

Review

Corrosion inhibitors for steel reinforcement in concrete: A review

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Accepted 16 August, 2011

Inhibitors are added to concrete to improve its quality and integrity. In recent years the use of these inhibitors in producing high performance concrete has increased significantly as a result of aggressive environment. This report is based on the corrosion inhibitors used in concrete and also on the published literatures. Most authors agreed that reinforcement corrosion is the most important causes of premature failure of reinforced concrete structure worldwide and generate a great research concern due to its effects on global economy. The report presents information related to basic mechanism of corrosion protection methods to extend the service life of reinforced concrete structures which include inhibitors, sealers and barriers. Environmental sustainability issues concerning the present inhibitors being used were examined, viability and versatility of green inhibitors to concrete was also x-rayed.

Key words: Concrete, chloride attack, corrosion, reinforcement, inhibitor, admixture, carbonation, sulphate attack.

INTRODUCTION

In the past, most of the design studies in the literature and research in reinforced concrete assumed that the durability of reinforced concrete structures could be taken for granted. However, many reinforced concrete structures are exposed during their lifetimes to environmental stress (for example, corrosion and expansive aggregate reactions) which attacks the concrete or steel reinforcement (Ormellese et al., 2009). Researchers and engineers are continuously in search of cost-effective means to prevent the corrosion of reinforcing steel for the duration of a concrete structure's design life. The cement paste in concrete is alkaline with a pH typically between 12 and 14. This paste forms a passive film surrounding reinforcing steel in concrete which further thicken iron oxide layer on the steel surface. Many researchers believe this alkaline environment facilitates the protective passive film around the steel (Broomfield, 2003; Soeda and Ichimura, 2003; Gaidis,

2004; Ormellese et al., 2006; Ormellese et al., 2009). The passive film is not invulnerable, though it can be damaged both chemically and mechanically. Some examples of chemical damage are carbonation, chloride ingress (seawater, de-icing salt, unwashed sea sand, admixtures etc) and sulphate attack. Proper design and preparation of concrete in accordance with relevant standards and timely maintenance of the structures under those conditions would guarantee them a long and efficient life in aggressive media. However, these requirements are not always met and adhered to. Preventive measures being used in the construction industry to salvage the service life of steel reinforcement in concrete structures are cathodic protection, inhibitors, coatings, penetrating sealers and chloride removal (Saraswathy and Song, 2007). One of the practiced methods popularly used for the control of steel corrosion in concrete is the corrosion inhibitors either preventive or curative.

In recent years, the use of these inhibitors in producing high performance concrete has increased significantly. Inhibitors are chemical substance that decreases the corrosion rate when present in the corrosion system at

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suitable concentration without significantly changing the concentration of any other corrosion agent (Soylev and Richardson, 2008). Many synthetic compounds (inhibitors) were developed to combat this endemic corrosion problem, but most of them are highly toxic to both human beings and environment (Satapathy et al., 2009). Inhibitors toxicity according to Uhlig (2004) is measured as lethal dose (LD) and lethal concentration (LC). LD₅₀ is the lethal dose of a chemical at which 50% of a group of animals are killed for 24 h exposure time, whilst LC₅₀ is lethal concentration in air or water which kills 50% of test population. Inhibitor biodegradation or biological oxygen demand (BOD) should at least be 60%. The BOD is a measure of how long the inhibitor will persist in the environment. Hence it becomes imperative to review the current inhibitors in order to find more appropriate, suitable and sustainable inhibitor.

BASIC MECHANISM OF PROTECTION

The present literature review is focused on the most commonly used inhibitors and is categorized and summarized as follows:

Inorganic inhibitors

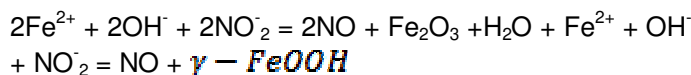
Macdonald (2003) investigated inhibitors in alkaline solutions and in cement extracts. The cement extracts experiment showed that sodium nitrite inhibited corrosion in the presence of chlorides while sodium benzoate did not. Moreover corrosion initiation was delayed with sodium nitrite, with the delay increasing with inhibitor content (Macdonald, 2003). Novokshcheov (2000) showed that calcium nitrite is not detrimental to concrete properties as it is the case for inhibitors based on sodium or potassium. A latter study by Skotinck (2000) and Slater (2001) showed that under long-term accelerated testing, calcium nitrite was found to be of better quality in terms of strength. Berke and Hicks (2004) further argued that 'calcium nitrite' does not increase corrosion rates after chloride protection values are surpassed and in contrast often lowers them. A major advantage to the use of calcium nitrite corrosion inhibitor is that the engineer can use rational procedures based on chloride exposure, concrete quality and quantity of calcium nitrite to design for service life on the basis of expected chloride-to-nitrite ratios. Samiento-Bustos et al. (2008) investigated the effect of LiNO₃, Li₂CrO₄ and Li₂MoO₄ inorganic inhibitors on the corrosion performance of 1018 carbon steel in the LiBr + ethylene glycol + H₂O. It was found that the inhibitor efficiency increases with the inhibitor concentration except for chromates where the highest efficiency was reached with 20 ppm of inhibitor. The highest efficiency was obtained with 50 ppm of LiNO₃, 95%, slightly higher than the obtained with Li₂MoO₄ and

