

CONCRETE CORROSION INHIBITING ADMIXTURES

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ABSTRACT

The harsh ambient conditions of the Gulf region necessitate the adoption of strict measures during construction to ensure that reinforced concrete structures have the durability to meet their design lives. Alongside the maintenance of good concrete practices, there are a variety of methods that may be employed to protect reinforced concrete from the environment, particularly the damaging effect of chloride-induced corrosion. Several of these options are often used in combination. One such technique is the inclusion of corrosion inhibiting admixtures.

Several types of corrosion inhibiting admixture are available and these employ different mechanisms to offset the corrosion of reinforcing steel in concrete. This paper discusses the mechanisms by which three, different, corrosion-inhibiting admixtures operate. These mechanisms are explained in terms of whether the admixture can be described to play an active, passive or combined active-passive rôle in reducing or delaying chloride-induced corrosion of the reinforcing steel.

KEYWORDS

Admixtures, corrosion inhibitor, chloride ions, reinforced concrete, permeability.

INTRODUCTION

Durability refers to the ability of concrete to maintain its integrity in service. The hot, saline environment in the Gulf region has often compromised this durability resulting in many instances of deterioration of concrete structures. With an increased awareness of the factors affecting durability, substantial improvements have been made in the quality of reinforced concrete. These have been achieved by both improving concrete practices and by effective use of appropriate technologies. One of the technology options available is the inclusion of materials that limit the corrosion of the reinforcing steel. The use of such corrosion inhibitors has become commonplace and there are several mechanisms by which available systems may operate.

This paper considers three different types of commercially available corrosion inhibitor. The mechanisms by which these systems operate are discussed.

CORROSION OF STEEL IN CONCRETE

Whilst carbonation of concrete can lead to generalised corrosion of the reinforcing steel, it is chloride attack which is of most significance in the Gulf region.

Reinforcing steel develops a passive, ferric oxide ($\gamma\text{-Fe}_2\text{O}_3$) layer in the alkaline environment of concrete. This passivating layer acts as a barrier to corrosion and is stable above pH 9. In the presence of chlorides and moisture, this passive layer may break down, even above the threshold alkalinity, resulting in the initiation of corrosion. This breakdown of the passive film is a localised phenomenon and results in the formation of a galvanic cell as illustrated in Figure 1.

