easy handling [2-4].

According to ISO 8044, a corrosion inhibitor can be defined as a chemical substance that, when present in the corrosion system at a suitable (preferably small) concentration, decreases the corrosion rate, without significantly changing the concentration of any corrosive agent [5].

According to the general service life model by Tuutti (Figure 1), corrosion inhibitors may have the ability to increase both the initiation time and the propagation period. In the first case, they can strengthen the passivity of carbon steel rebar by promoting an increase of the chloride

threshold necessary to initiate corrosion. They can also create a barrier effect, by limiting the diffusion of aggressive species, as chloride ions, even if the latter cannot be considered a real inhibitive effect. Corrosion inhibitor can further influence the corrosion propagation phase, by producing a reduction in the rebar's corrosion rate [3, 6].

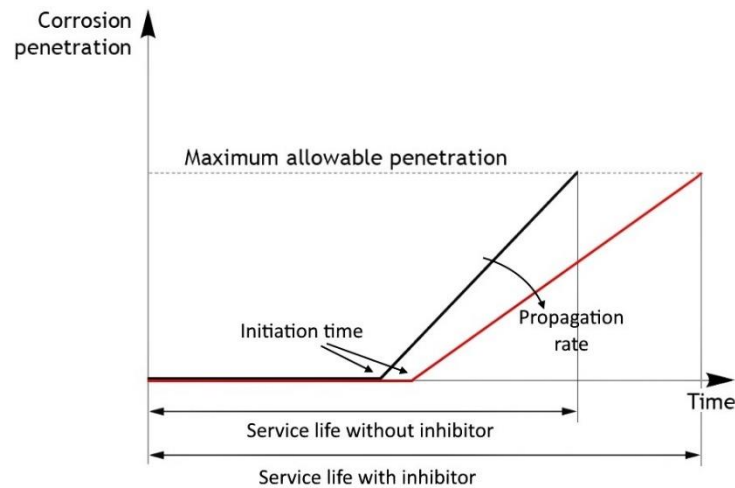


Figure 1 - Influence of the inhibitor on the service life

According to the application method, inhibitors in concrete can be classified in admixed corrosion inhibitors, directly added to the fresh concrete as preventative method, or in migrating corrosion inhibitors, applied on the surface of the hardened concrete as a curative repair technique.

The substances can be both organic and inorganic in nature. Nitrites were firstly used in concrete from the 50s. Besides the well-established effective nitrite-based inhibitor, new organic and inorganic substances have been investigated as alternative to overcome the safety and environmental issues related to nitrites. During the 1990s, a wide number of organic inhibitors were developed, including amines, alkanolamines, carboxylates and emulsified mixtures of esters, alcohols and amines [2-4]. More recently, nitrate ions was suggested as possible alternative inorganic inhibitor, by virtue of its harmless and compatibility with the concrete matrix, enough to be commonly used as set accelerator [7].

The present literature review is focused on the effectiveness of the most commonly used inhibitors as nitrites, nitrates, organic compounds, to face chloride-induced corrosion. A final section is dedicated to the use of green compounds, natural substances typically extracted from plants for corrosion prevention. These inhibitors have become priority for researchers: they are suggested as substitute of chemicals inhibitors, which are environmentally hazardous substances.

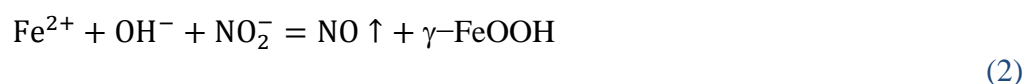
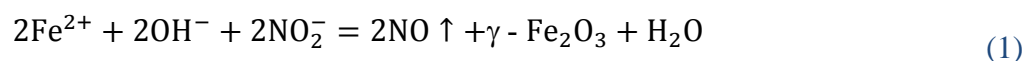
2. NITRITE-BASED INHIBITORS

The first literature reference regarding the investigation on nitrite as concrete inhibitor is dated in the late 1950s in the Soviet Union, where a mixture of nitrite and nitrate (NO_3^-) of sodium and CaCl_2 were used as a protection strategy against corrosion caused by de-icing salts. Due to loss in compressive strength and risk of alkali-aggregate reactions, the use of calcium nitrite ($\text{Ca}(\text{NO}_2)_2$) was investigated [8-9].

Commercial calcium nitrite was introduced only in the middle of the 1970s, in Japan and United States. Over the 1980s and 1990s, nitrite-based inhibitors were used as protection strategy in large structures, as viaducts and bridges, worldwide [10-13].

Inorganic nitrite compounds (NO_2^-) are anodic inhibitors, they directly interferes with the anodic dissolution reaction of steel during chloride- or carbonation-induced attack.

Nitrite ions, dissolved in the alkaline pore solution, react with the ferrous ions of the reinforcements forming stable iron oxides that preserve the surface passive layer [14-15]. The redox reactions (1) and (2) show the mechanism:



Ferrous ions (Fe^{2+}) are oxidized to ferric ions (Fe^{3+}), forming a passivating ferric oxide layer on the steel surface because they are insoluble in the alkaline pore solution and block the transport of ferrous ions into the concrete electrolyte [3].

The nitrite inhibitory effect is based on its ability to reduce itself, oxidising the ferrous ions: nitrite is not integrated into the passivity film, but it competes against chloride [16-19].

The effectiveness of nitrite corrosion inhibition in chloride-induced attack can be evaluate considering the molar ratio between the nitrite and chloride ions concentrations, $[\text{NO}_2^-]/[\text{Cl}^-]$. Ratios higher than 0.5-0.6 are required to prevent corrosion [3, 13-19]. If chloride ions are present in the concrete pore solution, nitrites will compete with them forming ferritic ions and the passive layer on the reinforcement's surface. Hence, the inhibitor concentration required for protection is determined by the level of chlorides to which the concrete structure will be exposed, determined by the atmospheric aggressiveness.

