

Evaluation of surface applied corrosion inhibitor performance on reinforced concrete structures

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ABSTRACT

Surface applied corrosion inhibitors (SACI) are widely used to mitigate the corrosion process of steel reinforcement in concrete. But they remain controversial as to their effectiveness and the ability to compare materials from different manufacturers and technologies. They are applied onto the surface of hardened concrete and penetrate towards steel reinforcement. This paper discusses the corrosion inhibition performances of dual-phase surface applied corrosion inhibitor and the efficiency of the corrosion inhibitor is assessed by selected testing procedures in BAM laboratories.

KEYWORDS: corrosion, inhibitor, concrete, steel, reinforcement, protection.

1. Cost of corrosion

Concrete is the most commonly used construction material in today's world. Local availability of ingredients such as cement, sand and gravel, ease of forming and high compressive strength made concrete superior to masonry for constructing new structures. On the other hand, strong concrete could not provide adequate tensile strength and thus engineers had to incorporate steel to overcome this weakness. The steel-reinforced concrete led to innovative construction solutions for all types of structures and has become the first choice for designers and builders. Despite the all advantages, corrosion of the steel reinforcement represents a major problem for the longevity of the structures. The physical protection of concrete cover and the high alkaline environment provided by the

cement paste are not long-lasting due to several other factors.

Over the past half-century, corrosion has emerged as the most significant cause of concrete deterioration. Apart from the significant refurbishment costs, the loss of access or functionality also results in considerable economic loss. Taking the five major sectors of infrastructure: utilities, transportation, manufacturing industry, and government, the total annual cost of corrosion-related repairs throughout the world is estimated at US\$2.5 trillion, corresponding to about 3.4% of the world's Gross Domestic Product (GDP) (2013) [1]. Corrosion related refurbishment work in reinforced concrete structures such as roads, bridges, marine structures, industrial buildings, commercial and residential buildings account for

a significant share of the total direct cost of corrosion. The indirect cost corrosion damages to the public are difficult to estimate but, based on a life cycle analysis of corrosion maintenance, repair, and rehabilitation for bridges in the USA, the cost in terms of lost productivity, traffic delays, etc. could be as high as the direct costs [2].

2. Corrosion of steel

Corrosion could be described as the transformation of a refined metal (in this case steel) into its more stable form (oxide compounds), with the consumption of oxygen and water. These electrochemical reactions take place at two distinct locations on a metal component, the anode (1) and the cathode (2) [3].

$$Fe \rightarrow Fe^{+2} + 2e^{-1}$$
 (1)

$$2e^{-} + H_2O + \frac{1}{2}O_2 \rightarrow 2OH^{-}$$
⁽²⁾

The hardened concrete protects the steel reinforcement against corrosion in different ways. The highly alkaline environment created by the cement matrix surrounding the reinforcing bars results in the formation of a passive layer around the steel. This passive film is only a few nanometers thick and is composed of hydrated iron oxides with a varying degree of Fe²⁺ and Fe³⁺ [4]. This protective film is maintained if the highly alkaline environment provided by the concrete matrix persists. However, deterioration of the concrete harms the passive condition of the reinforcement.

In chloride attack, chloride ions are diffused through the concrete to the steel. This disrupts the passive layer at a local place at the rebar and leads to corrosion. Besides, carbonation is also resulting with breakdown of the passive layer and furthermore increases the free chlorides by releasing the bound ones. The exposure to carbon dioxide dissolved in the water initiates the carbonation process of the concrete, which reduces the pH of the cement matrix. Once the passive layer breaks down, corrosion reactions start, attacking the reinforcing bars. Water and oxygen are the only ingredients, which are needed for the reactions to continue. Depending on the corrosion rate, the volume expansion of the corrosion products on the reinforcement bars could push off the concrete cover and eventually corroded steel reinforcement lose adhesion to the concrete, which compromises the structural integrity.

3. Protection of steel reinforcement

Corrosion of steel in the concrete is called no as an electrochemical process. A typical corrosion cell requires both an anodic site, where the metal is dissolved, and a cathodic site, where oxygen is reduced, and hydroxyl ions are produced; it also requires electronic conduction paths (through the reinforcing steel) and ionic or electrolytic conduction paths (through the pore-electrolyte). To reduce the rate of corrosion, a reduction in the rate or elimination of the associated processes is required [5].