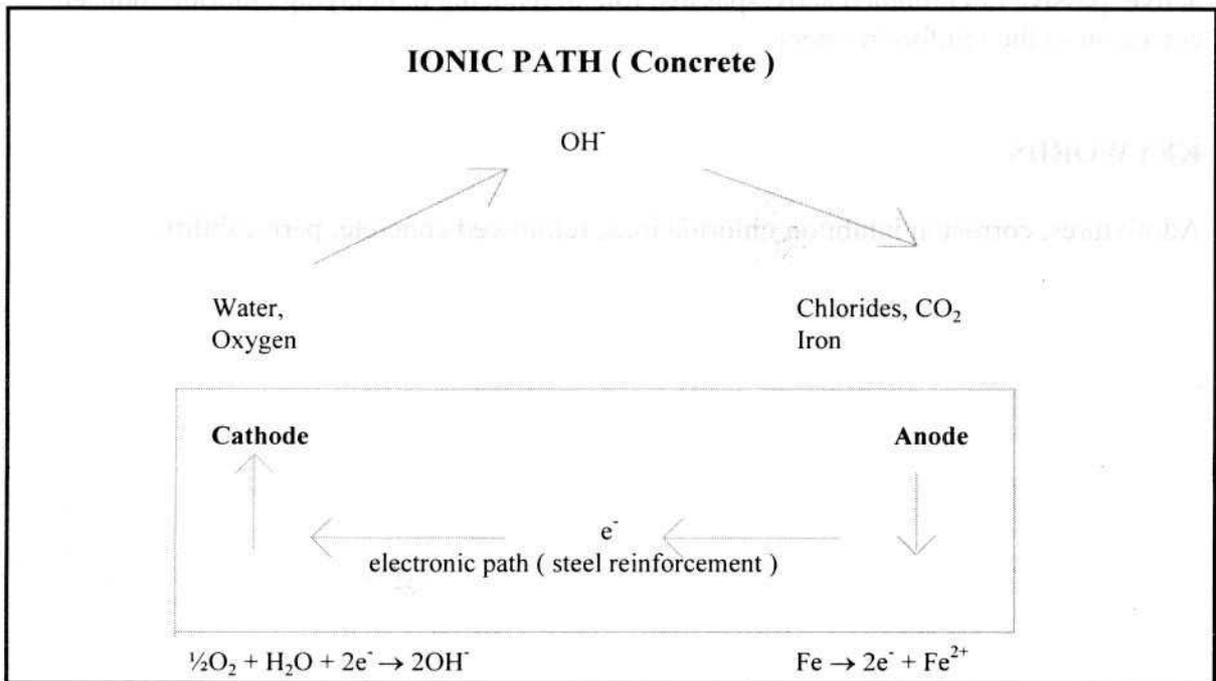


Fig. 1. Galvanic cell

The local active areas become the anodes whilst the remaining passive areas on the steel are cathodic. The cathode is where the reduction of dissolved oxygen takes place.

The galvanic cell may be termed “macro” or “micro” depending upon the distance between the anode and the cathode on the reinforcement. This separation depends upon several factors; including the porosity, the degree of paste saturation, and chloride quantity and distribution within the pore matrix. The degree of separation determines the pattern of chloride attack on the steel reinforcement. If chloride ions attack the ferrous ions they combine to create a ferrous chloride complex (rust) and initiate pitting corrosion. Without treatment, chloride ions continue to attack newly exposed ferrous ions and complex to form more rust. Growth of the corrosion pits continues and the increasing level of corrosion products leads to staining, cracking and spalling of the concrete.

Cathodes provide the environment for soluble iron chloride complexes to form. Such complexes can migrate to oxygen and pH rich areas where the complex breaks down forming iron hydroxide precipitate that releases the chloride to further react with the steel. Alternatively, the complexes may migrate away from the reinforcement permitting corrosion to continue.

Cracking and spalling of concrete cover is a consequence of the increased volume of the corrosion products over the original steel. The high specific volumes of the possible corrosion products, given in Figure 2, illustrate the problem.

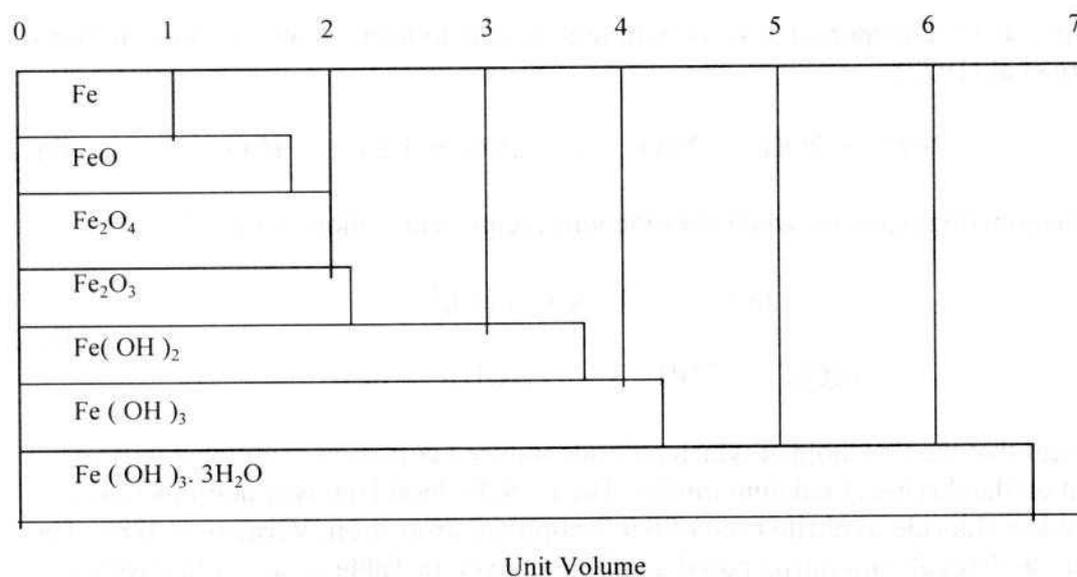


Fig. 2. Specific volumes of iron oxides and hydroxides, Jestesan et al (1985)