An experimental work confirmed that after 5 years, concrete samples with nitrite concentrations higher than the required one were still in passivity condition [18-19]. Ann et al. [16] showed the relation between carbon steel corrosion rate and the molar ratio (Figure 2): when the molar ratio is higher than 0.7, corrosion of rebar is negligible. Consequently, nitrite-based corrosion inhibitors have a direct effect on the critical chloride threshold. By increasing the dosage of corrosion inhibitor, the critical chloride threshold may increase from 0.4% with respect the cement weight, the typical value for carbon steel rebar [1], up to 3% at the maximum allowable dosage [11-19].

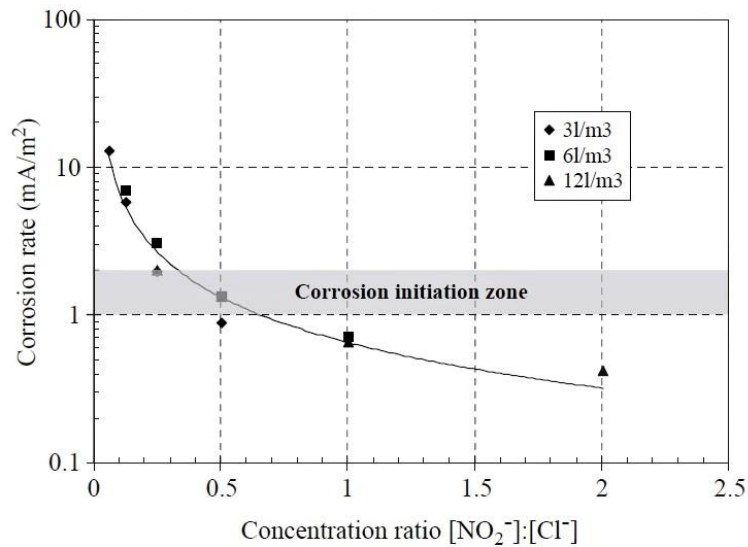


Figure 2 - Corrosion rate trend in function of $[\text{NO}_2^-] / [\text{Cl}^-]$ ratio [16].

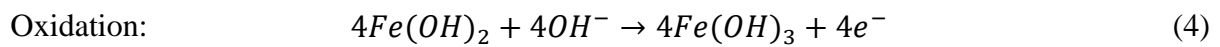
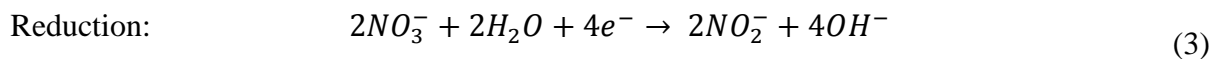
More recently, the inhibitive effect of nitrites was studied in combination with the use of Layered Double Hydroxides (LDH), a kind of anionic clay minerals that can be used as a new class of smart functional additives with unique benefits. Nitrite ions encapsulated were able to provide a corrosion protection for carbon steel, in both synthetic pore solution and concrete. In fact, based on an ion-exchange principle, the synthesized LDH-NO₂ is able to absorb Cl⁻ ions and release of OH⁻ and NO₂⁻ ions simultaneously, this increasing alkalinity and inhibition [21-22].

3. NITRATE-BASED INHIBITORS

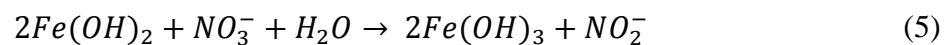
An inorganic alternative to nitrite-based inhibitor is calcium nitrate (Ca(NO₃)₂). Nitrate is a polyatomic ion, mainly produced for agricultural use as fertilizers because of its high solubility and biodegradability. The second major application of nitrates is as food preservatives [23]. Comparing to nitrite compounds, nitrates are cheaper and less harmful to the environment; in addition, they are commonly used as set accelerator, demonstrating their perfect compatibility with concrete [24].

The first research regarding nitrates dates back to 1987: D'yachenko et al. investigated the inhibiting efficiency of nitrate and nitrite mixtures with respect chloride-induced corrosion on reinforced concrete samples [25]. More recently, the effect of nitrite and nitrate in alkali-activated slag and in layered double hydroxides has been investigated [26-28].

The inhibiting mechanism of calcium nitrate for the corrosion of steel in concrete was suggested firstly by Justnes in 1994 and better clarified later, in 2000 [29]. Like nitrite, it is considered an anodic corrosion inhibitor, able to favour carbon steel passivation. Nitrate behaviour as corrosion inhibitor can be understood through the mechanism of the related nitrite ion, as previously described. Justnes exploited this mechanism and extended it to the nitrate behaviour; in particular, he assumed that the oxidation action of nitrate is the consequence to its easy reduction to nitrite. The two half-reactions illustrating the mechanism are:

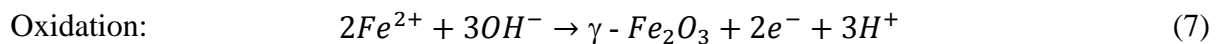
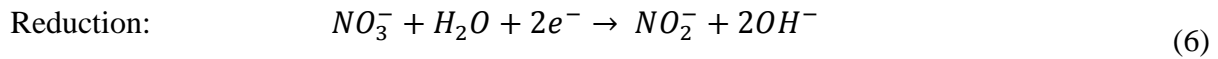


They are combined to give the total reaction:



Nitrate (NO_3^-) should be an even better inhibitor than nitrite (NO_2^-), since the amount of moles of ferrous oxide that reacts with one mole of inhibitor is doubled with respect to the nitrite reaction. However, the experimental results obtained by Justnes did not confirm this enhanced inhibition efficiency: calcium nitrate did not appear to work when subjected to rapid solution tests as well as the corresponding nitrite compound [29]. This suggested that the kinetic of the redox reactions regarding nitrate are slower than nitrite. Justnes himself, and other studies, assessed the delay in this inhibition mechanism evolution [7, 30-32].

An alternative hypothesis regarding the inhibiting mechanism of nitrate was suggested by Saura et al. in 2011 [33]; in particular, the behaviour and the efficiency of sodium nitrate ($NaNO_3$) was analysed. In contrast to Justnes hypothesis, the authors considered a different ferrous oxide compound reaction. The two proposed half equations are:



The above mechanism was assessed in simulating concrete pore solution and the $\gamma-Fe_2O_3$ formed layer was proved to be stable in alkaline environments, inducing a strong protective effect on the steel surface. Nevertheless, problems in the passive film stability were observed in neutral or low-pH solutions; as consequence, it was assumed that nitrate protective effect could be limited in carbonation-induced corrosion [33].