Li₂CrO₄ around 90. The passive current density was decreased for more than two orders of magnitude with the addition of inhibitors; however, the lowest value was obtained with 20 ppm of Li₂CrO₄. In a similar way, the pitting potential value was lower with 5 ppm of inhibitor regardless of its chemical composition, whereas with 20 ppm of Li₂CrO₄ was the highest, 150 mV nobler than that obtained with the uninhibited solution.

The noise resistance data indicated that in absence of the inhibitors, transients' data were present indicating film rupture/repassivation events. With 5 ppm of inhibitors, the frequency of these transients was similar to that obtained in absence of inhibitor, but they decreased as the inhibitor concentration increased. Adsorption isotherms suggested a different adsorption mechanism for each inhibitor. Finally, impedance results suggested that the corrosion process when nitrates were added was under charge transfer control, whereas in the case of molybdates or chromates was under diffusion control. According to De Schutter and Luo (2004), they reported that calcium nitrite inhibitor increases the early age compressive strength (28 days). The effect on the ultimate strength seems to depend on the amount of inhibitor added to the concrete. A calcium nitrite-based corrosion inhibitor increases somewhat the air content as well as the workability of the fresh concrete. But Kondratova et al. (2003) warned that the addition of calcium nitrite influences the hydration process of cement paste. Apparently, calcium nitrite has the function of accelerating and stabilising the formation of the crystal phase of calcium hydroxide which leads to an increase in the micropore diameter in the hardened cement paste and thus to an increase in chloride permeability compared to concrete without inhibitor. They also reported that calcium nitrite can decrease the resistivity of concrete and also tends to increase concrete chloride permeability values. Tritthart and Banfill (2001) suggested that users of nitrite inhibitors must be aware that a threshold free nitrite concentration needs to be achieved such that the chloride/nitrite ratio remains below 1.5. This requires all sources of chloride to be analysed for the concrete in question.

The results can be used to give guidance for the satisfactory use of nitrite inhibitors. Also Mammoliti et al. (1999) concluded in their work that the results obtained from tests performed in synthetic pore solution using nitrite base inhibitors were contradictory to those reported in previous studies. All inhibitors were unsuccessful in increasing the chloride threshold value of steel exposed to chlorides and all had a minimal effect on corrosion rates once corrosion was initiated. The most surprising behaviour was illustrated by 'calcium nitrite'. Samples immersed in solutions containing this inhibitor had the highest incidences of pitting corrosion accompanied by higher current density values. Samples also had more difficulty repassivating at higher chloride levels. This behaviour is most likely attributed to the lower pH values

observed in solutions containing this inhibitor. These results, however, do not support the proposed mechanism for nitrite inhibition (Abdulrahman et al., 2011a, 2011b) as shown in the following equation:



From this equation, it suggest that a more coherent, homogeneous passive film forms due to nitrite acting as a catalyst for film formation; however, no apparent film enhancement was observed in synthetic pore solutions. Montes et al. (2004) reported the detrimental effects of calcium nitrite inhibitor (CNI) on the properties of concrete and that it has apparently poor performance in preventing corrosion of steel reinforcing bars. Based on the results of the experimental program obtained, the following conclusions were drawn: the w/c ratio plays an important role in the development of cracking due to corrosion. The lower the w/c ratio, the less cracking to be expected and this effect is more evident when fly ash and CNI are included in the low w/c ratio mixture. This suggests that the combination of low permeability concrete and corrosion protection of the steel using CNI together is effective in reducing cracking in concrete by decreasing cracking– corrosion interaction phenomenon. With regard to 'linear polarization resistance' results, it was concluded that cracking of the concrete strongly affects the rate of corrosion, reaching values as high as ten times its uncracked condition. In general, for the concrete characteristics and exposure conditions evaluated in their work, it was found that CNI alone does not always provide corrosion protection of the steel reinforcement in concrete. Even for uncracked concrete without fly ash in a 0.45 w/c ratio concrete, CNI failed to prevent corrosion. However, the combination of good quality concrete (w/c = 0.29 or 0.37) and the use of CNI at an addition rate of 12.5 L/m³ plus the use of 20% of fly ash appears to be the desirable approach to reduce the effect of chloride induced corrosion of steel reinforcement.