CORROSION INHIBITORS

A corrosion inhibitor is a substance that, when added to an environment, effectively checks, decreases or prevents the reaction of the metal with the environment, NACE (1984).

According to ACI 116R-90, it is a chemical compound, either liquid or powder, that effectively decreases corrosion of steel reinforcement before being embedded in concrete, or in hardened concrete if introduced, usually in very small concentrations, as an admixture. Corrosion inhibitors fall into several classes, including the following: passivators, precipitators, cathodic, anodic, oxygen scavengers and film-forming / adsorption, NACE (1984).

In reinforced concrete, for simplicity, corrosion-inhibiting systems can be considered as active, passive or active-passive, Nmai (1995). Active systems provide corrosion inhibition through a chemical reaction between the active ingredients of the inhibitor and the reinforcing steel. This provides a protective film or oxide layer at the steel's surface. A passive system is one in which the ingress of agents necessary to support corrosion is reduced or inhibited by permeability reduction. Examples include pore-blocking materials, surface sealants, waterproofers and pozzolanic additives. An active-passive system combines both protection at the steel and reduces the permeability of the concrete matrix.

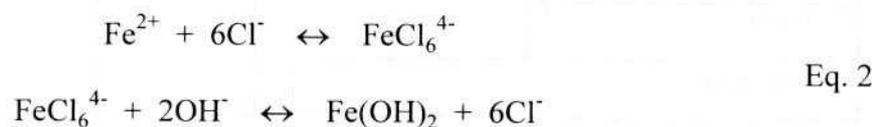
Active Inhibitor

“Calcium nitrite based admixture” is the classic example of an active inhibitor. It is an anodic inhibitor and delays corrosion by re-passivating defects in the passive, ferric oxide layer on the steel. Such defects are ferrous oxide ions that are susceptible to chloride attack.

Nitrite ions have been reported to react with ferrous ions to form an oxide film as follows, Rosenberg et al (1977).



A typical competing reaction, when chloride ions are present, follows in Eq. 2.



It is apparent that the threshold at which chloride induced corrosion is initiated will be dependent on the dosage of calcium nitrite. The U. S. Federal Highway administration recommends a chloride to nitrite ratio of 0.9 for optimal protection, Vermani (1988). The dosages for a 30% calcium nitrite based admixture, given in Table 1., are in line with this recommendation.

Based upon FHWA recommended 0.90 chloride to nitrite ratio		Currently utilized industry limits	
Chloride threshold kg / m ³	Recommended dosage of calcium nitrite admixture ltrs / m ³	Chloride threshold kg / m ³	Recommended dosage of calcium nitrite admixture ltrs / m ³
3.62	15.0	5.87	14.83
4.21	17.5	6.82	17.30
4.80	20.0	7.72	19.78
5.40	22.5	8.36	22.25
5.99	25.0	8.90	24.72
6.59	27.5	9.26	27.19
7.18	30.0	9.50	29.66

Table 1. Recommended dosages of 30% calcium nitrite based admixture

This type of inhibiting admixture has, in the past, been used successfully where the inclusion of cast-in chlorides could not be avoided. In such situations, it is relatively straightforward to calculate the level of chloride ions and, therefore, determine the dosage of the calcium nitrite admixture necessary to prevent chloride-induced corrosion. Successful use against later ingress of chlorides depends upon an assessment of the level of chloride ions expected at the surface of the steel within the life expectancy of the concrete structure. Whilst this involves more complex calculations, calcium nitrite admixtures have been successfully used in this manner for many years.