The efficiency of nitrate-based compounds is still today an active topic. Many case studies are present in literature and most of them show conflicting results about the real inhibition effect. The first documented beneficial effect goes back to 1995, when Meland et al. [34] investigated a deteriorated reinforced concrete structure subjected to 22 years of external contamination by calcium nitrate. They found that the carbon steel rebars in severely nitrate-polluted areas (NO_3^- concentration higher than 1.5%) were in perfect condition with only surface rust. In the same years, Vogelsang [35] studied the effect of nitrate on carbon steel samples immersed in alkaline solutions. He proved that calcium nitrate and nitrite had identical corrosion inhibiting properties in pitting-induced corrosion by chlorides contamination.

Justnes and Nygaard [7] reported additional validation of nitrate inhibition effectiveness in chloride-induced corrosion by long-term macro-cell tests in concrete. Concrete samples were cast with Ordinary Portland Cement, a W/C ratio 0.55 and calcium nitrate was added in

concentration 3.86% by cement weight. To induce corrosion, samples were wetted with a 5% NaCl solution. As reported in Table 1, a retarded inhibition action of calcium nitrate was observed: after 14 months, corrosion rate was reduced by a factor of five, to almost negligible values, similar to the value of the unpolluted concrete (time 0). No indication are reported regarding the critical chloride threshold in the presence of calcium nitrate, but only the percentage of chloride in the surrounding environment.

Table 1 - Potential measurement and corrosion rate evaluation in time [7].

Time	E_{corr} (mV CSE)	Corrosion rate (µm/year)
0	-360	2.1 ± 1
3.5 months	-600	13 ± 4
5 months	-600	12 ± 2
10.5 months	-330	19 ± 3
14.5 months	-300	2 ± 1

In 2000, another Justnes' study [29] demonstrated that 2% of calcium nitrate by weight of cement was sufficient to delay chloride-induced corrosion of carbon steel embedded in concrete. Al-Almoudi et al. [11] achieved similar conclusions in 2003: the corrosion of steel reinforcements in concrete mortars was effectively inhibited by calcium nitrate if contaminated by 0.8% of chloride ions. Pitting initiation was delayed and rebars corrosion rate reduced by calcium nitrate in dosages higher than 3% by cement weight.

Different results were obtained in a subsequent study of Dhouibi et al. [36]: electrochemical impedance spectroscopy (EIS) on concrete specimens with admixed calcium nitrate (concentrations 2%, 4% and 6% by weight of cement) showed that the long-term corrosion inhibition effectiveness was not achieved.

The results seem in partial agreement with Diamanti et al. [30]. The inhibition effect of nitrites and nitrates was studied in simulated concrete pore solution polluted with chlorides 0.1 mol/L or 0.3 mol/L. The inhibition effect, measured by means of the pitting potential determination (Figure 3), was significantly improved in presence of nitrites 0.1 mol/L, while in presence of nitrates the inhibition was achieved only adding nitrates 7 days before chlorides, above all in the presence of the highest inhibitor dosage.

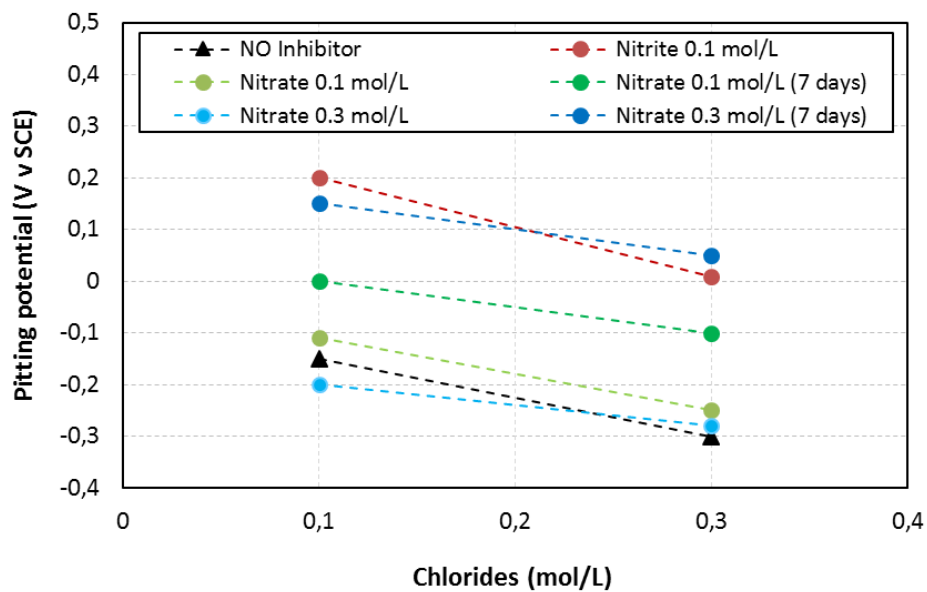


Figure 3 – Effect of nitrites and nitrates on pitting potential

Most of the recent works seem to be in line with Justnes, confirming the effective inhibition mechanism on chloride-induced corrosion of calcium nitrate at concentrations higher than 3% by weight of cement. Ostnor and Justnes [37] showed effective corrosion rate reduction of steel reinforcements embedded in concrete structures exposed to marine tidal zones: adding 3% of cement mass of $\text{Ca}(\text{NO}_3)_2$, the rebars were protected against chloride-induced corrosion. More recently, a mixture of nitrate and nitrite was incorporated into alkali-activated slag. Initially, nitrites and nitrates are sequestered into the hydrotalcite, to avoid inhibitors leaching. As chlorides enter into concrete, hydrotalcite releases nitrite and nitrate and immobilise

chlorides. As such, the ratio between inhibitor and chlorides is maintained, contributing to mitigate corrosion initiation [26-28].