3.1 Hydrophobics in concrete protection

Chloride ions diffuse into concrete along with the water and damages the protective passive layer around the steel reinforcement and initiate or accelerate the corrosion process. Water is the main chemical compound along with oxygen, which are both consumed in corrosion reactions. Therefore, reducing the water ingress and chloride ion diffusion result with reduction of the corrosion rate.

There are several different ways to reducing water ingress to the concrete. Hydrophobic treatment is one of the ways being used for a long time for keeping concrete dry and silicones are the most widely used chemicals for this purpose. Silanes are a diverse class of chemicals of organo-silicon molecules of various functions and sizes. The small size of silane molecules means that they can penetrate deep into the concrete, where they can form chemical bonds with the hydrated components of the cement matrix due to their silica structure. After reacting with concrete, silane molecules repel the water and stop further chloride ions from penetrating the concrete [6,7,8]. The water already present in the concrete can evaporate through open pores since this water-repellent layer created by silanes is in the molecular level by size and naturally considered as 'breathable'.

3.2 Corrosion inhibitors

NACE International defines corrosion inhibitor as "a chemical substance that, when added in concentration to an environment, small effectively decreases the corrosion rate". Based on the electrochemical mechanism of action alone, all inhibitors fit into one of three broad classes: (a) anodic, (b) cathodic and (c) mixed, depending on whether they affect the anodic reaction, the cathodic reaction, or both [9]. These inhibitors are chemical compounds, which can be transported to the steel reinforcement surface in different ways. They can be added to concrete admixtures and mixed directly with the fresh concrete. But this method is limited to fresh concrete and only applicable for new structures. The refurbishment of existing structures accounts for a large part of construction activities in Europe. In the light of this fact, various types of surface-applied corrosion inhibitors (SACI) have been developed over the last decades to stop ongoing corrosion processes in old concrete.

Silanes are used as an effective corrosion inhibitor due to their excellent hydrophobicity on concrete surfaces. Besides silanes, amines (e.g. aminoalchohol, aminocarboxylates) and sodium monofluorophosphate (MFP) are known as SACIs for protecting steel reinforcement. However, the efficiency of these inhibitors on reinforced concrete are limited under certain conditions. For instance, MFP shows very little effectiveness on the corrosion rates of steel in both non-carbonated and carbonated concretes [10]. Several experimental studies and field surveys revealed that the amine-based inhibitors (aminoalcohol and aminocarboxylates) also have very limited impact on inhibiting ongoing corrosion [11,12,13,14].

4 Dual phase corrosion inhibitor

In the light of research carried out over the past two decades, scientists succeeded in combining silanes and selected corrosion inhibitors to develop a new type of surface-applied corrosion inhibitor. This material is a clear liquid with a combination of high-quality blended silanes and selective corrosion inhibitors (including latent phase inhibitors) and is designed to break the corrosion mechanism in reinforced concrete structures in various conditions. Silane enables the inhibitor for deep technology penetration into the concrete and chemical bonding, which avoids wash out over time. In addition, the high alkali-resistant nature of silanes leads to long service life when used on concrete surfaces. While the silane backbones of the material guarantee high water repellency and the exclusion of water and chloride ions, selective corrosion inhibitors stop the corrosion reactions and help the reinforcement bar to restore its passive layer. The presence of a latent phase inhibitor lies dormant within the concrete until activated by moisture, which then penetrates the surface through cracks in concrete and sustains effective corrosion protection even after the silane barrier diminishes. This phenomenon leads to an extension of the service life of the structures and the maintenance-free period with reduced refurbishment costs.

4.1 Functionality

Dual phase corrosion inhibitor employs dual functionality. The silane base (alkylalkoxysilane) provides similar benefits to the water-repellent sealers, and the integral corrosion inhibitors are carried into the concrete along with the silane. The latent phase inhibitors remain inactive in the concrete until the water repellency diminishes over time, or until the concrete cracks. They then become mobile and are carried deeper into the concrete. Dual phase inhibitor has a surface tension roughly 1/3 that of water, and low viscosity to improve penetration into concrete. Its special blend of silanes provides a balance between drying time and penetration over a wide temperature range, as well as lower VOC content and a higher flash point than many traditional silane-based inhibitors.

The most observable property of dual phase inhibitor is water repellency on the concrete surface. The silane component of dual phase inhibitor provides the same benefit with the added feature of its ability to act as a corrosion inhibitor. The alkylalkoxysilane structure of the dual phase inhibitor protects concrete from penetration of liquid water, but it keeps concrete permeable to water vapor. Thus, while keeping additional water from penetrating into the concrete, it will allow any moisture contained in the concrete to evaporate. Dual phase inhibitor utilizes multiple silane functionalities to create different effects on the concrete substrate. These include the formation of a hydrophobic shield as well as a corrosion inhibition effect.