Passive Inhibitor

“Hydrophilic, pore-blocking admixture” is an example of a passive corrosion inhibitor. This employs a dual system to afford an improvement in the impermeability of the concrete. The reduced permeability to water and water-borne chloride has been successfully used for many years to protect against the detrimental effects of corrosion, particularly in concrete structures in marine environments subject to wetting and drying.

The admixture is based on a combination of fatty acids and hydrocarbon resin. The mechanism by which it operates can be described as follows.

From the onset of cement hydration, the Ca(OH)_2 liberated reacts with the fatty acids to form insoluble hydrophobic compounds, mainly as calcium salts. With the migration of water out of the concrete, the capillaries and voids are lined with this water repellent material. This causes a reversed angle of contact in which the surface tension forces now push the water out of the pore instead of into the pore, Ramachandran (1995). The hydrocarbon resin is deposited in the capillaries as they are formed, augmenting the waterproofing effect. Under subsequent water pressure in the hardened concrete, the hydrophobic solid blocks the capillary pores and interstices. As well as reducing water permeability, the restricting effect of the hydrophobic lining and the pore-blocking solid also reduces the migration of chloride ions.

Table 2. summarises two key water permeability measures for a concrete containing the hydrophilic, pore-blocking admixture in comparison with an equivalent control concrete without the admixture. The results clearly demonstrate the reduction in permeability imparted by the inclusion of the corrosion-inhibiting admixture.

Permeability test	Concrete control	Concrete with hydrophilic, pore-blocking admixture
Water absorption, BS1881 (%)	2.2	0.6
Depth of water penetration, DIN1048 (mm)	5.0	nil

Table 2. Permeability measures for 28-day old concrete containing hydrophobic, pore-blocking admixture

Concrete beams to the same mix designs have also been assessed for their ability to resist intrusion of chloride ions over a twelve month exposure period, when placed in a marine environment. The increase in chloride content of the concrete containing the inhibitor was less than half that of the control, in the 0–10mm depth range, in both a tidal zone and a splash zone.

Active-Passive Inhibitor

“Organic corrosion inhibitor” contains elements to impart both active and passive inhibition of corrosion. This admixture is a classic mixed inhibitor, affecting both anodic and cathodic reactions of corrosion. It contains an amine film-forming component that forms a protective film at the reinforcement surface. It also contains a waterproofing component that reduces chloride, oxygen and moisture permeability. Together, these form a synergistic corrosion inhibiting system.

In a similar mechanism to that in the hydrophobic, pore-blocking admixture, the time to corrosion initiation is reduced based on waterproofing organic esters. These partially hydrolyse and bind with the calcium ions provided from the $\text{Ca}(\text{OH})_2$ in the initial hydration mechanism of cement. This binding creates fatty acids and their calcium salts that provide a hydrophobic coating within the pores. The diameter reduction in the pore, induced from the hydrophobic, calcium salt lining, also reduces chloride ion migration through the capillary pore matrix. This provides passive system corrosion inhibition by increasing the time it takes to reach the chloride threshold level at the steel reinforcement in concrete.

This reduction in chloride migration is particularly important when concrete cracks. Chlorides cannot easily diffuse laterally from the crack in concrete treated with this admixture, thus the spread of corrosion along the reinforcement is minimised, Krauss and Scanlon (1993).

Adsorption is an important step in the inhibition mechanism of organic, film-forming corrosion inhibitors. The amine in this admixture is particularly effective in adsorbing onto the steel reinforcement because of its chemical structure, comprising a polar “head” with a long hydrophobic “tail”. The polar end of the molecule is oriented towards the steel reinforcement and forms chelate bonds with the surface metal atom, Buffenbarger et al (1996). The consequence of such bonding is that the amine molecules are strongly attached to the steel surface. With the polar head multiple-bonded to the steel reinforcement, the hydrophobic tail is angled away from the steel surface. This can be visualised in the idealised view presented in Figure 3.