4. ORGANIC INHIBITORS

Organic compounds are filming inhibitors, able to adsorb on carbon steel rebar. By modulating the functional group responsible of the adsorption (as $R-NR_2$, $R-OH$, $-S^-$, $R-COO^-$ and $R-SO_3^-$) and the carbon chain length ($-R$), they can act both as a physical barrier, with a sort of steric effect, avoiding chlorides to come in contact with carbon steel rebar, and as an electrostatic repulsion effect if the chain R has a negatively charged end. Some compounds are chelating agents, and they can form five- to six-membered chelate rings with the carbon steel surface; typically the rings are formed thanks to the chemical bonding between two or more functional groups present in the inhibitor chemical formula, as $-NH_2$, $-OH$, $-SH$ or $-COOH$ [3-4, 38-39].

Amine and alkanolamines are by far the most common family of organic additives used in concrete.

Dimethyl-ethanol-amine (DMEA) is widely used as active principle in many commercial inhibitors. There are conflicting results regarding its efficiency. It is claimed to adsorb on carbon steel surface, forming a very thin and protective oxide layer that limits the attack by chlorides. Indeed, DMEA contains one hydroxyl and one amine group, which both work as nucleophilic ends, able to react with iron metal. In particular, the lone pair of electrons found in the hydroxyl and amine groups donate to the vacant d-orbital of iron atom, allowing the formation of a coordinate covalent bond [3, 4].

More recently, the role of DMEA in synergy with other additives has been explored; the corrosion resistance of steel rebars in concrete has been evaluated after the addition to the mixture of several pozzolanic materials (fly ash, silica fume and polypropylene fibers) and DMEA [41]. The inhibitor increased the overall compressive strength of concrete, up to the 20% after 90 days of curing. This is due to the adsorption process of the inhibitor on the metal surface and the stability of the adsorption layer. The study concluded that the best mixture proportion for

corrosion resistance of reinforced concrete was the one with 25% fly ash, 10% silica fume and 3% inhibitor. Indeed, a dosage from 10 L/m³ to 15 L/m³ of commercial inhibitor (containing DMEA about 20%) should be employed, for normal and severe conditions, respectively. Bolzoni et al. [42-43] confirmed the DMEA containing commercial inhibitor is able to increase the critical chloride content up to maximum 1.2-1.3 % with respect cement weight. Tests were performed on concrete specimen cast with OCP, a W/C 0.6 exposed to chloride penetration. Corrosion on concrete with inhibitor initiated 10 months later with respect the initiation of corrosion on not treated concrete.

Alternative substances were studied as alternative to DMEA [44-60].

Ormellese et al. investigated the use of several organic substances [39, 46-48]. They compared the efficiency of more than 80 pure organic compounds in inhibiting chloride-induced corrosion, in both solution and concrete. Triethylenetetramine (TETA), sodium benzoate, sodium glutamine and asparagine were able to avoid the initiation of corrosion in alkaline solution polluted with 1 mol/l of chlorides. The substances were able to increase the critical chloride content up to 1.5-2% with respect cement weight. Time-to-corrosion has been increased by a factor of minimum two. The substances were added to the fresh concrete in dosage 1% with respect the cement weight not to affect the workability of fresh concrete and the mechanical properties of the hardened concrete.

Xu et al. [49] investigated the use of TETA. They introduced TETA into chloride-contaminated concrete specimens applying a new technique called bi-directional electro-migration rehabilitation (BIEM). The technique is based on the application of an electric field to inject the inhibitor to carbonated or not-carbonated concrete specimens and extract the chloride ions from the concrete cover zone (Figure 4). The efficiencies of Cl⁻ extraction, OH⁻ enhancement and TETA migration increased as the BIEM current density, BIEM treatment time and W/C ratio

increased. The migration efficiency of the TETA in carbonated concrete resulted higher than in non-carbonated one.

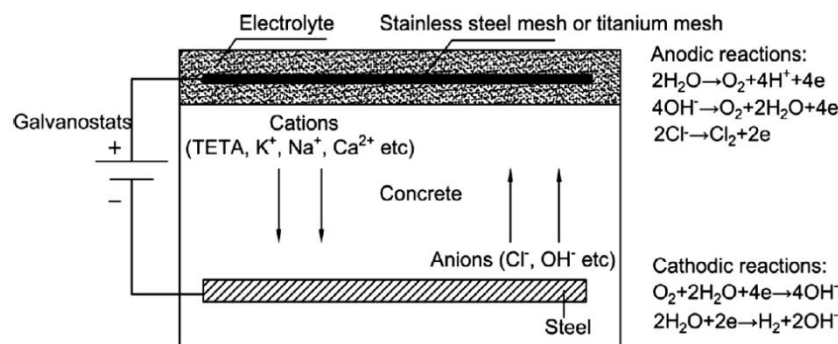


Figure 4 - Schematic of the working mechanism of BIEM [49].

Shen et al. [50] studied the anticorrosion performance of three nitrogen-based electro-migrating inhibitors: guanidine, 1,6-hexamethylenediamine (HMDA) and 3-aminopropyltriethoxysilane (APS). The application of these additives positively affects the concrete durability, by improving the water resistance and the ability of withstanding both chloride and carbonation corrosion initiation. In particular, HMDA reduced the water absorption and carbonation rate, while APS enhanced the hydrophobicity of concrete, thanks to the formation of Si-O-Si bonds with the silicate substrate. APS alkyl groups were able to prevent the wetting of the pores, by blocking the water molecules. The experiments revealed that both APS and HMDA demonstrated a more efficient prevention against external aggressive factors with respect to guanidine, which in turn can improve the alkalinity of cement mortar.

As previously mentioned, carboxylate compounds are another commonly employed category of organic corrosion inhibitors in concrete. Liu et al. [51] analysed the efficiency of benzoate and dimethylethanolamine: differently from conventional amino alcohol inhibitor, the new additive demonstrated to increase the chloride threshold and decreased the area affected by corrosion, even after 120 days of exposure. The inhibition mechanism is based on quick adsorption and buffering effect at initial time, followed by the deposition of a stable and insoluble layer on steel

surface after long-term immersion in chloride-rich environment. This deposited film slows down the dissolution of the oxide film. Carboxylate is a mixed type of corrosion inhibitor, since it can decrease the corrosion current density by inhibiting both the anodic and cathodic reactions, ensuring an overall 63% efficiency (calculated by mass loss method).