Ann et al. (2006) used calcium nitrite-based corrosion inhibitors to investigate the effects on the chloride transport, compressive strength and setting of concrete. Their conclusions are as follows: the corrosion rate reduced considerably by the addition of corrosion inhibitor at all levels of chloride ions in mortar and the chloride threshold level was raised by an increase in the dosage of corrosion inhibitor, ranging from 0.22 to 1.95% by weight of cement. Nitrite free specimen produced the values ranging from 0.18 to 0.33%. It was also observed that the threshold mole ratio of (NO₂⁻):[Cl⁻] ranged from 0.34 to 0.66 for preventing corrosion. However, addition of corrosion inhibitor resulted in an increase in the total charge passed in the test of rapid ion penetration using a 60 V DC which may imply the increased chloride transport and thus offset the beneficial effect in

increasing the chloride threshold level. Calcium nitrite-based raises the compressive strength at early ages when compare to control non chloride contaminated sample. However, at 900 days, the strength trends reverse (Ann et al., 2006). In addition, an increase in the dosage of corrosion inhibitor resulted in decreased concrete setting by about 1 h, when 12 l/m³ inhibitor was added. However, Ngala et al. (2002) posted a thought provoking question about nitrite base inhibitors in their research that:

- i) Can nitrite ions penetrate through concretes of different quality in adequate amounts to retard corrosion which has become established on embedded steel if recommended methods of surface application are used?
- ii) Is there a significant risk of intensified corrosion of embedded steel developing as a consequence of inadequate treatment of concrete which has been exposed to varying levels of carbonation and/or chloride contamination?

Ngala et al. (2002) then concluded that on the basis of the performance recorded from relatively short-term laboratory investigations of the sort undertaken with a calcium nitrite-based treatment for corroding reinforced concrete, it appears that nitrite ions can be transported through realistic thicknesses of cover concrete of high water/cement ratio. Their effect was to cause some reduction in the corrosion rate of moderately pre-corroding steel in noncarbonated concrete with modest levels of chloride contamination and in carbonated concrete without chloride. In the case of non-carbonated concrete with higher levels of chloride contamination and, particularly in the case of carbonated concrete with even low levels of chloride, it was found that the inhibitor was ineffective under the conditions studied. Some evidence was obtained of enhancement of the severity of pitting under these conditions for the more severely contaminated concretes. It must be emphasized that no short-term laboratory investigation can fully simulate the performance of concrete repair systems that are used and exposed under different circumstances on real structures. It seems, however, that there is a need for caution in applying systems of the type investigated. In general, evidence of medium to long-term performance should be sought from well monitored field trials that can only be of real value in cases where thorough investigation of the structure concerned to establish the causes of corrosion has been undertaken. Based on the limited evidence of the present investigations, calcium nitrite-based remedial treatments would appear to be potentially applicable only to non-carbonated concrete contaminated with relatively low levels of chloride or to carbonated concrete without chloride, where the initial rates of corrosion of embedded steel are fairly low.

The effect of sodium molybdate and sodium nitrite as steel corrosion inhibitors in saturated calcium hydroxide solutions polluted with sulfuric and nitric acids (acid

atmosphere) was investigated by Tommaselli et al. (2009), they concluded that: both compounds showed significantly inhibitory effects. However, sodium molybdate in low concentration (0.013% total solution mass) showed an efficiency of approximately 67% while sodium nitrite in the same concentration displayed 52% efficiency. The two compounds displayed similar inhibitory effects within a high range of inhibitor concentrations (0.040% total solution mass).

Organic inhibitors

The use of organic compounds to inhibit corrosion of mild steel and iron has assumed great significance due to their application in preventing corrosion under various corrosive environments (Ali et al., 2008). A variety of organic compounds have been reported to be effective as corrosion inhibitors during acidization in industrial cleaning processes (Ali et al., 2008). The development of corrosion inhibitors is based on organic compounds containing nitrogen, oxygen, sulfur atoms and multiple bonds in the molecules that facilitate adsorption on the metal surface (Cruz et al., 2004). The corrosion inhibition efficiency of organic compounds is related to their adsorption properties. Adsorption depends on the nature and the state of the metal surface on the type of corrosive medium and on the chemical structure of the inhibitor. Studies report that the adsorption of the organic inhibitors mainly depends on some physicochemical properties of the molecule related to its functional groups, to the possible steric effects and electronic density of donor atoms; adsorption is supposed also to depend on the possible interaction of p-orbitals of the inhibitor with d-orbitals of the surface atoms, which induce greater adsorption of the inhibitor molecules onto the surface of carbon steel, leading to the formation of a corrosion protecting film (Cruz et al., 2004). Ormellese et al. (2009) researched about 80 organic substances as: primary and tertiary amines and alkanolamines, aminoacids, mono- and poly-carboxylates. Such substances are selected with the purpose of analysing the effect of functional groups (aminic or carboxylic), the position and number of the substituent and to study the influence of either electron-donor (nucleophile groups like oxidrilic, aminic and alkylic groups) or electron-attractor groups (electrophile agents like halogen, carboxylic group and atoms with high electronegativity), as well as the effect of carbon-chain length.