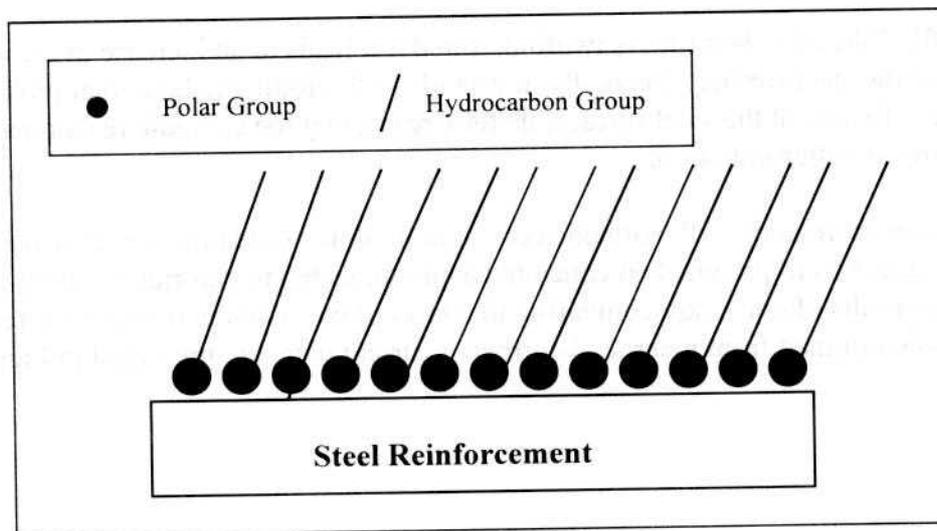


Fig. 3. Idealised view of film-forming amine on surface of reinforcing steel

The hydrophobic tail provides two important functions. It attracts excess non-absorbed amines and similarly structured waterproofing esters to the reinforcement site by providing a structure for stacking between hydrophobic molecules. This effectively allows molecular monolayers to build and create an increase in layer thickness at the reinforcement. Additionally, thermodynamic stability is conferred with trans-conformation stacking, Buffenbarger et al (1996), as illustrated in Figure 4.

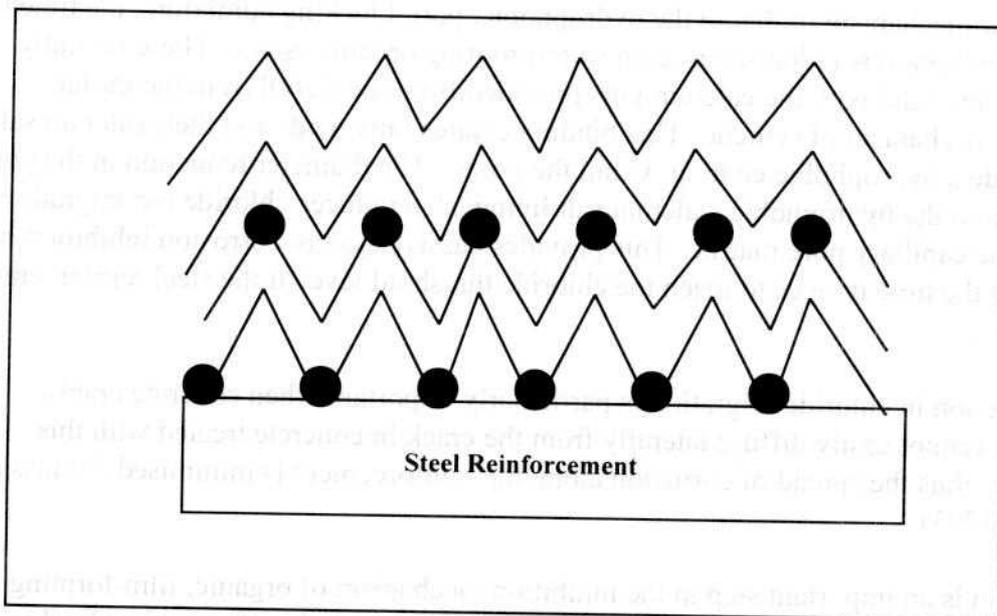


Fig. 4. Stacking of film-forming amine and ester hydrophobic tails near the reinforcing steel.