A comprehensive comparison of two carboxylate compounds (sodium tartrate and sodium benzoate), one long chain salt of an amino-acid (sodium glutamate) and two amines (DMEA and TETA) was the subject of another research study [52]. Sodium tartrate showed the overall best inhibitive performance, due to its adsorption strength, excellent surface coverage and the chloride ions repulsion produced by the exposed carboxylate anions. Similarly, sodium benzoate also presented a considerable adsorption energy and a uniform distribution when adsorbing on γ -FeOOH. Sodium glutamate demonstrated the highest adsorption among the anionic inhibitors, with a carboxylate distribution similar to tartrate, reaching a high pitting potential. On the contrary, amine-based inhibitors showed poor inhibition effect, because of a weak repulsive interaction with chloride ions. Tartrate, benzoate and glutamate, all resulted in a good inhibition effect at low chloride concentration (0.1 M NaCl), with an increase of pitting potential larger than 650 mV with respect to the reference solution, while DMEA and to a lower extent TETA were less performing. In the case of a higher content of NaCl (i.e. 0.3 M), amines did not produce any significant inhibitive action, with a substantially unaltered E_{pit} . On the contrary, benzoate and glutamate allowed a small increase in pitting potential, while tartrate was the only species that kept a good inhibitive performance, with pitting potential almost 500 mV higher than in the reference solution. The results of the increase in pitting potentials are summarized in Figure 5.

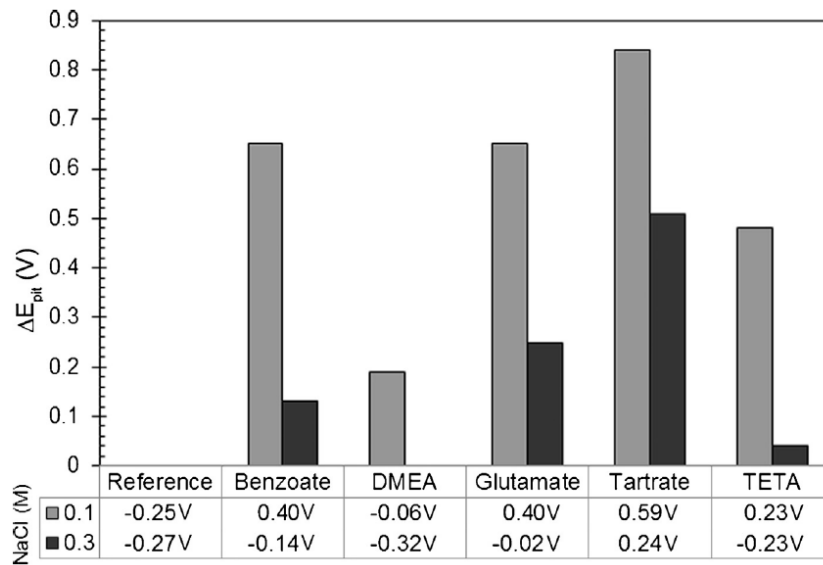


Figure 5 - Increase of the pitting potential, ΔE_{pit} , in presence of different species of inhibitors (in concentration 0.1 M) in SCP solution, with the addition of 0.1 M or 0.3 M NaCl. Pitting potential values, E_{pit} , are expressed in V SCE [52].

Wang et al. [53] (SO) studied the inhibitive action of sodium oleate. It inhibited pitting corrosion of carbon steel at early stages of exposure. With extended test time, carbon steel showed passive behaviour and SO could effectively decrease the passive current density. Thanks to its action, the final number of pits decreased, and the distribution of the inhibitor on the surface was found to be very homogeneous. The molecular simulation results showed that the HOMO of SO is mainly distributed on the oleic acid group, while the LUMO of SO is mainly distributed in the middle of the long carbon chain.

Corrosion inhibitors based on sulfonates are promising organic alternatives to amines. In one study, the application of tri-ethanol ammonium dodecylbenzene sulfonate (TDS) is analyzed. TDS is characterized by low pollution and cost-efficiency. TDS molecules are adsorbed on the passive film through physical or chemical ways, thanks to the presence of the electronegative S atom and the benzene ring. With more TDS added into the alkaline simulated concrete pore solution, both the pitting potential and charge transfer resistance increased, while the corrosion

current density and the double layer capacitance decrease significantly. Moreover, TDS reduced the donor density of the passive film, ensuring a more stable passive film [54].

Another study by Wang et al. [53] focused on the use of calcium lignosulfonate (CLS). The adsorption of CLS occurs particularly at the corroded areas of the steel surface, due to the interactions involving the electrons of the sinapyl alcohol monomer and the vacant d-orbitals of iron atoms. CLS inhibited pitting corrosion of carbon steel at both early stages and extended test times of exposure. A concentration of 0.001 mol/L corresponded to an inhibition efficiency larger than 97%; even in 7200 h weight loss test, CLS still showed high inhibition efficiency over 90%. With longer immersion time, a homogeneous adsorption film forms on the surface.

Organic inhibitors such as aminoethanol, diethanolamine, alkanolamines and carboxylates have been studied as efficient inhibitors for rebar corrosion, but their synthetic strategy and toxic nature limit greatly their usage. Polymeric inhibitors have recently gained attention as a valid alternative, due to their multiple adsorption sites availability, easy synthesis, low cost and capability of adsorbing larger surface. Nevertheless, works carried out with polymers are still rare and scanty.

The use of linear polyesters has been the subject of a recent research study. In particular, two linear macromolecules have been considered: the aliphatic polyglycerol azealate (PGAZ) and the aromatic 4-1-4-methoxyphenyl cyclohexylhenyl 9-oxodecanoate (MPOD). The two polyesters were synthesized and evaluated for rebar corrosion in alkaline solution at selected concentrations of 10, 100, 1000 ppm. A maximum inhibition efficiency of 71.8% was reported for MPOD and a minimum efficiency of 57.7% was found for PGAZ, primarily due the difference in aromaticity [55].