Creation of the hydrophobic properties begin when the silane hydrolyzes to form silanol and alcohol. Next the silanol group condenses, forming a bond to hydroxides on the concrete surface. Fig. 1 [15,16] depicts the chemical reactions associated with this process.





Fig. 1: Reaction of alkyl alkoxy silane with water (hydrolysis) to produce silanol and alcohol followed by condensation and bonding to the pores of the concrete substrate.

The R in the figure represents the hydrophobic portion of the chemical compound. CH_3OH is the methanol produced when dual phase inhibitor reacts with water. The substrate in this case is the pores in the concrete. This series of reactions leads to the formation of the hydrophobic layer (in molecular level) observed on and in the surface of the concrete treated with dual phase inhibitor.

Alkylalkoxysilanes can react within the concrete to reduce the conductivity of the electrolyte. The reaction increases the resistivity of the concrete immediately adjacent to the reinforcing steel which in turn slows down the electrochemical reactions for the corrosion process.

5 Experimental studies in BAM

The test specimens used for this investigations are listed in Table 1.

Table 1. Test specimens

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Test Series	Absorption test		Reference
Name	MP-I	MP-III	Ref
CEM-I	6	6	6
CEM-III	3	3	0

The investigations were performed with mortar specimens manufactured with CEM I and CEM III. The mortar formulation corresponds with the standard formulation in DIN EN 196 [17] Engin Cueneyt Seyhan – et... / VIII CONGRESO ACHE – SANTANDER 2020 whereby the w/z value differs from the standard according to the customer. The used w/z value was 0.6. The test setup for the specimens is shown in Figure 2. The mortar cover was 6 mm. The electrolytic coupling of the reference electrode was achieved by application of a chloride-containing electrolyte in a saddle cell. This cell was attached to the specimen by means of silicon. The advantage of the saddle cell is that the investigations can be performed in a nonwater-saturated mortar as a coupling electrolyte at the bottom of the specimen is not necessary. The electrolyte used consists of artificial seawater prepared according to DIN EN ISO 15711 [18]. Saturated silver/silver chloride electrodes were used as reference electrodes for the electrochemical tests.



Fig. 2: Schematic representation of the test setup for the MP 8500 and reference specimens

The electron-conducting connection was prepared by means of a stainless steel wire made of material 1.4576 which was welded through WIG-welding. After welding the specimens were sandblasted and degreased before concreting.

Figure 3 represent the test setup with all specimens using saddle cells. The potential recording was realized by a data logger of type Keysight 34972A; the measured values were recorded every minute.



Fig. 3: Exemplary experimental setup using saddle cells

The measuring arrangement enables a precise chloride contamination above the working electrode. Furthermore, the combination of inhibitor and hydrophobing can be realistically applied at the surface and not at the entire lateral surface of the specimen.

Following the potential measurements, after a 16weeks drying phase under laboratory conditions 20°C and 40% relative at humidity electrochemical polarization tests were carried out. The current versus potential curves were recorded with Gamry Interface 1000 potentiostats and the corrosion current was calculated by means of Tafel fitting. Figure 4 shows the measuring setup for the polarization tests. As counter electrode a mixed metal oxide coated titanium mesh was used; the electrolyte in the cell was water. Prior to starting the polarization tests, the specimens of the series passive were exposed to water for one hour passive); the filling level (series was approximately 5 mm from the bottom of the specimen. The saddle cells were filled with chloride-containing solution. After 24 h exposure in water and exposure to artificial seawater the specimens were measured again (series active). This serves to prove the efficiency of the inhibitors regarding the corrosion rate in the active and passive condition.



Fig.4: Measurement setup for electrochemical polarization tests

5.1 Results of electrochemical investigations with preventive application of dual phase corrosion inhibitor

The following series were treated with MP 8500, before the electrochemical measurements. After an exposure time of 28 days the saddle cells were assembled and filled with artificial seawater; simultaneously the potential measurements were started.

The series MP 8500-I and MP 8500-III were treated as described above. For series MP 8500-I three out of six specimens were active after completion of the measurement, see Fig. 5.



Fig. 5: Potential versus time for series MP 8500-I

For series MP 8500-III (CEM III) two specimens exhibit potentials lower than -350 mV after three days; the third specimen was active after 50 days, see Fig. 6.