Electrical impedance spectroscopy studies have shown the ability of the film to form a protective, corrosion-resisting layer on the steel reinforcement. Fourier Transform Infrared studies have demonstrated the adsorbed film to be several layers in thickness and irremovable by water and chemical washes.

The benefit of the adsorbed film is twofold. Firstly, it leads to an increase in the chloride threshold at the steel surface. Secondly, it provides a hydrophobic layer that minimises the availability of water at the steel surface, thereby restricting the cathodic reaction and the rate of corrosion after initiation.

Overall, the performance of the organic corrosion inhibitor is demonstrated by the time-to-corrosion results from pre-cracked concrete beams subjected to chloride ponding with 6% NaCl. The results of one study comparing the onset of corrosion in treated concrete with a control, as determined from macrocell corrosion current data, are presented in Figure 5.

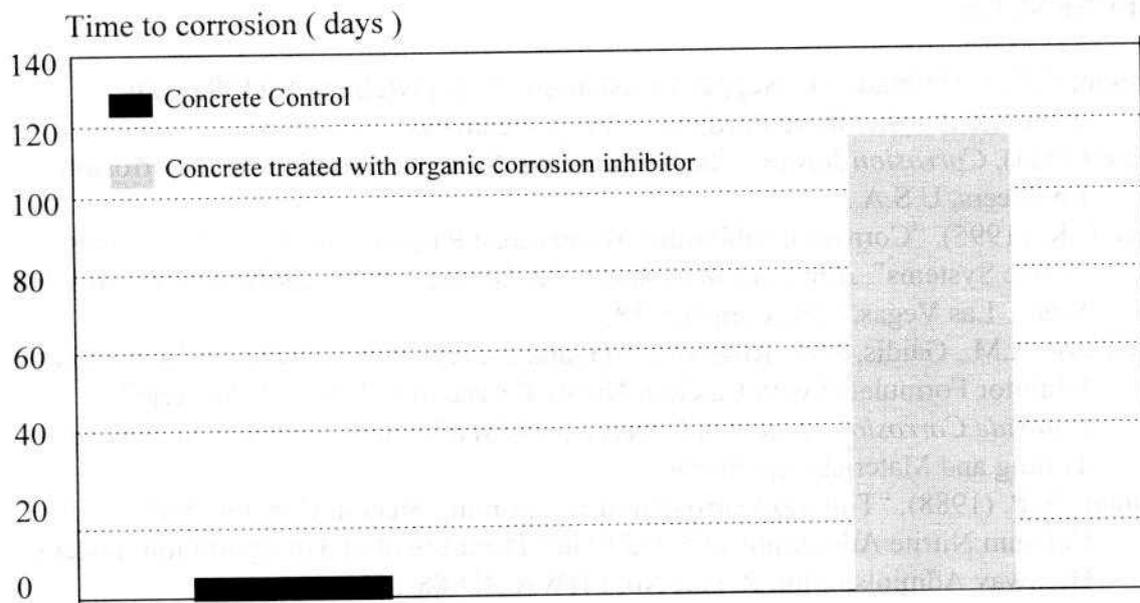


Fig. 5. Time-to-corrosion data for pre-cracked beams subjected to chloride ponding

SUMMARY

There are various methods employed in the Arabian Gulf for inhibiting corrosion in reinforced concrete. These include; good concrete practices, the use of epoxy-coated rebar, inclusion of pozzolans (e.g. microsilica), use of corrosion inhibiting admixtures, application of coatings and cathodic protection. Generally, several of these options, or others, are adopted, in conjunction, to try and combat the harsh ambient conditions to which concrete is subjected in the region.

The use of corrosion-inhibiting admixtures has been commonplace for some years, contributing to the success in building structures, which will meet their design lives. This paper has highlighted the mechanisms by which three different, commercially available admixtures operate. All these admixtures have been used successfully in the region.

ACKNOWLEDGEMENT

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