Bhuvaneshwari et al. [56] investigated a novel azomethine-based polyester (PAME). A maximum inhibition efficiency of 98% at 1000 ppm PAME concentration was found. The formation of a highly protective PAME film on carbon steel has been demonstrated. At larger

polymer concentrations, the thickness of the protective layer increased, accompanied by an increase in inhibition efficiency. PAME contains both the azomethine and the polyester functional groups. According to the proposed mechanism, the whole macromolecule is expected to be adsorbed on the metal surface, with an almost flat orientation, arranging parallel to each other and covering the entire metal surface, preventing the access of aggressive species, as chlorides. The final configuration of the adsorbed macromolecule on the steel surface is depicted in Figure 6. The adsorption isotherm calculated for PAME inhibitor in presence of chloride contaminated SPC solution follows the Langmuir adsorption isotherm.

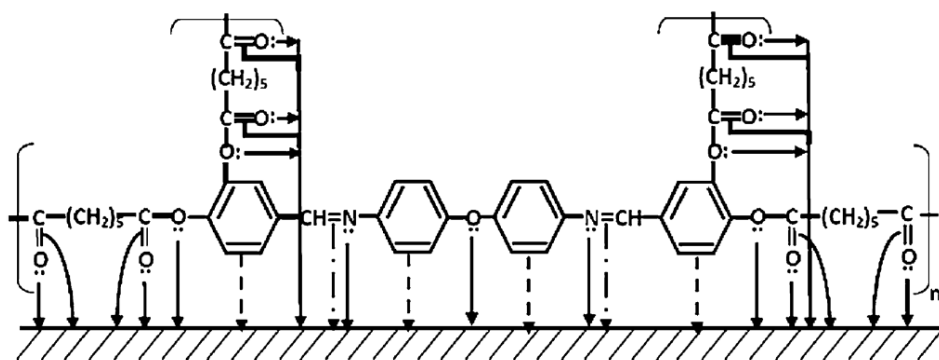


Figure 6 - Adsorption of PAME inhibitor on steel surface [56].

A further research [57] examined the effect of another promising polymeric inhibitor, polyacrylamide (PAM) on the corrosion inhibition on carbon steel. Tests were performed in alkaline solution, with increasing pollution by chlorides. The maximum inhibition efficiency (of about 99%) was achieved with 0.15 wt% PAM. The inhibitive performance is due to the generation of an adherent adsorption film on steel, following the Langmuir adsorption isotherm. The critical chloride concentration with 0.15% PAM is approximately 2 times larger than the one observed in the absence of the inhibitor. The effect must be confirmed by concrete tests. PAM molecules adhere spontaneously; in particular, the acylamino functional group ($-\text{CONH}_2$) has the strongest adherence to steel surface.

Hu et al. [58] investigated the inhibition effect of organic core-shell corrosion inhibitors (CSCI) on the corrosion of rebars in a synthetic alkaline solution. In particular, polyethylene oxide-b-polystyrene (PEO₁₁₃-b-PS₁₁₇₁) di-block copolymers were selected to prepare the CSCI. Dialysis method was used to realize both empty CSCI and CSCI containing benzotriazole (BTA). The encapsulated amount of BTA was about 1.05 g/L. CSCI efficiently increased the corrosion resistance of the steel reinforcements. At a concentration of about 2.27 x 10³ wt%, BTA-containing CSCI improved the corrosion resistance of the rebars with an inhibition efficiency even higher than 93%. Both empty and BTA-containing CSCI efficiently adsorbed on the reinforcement surface, stopping the adsorption of chlorides. Furthermore, BTA released from BTA-containing CSCI reacted with the metal, forming [Fe_n(BTA)_p]_m complexes at the corrosion sites. The superior inhibition ability of BTA-containing CSCI was attributed to their adsorption and smart release of BTA, with the subsequent alteration of products composition on the reinforcement surface. A graphical representation of the working mechanisms of both empty and BTA-containing inhibitors is shown in Figure 7 [58].

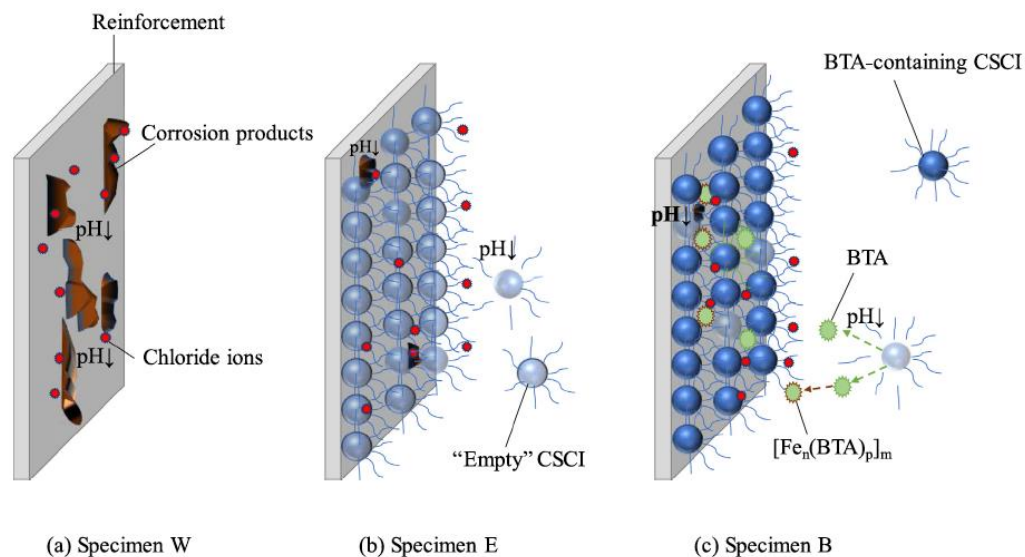


Figure 7 - Inhibition mechanisms of CSCI on the corrosion of the reinforcement in SCP solution, compared to the situation in absence of inhibitors (a, specimen W), in the case of empty CSCI (b, specimen E) and BTA-containing CSCI (c, specimen B) [58].