Amines and alkanolamines are largely used as constituents in commercial products due to their high water solubility and their negligible influence on properties of both fresh and hardened concrete. The functional group responsible for amines and alkanolamines adsorption on metal surface is the lone pair of the nitrogen atom: iron ions on metal surface act as a Lewis acid because they accept electrons from a

donor group. Amines adsorption is influenced by the electronic properties of the functional groups, R, bound to the nitrogen atom. Organic carboxylate substances were tested to study the effect of the delocalization of the electrical charge of the carboxylate anion ($-\text{COO}^-$), the functional group responsible for the adsorption on carbon steel surface. Carboxylates adsorption is influenced by the presence of electron-donor or electron-attractor groups, R, bound to the carboxylate anion. Ormellese et al. (2009) concluded as that:

- i) Amines showed poor inhibition effect with very scattered result when their volatility increased.
- ii) Aminoacids showed some inhibition effect but not sufficient for an industrial applications.
- iii) Carboxylate substances especially poly-carboxylates showed very good inhibition effectiveness making them the most promising candidates among the tested substances. A confirmation on concrete slab specimens is required to check compatibility with concrete and long-term effectiveness. As far as carboxylate substances, a strong link was found between inhibiting properties and molecular structure. The inhibition action is influenced by one or more of these factors:

Electron-attractor or electron-donor effect

Electron-donor substituent that gives up electrons, promotes the adsorption process through the negative charge localisation on oxygen and on carboxylic group (adsorption is a combination of inductive and resonance effect on electron density of the molecule); on the opposite, high electronegative substituent tends to be electron- attractor then weakening adsorption process being electrons not available for it.

Electrostatic effect

Adsorbed molecules with a negatively charged substituent or a lone pair electron develop a repulsive action towards chloride ions, avoiding chloride to be in contact with the carbon steel passive layer.

Steric effect

Alkylic chain or voluminous substituent groups form a sort physical barrier that blocks or delay chloride arrival to the metal surface.

Lateral interaction effect

Some repulsion effect between adsorbed molecules is possible because of the presence of highly polar group.

Benzina et al. (2008) and Gaidis (2004) investigated the effectiveness of an amino-alcohol based corrosion inhibitors using simulated pore solutions and mortar specimens. Their investigations were conducted in order to check the most efficient mode of use of an amino-alcohol based mixed corrosion inhibitor both in the two cases of simulating solutions and real mortar specimens. In order to get a rapid result, tests were first carried out in simulated pore solutions: the inhibitor showed an acceptable inhibitive action when it was introduced before the chlorides. In the case of mortar specimens, it was obviously noticed, contrary to the case of simulated pore solutions that the inhibitor was effective even with the presence of chlorides: the curative mode of use is efficient since the inhibitor reacted against existing corrosion and was able to slow down its progression in the two cases of presence or absence of chlorides. The inhibitor efficiency greatly depended on the environment and the way of use. Its dilution at 1 ml/50 ml in water can be considered as a suitable mean that can insure diffusion in the case of mortar specimens with standard mix. Several authors worked on N-heterocyclic organic compounds and their derivatives (El Azhar et al., 2001; Tritthart, 2003; Gaidis, 2004; Baddini et al., 2007; Ali et al., 2008; Gece, 2008; Hong, 2008; Noor and Al-Moubaraki, 2008; Saliyan et al., 2008; Yıldırım and Çetin, 2008; Obot et al., 2010).

The organic compounds used were confirmed satisfactorily good for corrosion inhibition of mild steel in acids and chloride media based on the adsorption of the molecules on the metallic surface and follows Langmuir isotherm adsorption model. But they were unable to investigate their effects on concrete properties. Benzina et al. (2008) investigated the use of benzotriazole (BTAH) as corrosion inhibitor for carbon steel in simulated pore solution. They concluded that the addition of BTAH into a simulated chloride-contaminated pore solution caused a significant increase in the corrosion resistance of the carbon steel (CA-50). The improvement of corrosion resistance by the BTAH (1.5 wt %) addition was superior to that associated to the addition of nitrite (1.5 wt %) to the electrolyte suggesting that BTAH is a potentially attractive alternative to nitrites for inhibiting corrosion of steel reinforcement in concrete. The increase in corrosion resistance was associated with the formation of a complex layer of $[\text{Fe}_n(\text{Cl})_p(\text{BTA})_m]$ that spreads over the steel surface with immersion time acting as a partial barrier to the access of environment aggressive species to the metallic substrate. Also, short and long terms effects on the properties of concrete were not investigated vis-à-vis its compatibility and the exposure time were too short for generalize inference. Ngala (2003) investigated the uses of sodium monofluorophosphate as a remedial treatment of reinforced concrete, they concluded that on the basis of the performance recorded from relatively short-term laboratory investigations of the sort undertaken with