Jiang et al. [59] investigated the corrosion inhibition action of deoxyribonucleic acid (DNA) on steel rebars in alkaline solution. DNA-based corrosion inhibitor greatly increased the corrosion resistance of the steel reinforcements, forming a dense and adherent film on the steel surface, able to effectively reduce the corrosion attack and provide a superior corrosion resistance. In this study, a mixed solution of oligonucleotides was selected as DNA corrosion inhibitor, with random genetic sequences ranging from 20 to 80 nucleotides in length. Deoxyribonucleic acid demonstrated excellent inhibition properties in alkaline solution, with different concentrations of NaCl (from 0.01 to 0.1 mol/L). At a DNA content of 0.0025%, the highest efficiency was measured. At the early stage, corrosion was inhibited by the adsorption of DNA on the steel surface, with the adsorption film mainly inhibiting the cathodic reaction. During the mid and late stages of the corrosion process, due to the increase of NaCl concentration, DNA adsorbed preferentially on the steel surface where the corrosion reaction was active, which mainly inhibited the anodic reaction. Consequently, DNA can be classified as a mixed type inhibitor. XPS results confirmed the electrochemical outcomes and provided further evidence of the physisorption of DNA on the steel reinforcement surface.

5. GREEN INHIBITORS

Although the previous families of inhibitors are able to efficiently protect reinforced concrete from corrosion, some of them usually unavoidably bring negative impacts in terms of toxicity towards both the environments and humans. These hazardous effects may be encountered either during the inhibitors synthesis or during their application in field, causing both reversible and irreversible health damages, including problems to kidneys, liver and enzymatic systems in general. Therefore, research studies are increasingly focusing on the development of novel natural solutions for corrosion inhibition in concrete. Green corrosion inhibitors are cheap, easily produced, nontoxic, biodegradable and environmentally biocompatible. They are generally made of extracts from natural plants or vegetal waste, which are typically abundantly available in

many countries. The majority of green inhibitors molecules usually contain multiple bonds, aromatic rings, polar functional groups and electronegative atoms, like P, N, S or O. The latter are able to coordinate with metal cations to form protective layers on the metallic surface of the reinforcements, to inhibit the development of the corrosion process [60]. Another mechanism proposed is based on onium cations (e.g. ammonium or phosphonium) deriving from the inhibitors and adsorbed on the cathodic sites of the metal surface, stopping the corrosion reaction: decisive factors are the size, possible aromaticity and conjugated bonding, the ability to form a compact layer at the metal surface and their solubility in the environment [61]. To summarise, the inhibition mechanism of green inhibitors stems from a combination of many processes, namely the adsorption onto the carbon steel rebar surface, the influence on the anodic and/or cathodic reaction, the decrease in electrical resistance and the effects on diffusion rate [62-64].

The vast majority of green inhibitors are extracted in different ways from several parts of plants and trees, in particular leaves. Ben Harb et al. [65] proposed the use of dried olive leaves extracts as corrosion inhibitors for mild steel in synthetic alkaline chloride solution, exploiting four organic solvents of different polarity: hexane, methanol, ethyl acetate and dichloromethane. The leaves were obtained from wastes of the common species *Olea europaea L.*, grown in arid zones of Saudi Arabia. The leaves extract is characterized by a high content of antioxidant molecules, mainly polyphenols (oleuropein, hydroxytyrosol and derivatives), which contain several N and O heteroatoms, within polar functional groups (-OH, -NH₂), and double bonds. The corrosion inhibition mechanism is due to the adsorption of such phytochemicals, rich in π -electrons, on the carbon steel surface. The results showed that the extract behaves as a mixed type inhibitor in a 0.1 mol/l NaOH and 0.5 mol/L NaCl solution, with a prevailing influence on the anodic process. The best inhibition efficiency (about 92%) is obtained in the case of the extraction with methanol. Indeed, the results showed that the efficiency of the olive leaves extract increases with the polarity of the extraction solvents. This was explained by the fact that the adsorption

mechanism could be directly affected by polarity, since it allows the formation of strong bonds, but also by the size of organic molecules and the number of functional groups.

Anitha et al. [66] studied the use of *Rosa Damascena* leaves as a green corrosion inhibitor on carbon steel in alkaline solution with 0.05 mol/L NaCl. The main phytochemical constituents in the leaves extract include complex aromatic molecules, namely tannins, alkaloids, phenols and saponins. A comparative analysis was performed to evaluate the influence of the extraction solvent employed in the powder production, by means of acid extraction in H₂SO₄ (RDAE) or alcoholic extraction in ethanol (RDEE). A maximum protection efficiency of 82% was found for RDAE, with an inhibitor concentration of 12 % v/v. The inhibition performance of the RDEE was slightly less effective, as shown in Figure 8.

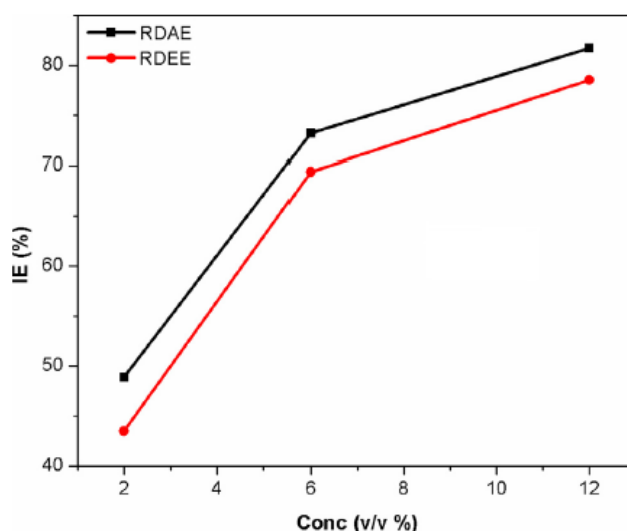


Figure 8 - Plot of inhibition efficiency (IE, %) vs. concentration of RDAE and RDEE (v/v %) [66].

Asaad et al. [67] studied the inhibitive effect of extracts from oil palm leaves (species *Elaeis guineensis*, EG) doped with silver nanoparticles (AgNPs), obtaining a cheap, eco-friendly and non-toxic corrosion inhibitor (EG/AgNPs). Silver NPs were selected due to their limited cost and lower environmental impact with respect to other metallic NPs, while the oil palm *E. guineensis* was chosen for the abundance of leaves as waste by-product in the palm oil production. The

composition of the leaves extract is very complex, and includes several phyto-constituents with anti-corrosion properties, namely tannins, alkaloids, coumarins, flavonoids, carbohydrates, saponins, terpenoids and phenolic compounds, most of which contain aromatic rings and polar functional groups. This novel composite additive was incorporated in reinforced concrete specimen immersed in seawater. The addition of just 5% EG/AgNPs inhibitor in concrete ensured a greatly enhanced corrosion resistance, due to the formation of a protective thin layer over the steel reinforcements. In particular, the inhibition effect was attributed to the adsorption of EG/AgNPs over the metallic surface along with the formation of an extra amount of dense, crystalline calcium silicate hydrate (C-S-H) gel in concrete, which could efficiently block the entry of chlorides in the capillary pores. A maximum inhibition efficiency of almost 95% was registered. The evolution of corrosion rate of the steel rebars during the year of immersion in seawater is showed in Figure 9. The overall corrosion inhibition mechanism of EG/AgNPs in reinforced concrete resulted as a mixed type, since it acted on both the anodic and the cathodic process.

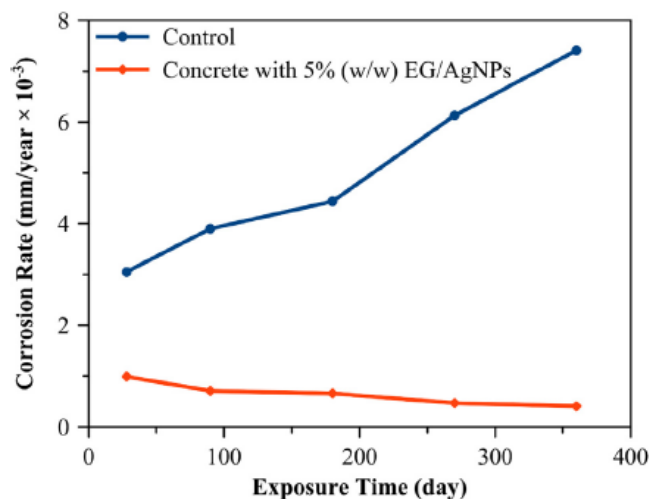


Figure 9 - Corrosion rate of reinforced concrete with and without EG/AgNPs, exposed to seawater for 1 year. The curves were obtained through LPR measurements [67].

The mucilage (or slime) of *Opuntia ficus-indica* (OFI) was exploited as corrosion inhibitor for carbon steel rebars in a mortar exposed to a chloride-enriched environment [68]. OFI, also known as Nopal, contains several compounds that typically work efficiently as anti-corrosion agents, like amino acids and long-chain carbohydrates. The experimental results indicated a possible correlation of direct proportionality between Nopal slime concentration and inhibitor coverage on the metallic surface, until reaching a maximum coverage of approximately 42% for a slime concentration of 8%. The final findings suggested that the addition of small concentrations of Nopal slime (between 4% and 8%) ensures a sufficient corrosion inhibition for steel in chloride contaminated mortar, with 8% as the best performing mixture. In particular, the slime addition enhances resistance to water penetration resistance, increasing impermeability against aggressive agents (i.e. chlorides and CO₂).

In a Chinese research study, the corrosion inhibition effect of ginger extract in reinforced concrete was compared to three other commonly used corrosion inhibitors (i.e. calcium nitrite, a commercial organic corrosion inhibitor and kelp extract). The main components of ginger extract are 6-gingerol, 8-gingerol, cyclocurcumin and arginine. These compounds are easily absorbable onto the metallic reinforcement surface, which makes ginger extract a very promising candidate as green corrosion inhibitor. The corrosion inhibition performance was attributed to the formation of a stable carbonaceous organic film on the steel surface. The experimental findings showed that the ginger extract can act as an effective corrosion inhibitor, efficiently reducing the corrosion risk of steel rebars embedded in concrete. The optimum concentration of ginger extract for the inhibition performance was 2%, which was slightly reduced to 1–2% if the effects on the flowability and mechanical properties were taken into account as well. It was estimated that the overall optimum dosage of ginger inhibitor in concrete should be of about 8–12 kg/m³ [69].

6. CONCLUSION

Corrosion inhibitors have been successfully applied for preventing corrosion in many fields, as well as in concrete, due to their low costs and easy handling. In the case of chloride induced corrosion, they mainly delay the initiation of corrosion by increasing the critical chloride threshold or reducing the chloride penetration. Poor to negligible effect are reported on the corrosion rate reduction.

The present state of art allow to state:

- Nitrite-based inhibitor are the most efficient. They are able to increase the critical chloride threshold, according to their dosage: $[\text{NO}_2^-]/[\text{Cl}^-]$ ratios higher than 0.5-0.6 are required to prevent corrosion. The main concern is related to safety and environmental issues related to nitrites.
- Nitrate seems to be a valid alternative. Conflicting results are reported as regard both the inhibition mechanism and the effectiveness. They are anodic inhibitor, as nitrite, but they seem to have a delayed effectiveness in time. Some authors report an increase of the critical chloride threshold up to 2-4% with respect cement weight, others suggest a lower increase.
- Many promising organic substances, synthetic or naturally derived, has been proposed in the last 20 years. Some of them seem to be promising inhibitor: DMEA, TETA, sodium benzoate and some green compounds extracted from leaves, as dried olive, Rosa Damascena or oil palm. The main limitation of most of the papers recently published is twofold: most of tests are performed in alkaline solution, than confirmation in concrete in mandatory; short-term tests are performed. The data about their long-term performance in concrete is mandatory.

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Declaration

On behalf of all the authors of the submitted paper “Recent advances in the use of inhibitors to prevent chloride-induced corrosion in reinforced concrete”, I declare there are no conflict of interest in publishing the work.

Best regards

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