$\text{Na}_2\text{PO}_3\text{F}$ treatment for corroding rein-forced concrete, it appears that $\text{Na}_2\text{PO}_3\text{F}$ had very little effect on the corrosion rates of steel in both non-carbonated and carbonated concretes under the conditions studied. This is consistent with the observation that PO_3F^{2-} ions were not detected in the pore solution of the concrete. The slight reduction in the corrosion rate of moderately pre-corroding steel in non-carbonated concrete with modest levels of chloride contamination may be due to the leaching of chloride from the surface of the concrete. Slight variations in the extent of corrosion might also be expected to arise as a result of formation in the pore solution of the hydrolysis products of PO_3F^{2-} , viz. PO_4^{3-} , which can act as an inhibitor, and F^- , which is not inhibitive. They emphasized that no short-term laboratory investigation can fully simulate the performance of concrete repair systems that are used and exposed under different circumstances on real structures. It seems, however, that there is a need for caution in applying systems of the type investigated.

They advised that, evidence of medium to long term performance should be sought from well monitored field trials that can only be of real value in cases where thorough investigation of the structure concerned to establish the causes of corrosion has been undertaken. Based on the limited evidence of the present investigations, $\text{Na}_2\text{PO}_3\text{F}$ did not appear to be effectively transported into the concrete under the conditions studied and so did not provide substantial corrosion inhibition to the embedded steel. Morris and Vázquez (2002) evaluated migrating corrosion inhibitor (alkylaminoalcohol) in concrete containing various contents of admixed chlorides. Findings were as follows: under the conditions of the present study, the efficiency of the inhibitor strongly depends on the initial chloride ions concentration in concrete. The inhibitor was able to reduce the corrosion rate (CR) of steel in concrete only when the initial chloride concentration was approximately 0.2 wt % referred to the content of cement in concrete. In this case, the inhibitor was applied to concrete having no admixed chlorides and even when samples had w/c = 0.6 and were exposed to a marine condition for 1000 days, the CR decreased almost one order of magnitude to values typical of steel in passive state ($\text{CR} \ll 1 \mu\text{m year}^{-1}$). After this period of exposure, the concentration of total chlorides raised up to approximately 1% at the rebar surface due to the incorporation of chlorides coming from the environment. Specimens that were prepared with w/c = 0.6, no admixed chlorides and treated with the inhibitor show an increase in the electrical resistance measurements compared to the blank ones. This behaviour could be attributed either to an increase in the electrical resistivity of concrete or to the formation of a protective film on the rebar surface or to a combination of both factors. On the other hand, this inhibitor effect was negligible when applied to admixtures where a/c = 0.4 and the total chloride concentrations initially higher than

0.43% (reaching also 1% after 1000 days of exposure to the marine environment). Thus, the product cannot be recommended for concrete prepared with raw materials contaminated with chloride ions.

The performance of this inhibitor (measured in terms of the rebar corrosion rate (CR)) depends on the quality of concrete being better in the specimens with the highest w/c. This makes the inhibitor a promising product for those cases where low-quality concrete mixes determine the overall corrosion progress. The use of this inhibitor under immersion conditions does not show a substantial improvement in the corrosion resistance in any of the concrete designs containing admixed chlorides. Yet, the mix design showing the lowest CR in this exposure condition is, once again the treated one with no initially incorporated chlorides. Inhibition for CO₂ corrosion of N80 steel by quaternary alkoxymethyl amine (IMC-80-Q) and imidazoline in 3% NaCl solution was investigated under static and flowing conditions by using modified rotating disk apparatus (Jiang et al., 2005). They concluded that:

- i) Critical flow velocity varied from one inhibitor to another one even though for the same inhibitor it was also a function of inhibitor concentration.
- ii) IMC-80-Q should be adjusted to different concentrations at different flow velocities (150 mg/L for 0 to 5 m/s and 300 mg/L for higher flow velocities) to get the best inhibition efficiency. The optimum concentration was further enhanced by the entrained sand in the medium containing IMC-80-Q.
- iii) The adsorption of IMC-80-Q under static condition obeyed Langmuir isotherm when concentration was lower than 150 mg/L, but it changed into Freundlich isotherm as concentration was beyond 150 mg/L.
- iv) The optimum concentration of imidazoline under static condition was 100 mg/L, but it increased to 200 mg/L at 5 m/s.
- v) Under static condition, imidazoline exhibited better inhibition performance than IMC-80-Q did; in contrast, at 5 m/s, inhibition performance of IMC-80-Q was better than that of imidazoline.

In a related research, Sawada et al. (2005) and Kubo et al. (2007) electrochemically injected two organic base inhibitors (ethanolamine and guanidine) into saturated specimens of carbonated and non-carbonated concrete from external electrolytes under the influence of an electrical field applied between embedded steel cathodes and external anodes. The main conclusions of this investigation may be summarized as follows:

- i) The two organic base corrosion inhibitors studied ethanolamine and guanidine were both capable of being effectively injected into carbonated reinforced concrete of the sort investigated by means of relatively short-term electrochemical treatments of the type applied.

- ii) The cathodic current densities and electrochemical treatment durations required to cause substantial penetration of the aforementioned corrosion inhibitors through carbonated concrete cover of w/c 0.86 and thickness 35 mm were of similar magnitudes to those typically employed for electrochemical realkalisation of carbonated concrete. Accumulation of high concentrations of the two corrosion inhibitors in carbonated concrete at the level of the embedded steel (in the case of guanidine) and in the cover zone a few millimeters from the embedded steel (in the case of ethanolamine), occurred as a result of electrochemical treatments of the type applied.

- iii) The inhibitor penetration profiles observed in carbonated concrete were explicable in terms of the degrees of ionization of ethanolamine (pKa 9.5) and guanidine (pKa 13.6) in carbonated concrete which has a pore solution pH value < 9.5 except in the vicinity of the steel cathode where much higher pH values are expected to occur.

- iv) Electrochemical treatments applied to non-carbonated concrete of the type studied which had a w/c of 0.65 and a pore solution pH value > 13 were far less effective in causing injection of the corrosion inhibitors than those applied to carbonated concrete.

- v) In the case of ethanolamine, it is thought that the low degree of ionization of the inhibitor in the alkaline pore solution phase of non-carbonated concrete prevented significant migration of the inhibitor under an applied field. Similar considerations would presumably apply also to other organic base inhibitors with pKa values = 13.

- vi) In the case of guanidine, although penetration of the inhibitor was significantly enhanced by an applied field indicating that the higher pKa value allowed migration to occur, the application of a cathodic current density of 5A/m² for 2 weeks did not prove sufficient to cause the inhibitor to reach the steel cathode at a cover depth of 35 mm. Further work is therefore needed to assess whether the electrochemical injection of guanidine, or similar relatively strong organic base inhibitors, into non-carbonated concrete can be induced over conveniently short timescales for practical applications.

The effect of inhibitors (alkanolamine, M2 and a water-base inorganic, R2) on the corrosion of steel reinforcements in concrete was evaluated by using anodic polarization, electron spectroscopy for chemical analysis (ESCA) and Auger electron spectroscopy (AES) by Saricimen et al. (2002). The reinforcement corrosion in uncontaminated concrete specimens was evaluated by impressing +4 V anodic potential for accelerated corrosion of the steel bar and measuring the time-to-cracking of the concrete specimens. The effectiveness of the inhibitors in retarding reinforcement corrosion in the contaminated concrete specimens was evaluated by measuring the corrosion potentials and corrosion-current density. Their results indicated that the time-to-cracking

in uncontaminated concrete specimens incorporating inhibitors M2 and R2 was higher than that in the control concrete specimens. While the increase in the time-to-cracking in the concrete specimens incorporating M2 was marginal, a significant improvement in the corrosion-resisting characteristics of concrete incorporating R2 was indicated over the control specimens. The data on time-to-cracking in the uncontaminated concrete specimens and the corrosion rate of steel in the contaminated concrete specimens indicated the usefulness of corrosion inhibitor R2 in retarding reinforcement corrosion.

The electrochemical test results and surface analysis results using ESCA and AES techniques showed the better performance of inhibitor R2 compared to inhibitor M2 in retarding corrosion of steel in an environment of saturated calcium hydroxide in the presence of chloride ions.

Sealers and barriers inhibitors

Wang et al. (2007) study the influence of thermal curing on the fabrication and properties of thin organosilane films coated on low carbon steel substrates. In this study, low carbon steel substrates have been treated with the organofunctional silane of γ -GPS by thermal curing process. The surface of the film has been analyzed by EDS and RAIR. The following conclusions were drawn from the results:

- i) The optimum thermal curing process of γ -GPS films is as follows: the curing temperature is limited about 150°C and the curing time should not exceed 1 h.
- ii) The analysis of EDS showed that the thermal curing process variables was the dominating reason for the variation of the element composition in γ -GPS (10 vol.%) films. And the highest silicon atomic concentration was obtained under the condition of curing at 150°C for 1 h.
- iii) The RAIR is an effective tool for characterizing the film. SiOH groups and SiOSi linkages exhibit opposite evolutions when the films cured at elevating temperature and time, indicating that SiOH groups reacted with each other to form SiOSi linkages with small or branched chains and a more denser and cross-linked thin films may be prepared to supply the adhesion to metal substrates. Additionally, some non-hydrolyzed end groups (SiOCH_3) were also presented in the deposited films and oxidation of the epoxide groups was observed in RAIR at an elevating temperature.
- iv) Adhesion tests showed that the adhesion increased by increasing the curing temperature and then decreased after 150°C, which evaluated in good agreement with results obtained from EDS. The maximum adhesion can reach 3.65 MPa. In this report no information as per the coated reinforce bar performance in concrete.

According to Troconis et al. (2002), they reported that

combination of inorganic and surface coating application to reinforced rebar could reduce the corrosion rate drastically. They concluded as follows:

- i) Chloride diffusion and, therefore, corrosion rate is controlled by reducing the w/c ratio to 0.45 regardless of calcium nitrite content.
- ii) The use of ZnO reduces concrete porosity and chloride content at rebar level.
- iii) After the exposure period (≈ 500 days), the potential values (> -200 mV vs. Cu/CuSO_4) and cyclic curves of the steel in the probes with ZnO show passivation even though corrosion rates are high ($>0.1 \mu\text{A} = \text{cm}^2$).
- iv) When ZnO is used, an appreciable change in corrosion rate is observed when the inhibitor concentration is changed from 2 to 3%.
- v) After approximately 500 days' exposure to the saline medium, all the probes prepared with $\text{Ca}(\text{NO}_2)_2$ showed breaks in the passive film on the reinforcement.
- vi) The ZnO/ $\text{Ca}(\text{NO}_2)_2$ mixture at 2% showed the best results throughout the study period.

Pérez-Quiroz et al. (2008) assessed stainless steel reinforcement for concrete structures rehabilitation. Based on their investigation, they concluded that use of stainless and carbon steel reinforcing bars in the same concrete pore solution will not increase the corrosion risk on carbon steel, even when these bars are in direct (electrical) contact. In fact, the increase in the corrosion rate of carbon steel due to galvanic coupling of stainless steel with corroding carbon steel was less than that of the combination of non-corroded carbon steel with corroding carbon steel. Therefore, the judicious use of stainless steel with carbon steel in the high-corrosion risk areas of a concrete structure can be a cost-effective option for reducing corrosion and greatly extending the service life of concrete structures. Batis et al. (2003a) presented a study concerning the investigation of the protective effect of migrating corrosion inhibitors, against rebar corrosion, in specimens of repair fiber reinforcement mortars, in relation to these containing corrosion inhibitors. Based on the results of corrosion measurements, the following conclusions were made:

- i) All the categories of specimens containing corrosion inhibitor exhibited lower rebar's' corrosion as compared to that without inhibitor.
- ii) The correlation between strain gauge (SG) and mass-loss measurements for all categories of specimens provides comparative results of corrosion evaluation.
- iii) Specimens made with fiber-reinforced mortar containing corrosion inhibitor exhibited the best corrosion protection results. This can be attributed to the combined straightening of protective passive layer and the lower mortar porosity. The positive effect of fiber reinforcements is proven by the slow rate of cracking due to the tensile strength improvement by the fibers.

iv) The presence of migrating corrosion inhibitor provides lower galvanic currents between different mortar specimens resulting in better protection of the steel rebar against corrosion.

v) For the better corrosion protection of an existing concrete structure, the repairing process may include the use of migrating corrosion inhibitor as well in the repair mortar as in the rebars and the surrounding concrete.

Batis et al. (2003b) suggested blending of inorganic coating in presence of alkanolamine-base inhibitor for the protection of steel reinforcement in concrete. They concluded that:

i) Uncoated specimens exhibit the worst properties having the higher corrosion rate of the reinforcing steel bars.

ii) The acrylic dispersion coating provides adequate protection of reinforced concrete under aggressive corrosion environment.

iii) The inorganic coating alone results in poor protection.

iv) The simultaneous use of alkanolamine-based corrosion inhibitor and inorganic coating almost equals the protection offered by the acrylic dispersion.

Green corrosion inhibitor

Environmental concerns worldwide are increasing and are likely to influence the choice of corrosion inhibitors in the future. Environmental requirements are still being developed but some elements have been established (Uhlig, 2004). The biodegradation or biological oxygen demand (BOD) should be at least 60% and inhibitors should be nontoxic (Uhlig, 2004). The BOD is a measure of how long the inhibitor will persist in the environment. Toxicity is measured as LC_{50} or EC_{50} . LC_{50} is the concentration of the inhibitor needed to kill 50% of the total population of the test species. The results are quoted as milligrams of chemical per liter of fluid (or LD_{50} , milligrams per kilogram) for exposure times of 24 and 48 h. The EC_{50} is the effective concentration of inhibitor to adversely affect 50% of the population. In general, EC_{50} values are lower than LC_{50} values because the former are the concentrations required to damage the species in some way without killing it. Some chemicals are excellent inhibitors, but are quite toxic and readily absorbed through the skin (Uhlig, 2004). There is a growing demand for corrosion inhibitors that are less toxic and biodegradable compared to current formulations. Green inhibitors displaying substantially improved environmental properties will be the inhibitors most widely used in the future (Uhlig, 2004). Among the numerous organic compounds that have been tested and are applied industrially as corrosion inhibitors, those that are non-toxic are now far more strategic than in the recent past. In the past two decades, the research in the field of "green"

corrosion inhibitors has been addressed toward the goal of using cheap, effective molecules at low or "zero" environmental impact (Moretti et al., 2004).

The known hazardous effects of most synthetic organic inhibitors and restrictive environmental regulations have now made researchers to focus on the need to develop cheap, non-toxic and environmentally benign natural products as corrosion inhibitors. These natural organic compounds are either synthesized or extracted from aromatic herbs, spices and medicinal plants. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost and are biodegradable in nature. The use of these natural products such as extracted compounds from leaves or seeds as corrosion inhibitors have been widely reported by several authors (El-Etre, 2003, 2006; Gunasekaran and Chauhan, 2004; Moretti et al., 2004; El-Etre et al., 2005; Sethuraman and Raja, 2005; Bouyanzer et al., 2006; Oguzie, 2006; Chauhan and Gunasekaran, 2007; Ismail, 2007; Ashassi-Sorkhabi and Asghari, 2008; Raja and Sethuraman, 2008a, 2008b, 2008c, 2009; Oguzie, 2008; Okafor et al., 2008; Radojicic et al., 2008; Zhang et al., 2008; Eddy, 2009; Ostovari et al., 2009; Satapathy et al., 2009; Solomon et al., 2009; Olusegun and James, 2010).

Conclusion

The following conclusions can be drawn from the studies and discussions of the published results in the literature reviewed. Most authors agreed that reinforcement corrosion is the most important cause of premature failure of reinforced concrete structure worldwide and generated a great research concern.

i) The uses of epoxy-coated steel had been questioned based on the deterioration of several structures built using epoxy-coated reinforcement has failed as a result of localized corrosion and high level of chloride attack.

ii) The use of galvanizing does not seem to offer sufficient guarantee for high chloride contamination.

iii) The uses of barriers such as water-proofing membranes and sealers though effective in checking corrosion, but required constant maintenance reapplication to the structure's life span.

iv) The uses of stainless steel reinforcement for concrete structures has been investigated and proved effective, but cost-effectiveness is the crux of the matter.

v) A viable alternative for controlling the corrosion phenomenon is the use of corrosion inhibitors when preparing the concrete, thereby reducing corrosion rates to technically tolerable levels, but limited information on the effects of inhibitors to the mechanical and physical properties of concrete due to difference types of environment to which the structure is exposed to.

vi) The uses of commercially available inorganic inhibitors (that is, nitrite base) can only delay corrosion initiation at the early stage, but reduces the compressive strength of the concrete structures as high as 20 to 40% as per long term performance and also decrease concrete setting by 1 h at high dosage. This, as a result of its function of accelerating and stabilizing formation of crystal phase of calcium hydroxide which leads to an increase in the micropore diameter in the hardened cement paste and thus to an increase in chloride permeability also decrease in concrete resistivity. Application of nitrite base inhibitors can only be made to non-carbonated concrete contaminated with relative low levels of chloride or to carbonated concrete without chloride. Calcium nitrite causes flash setting and freeze-thaw damage.

vii) The amines, alkanamines, aminoacids, mono- and poly-carboxylates organic inhibitor were found with the following characteristics: amines showed poor inhibition effect with very scattered result when their volatility increased. Aminoacids showed some inhibition effect, but not sufficient for an industrial applications. Carboxylate substances, especially poly-carboxylates showed very good inhibition effectiveness, making them the most promising candidates among the tested substances. A confirmation on concrete slab specimens is required to check compatibility with concrete and long-term effectiveness.

viii) Amino-alcohol base organic inhibitors were found effective in checking chloride ingress in the concrete, but its effects on the concrete properties were not investigated.

ix) N-heterocyclic organic compounds and their derivatives were confirmed satisfactory for corrosion inhibition of mild steel in acids and chloride media based on the adsorption of the molecules on the metallic surface and follows Langmuir isotherm adsorption model. But they were unable to investigate their effects on concrete properties and environment.

x) Benzotrazole (BTAH) was investigated as organic inhibitor into a simulated chloride contaminated pore solution and found to cause a significant increase in the corrosion resistance of the carbon steel as a result of formation of a complex layer of $[Fe_n(Cl)_p(BTA)_m]$ that spreads over the steel surface. Short and long term effects on the properties of concrete were not investigated vis-à-vis its compatibility and the exposure time was too short for such a generalized inference.

xi) The combination of $ZnO/Ca(NO_2)_2$ inhibitors shows a remarkable performance, but required further investigation as per its long and short term characteristics in concrete properties.

xii) Green inhibitor exhibits 73 to 98% inhibition efficiency. But it is still amazing to see reports wherein inhibition to the extent of 98% efficiency is achieved. It is certain that natural compounds emerge out as effective inhibitors of corrosion in the coming years due to their biodegradability, easy availability and non-toxic nature.

But its applications to mortar and concrete still need to be investigated.

ACKNOWLEDGEMENTS

This work was financially supported by Universiti Teknologi Malaysia (UTM) and Federal University of Technology, Minna, Nigeria. We are immensely grateful to both Institutions.

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