Fig. 6: Potential versus time for series MP 8500-III

5.2 Reference series without application of dual phase corrosion inhibitor

The potential measurement of the reference series was conducted similar to the MP 8500 series. The exposure with artificial seawater took place during the entire measuring period. Four out of six specimens were active already after one day, specimen Ref-6 was depassivated after 66 days and specimen Ref-5 after 74 days (see Fig. 7). The potential measurement was performed over a period of 142 days. A repassivation of the specimens during the test duration was not observed.



Fig. 7: Potential versus time for reference series

5.3 Electrochemical polarization tests

In the following, current density potential curves of all series for the "passive" and the "active" state are presented. The previously measured free corrosion potentials are shown in Fig. 8 and Fig. 9. After 24 hours of exposure to artificial seawater all series exhibit active specimens.



Fig. 8: Free corrosion potentials of specimens prior to polarization tests, passive



Fig. 9: Free corrosion potentials of specimens prior to polarization tests, active

The series MP 8500-I revealed more positive corrosion potentials than series Ref in passive state; the polarization currents are lower (Fig. 10). After 24h of chloride exposure 4 specimens shown lower free corrosion potentials and higher polarization currents then in the passive state (Fig. 11).



Fig. 11: Current density potential curves of series MP 8500-I, active

For series MP 8500-III one of the specimens became active during moistening. In Figure 12 the more negative free corrosion potentials of specimen MP 8500-III-8 can be observed as well as the higher polarization current. After 24h of chloride exposure a second specimen became active (see Fig. 13).



Fig.12: Current density potential curves of series MP 8500-III, passive



Fig. 13: Current density potential curves of series MP 8500-III, active

The series Ref passive exhibit a free corrosion potential of -270 mV to -135 mV (see Fig. 14). The polarization currents are comparable within this series. The polarization curves shown in Figure 15 show significantly more negative free corrosion potentials and up to two decades higher polarization currents for the active state.



Fig. 14: Current density potential curves of series Ref, passive



Fig. 15: Current density potential curves of series Ref, active

Figure 16 shows the measured potentials in the saddle cell (Ecorr-z) and within the electrolyte (Ecorr-El). The reference series do not reveal significant differences. The series MP partly

exhibit differences of the measured potentials (see red marked dots in Fig. 16). For the measured potentials in the cell describing an active corrosion system at the same time a more positive potential within the electrolyte was measured. These specimens reveal significantly lower values of the determined corrosion currents, see Fig. 17. In the reverse case (see series MP 8500-III) the corrosion currents are significantly higher.



Fig. 16: Free corrosion potential of specimens of test series active

The coloured gradation in Figure 17 enables a better attribution of the active (red), intermediate (orange) and passive (green) specimens.



Fig. 17: Corrosion currents calculated from the current density potential curves for the test series active

6. Discussion

Due to application of Dual phase corrosion inhibitor a partially delayed corrosion initiation could be observed at the series with CEM I. At several specimens no corrosion could be initiated

Engin Cueneyt Seyhan - et... / VIII CONGRESO ACHE - SANTANDER 2020

during the duration of the potential measurement. In the MP 8500-I series, 50% of the samples show potentials indicating active corrosion after the measurement. Compared to the reference series without application of Dual phase corrosion inhibitor, a positive influence of the preventive application regarding corrosion initiation can be observed. Compared to the reference series without application of Masterprotect a positive influence of the preventive application of Masterprotect on the corrosion inhibition can be determined. When considering the results of the polarization tests it becomes apparent that for specimens of the series MP 8500-I despite negative corrosion potentials which were comparable with those of the reference series (active) significantly lower corrosion currents were measured.

Furthermore, influence of the the hydrophobing on the potential measurement can be observed. If the potentials inside the saddle cell are more negative than in the electrolyte a significant voltage drop or a decoupling of the active areas, respectively, is given due to the hydrophobing. This results in a significantly smaller polarization current in the polarization tests. From a practical point of view this would decrease the driving voltage in a macro cell and reduce the corrosion rate. element Comparing specimens from series REF active with the specimen MP 8500-I-6 it becomes apparent that despite similar corrosion potentials the corrosion rate of specimen MP 8500-I-6 is up to two decades lower. As the specimen clearly revealed rather negative potentials during the long-term measurement than the specimen Ref-4, a significant influence of the determined corrosion current due to varying active surface ratios can be excluded. The lower corrosion current can hence be traced back to the inhibiting effect of MP 8500.

In the polarization tests of series MP-III all specimens exhibit low potentials indicating an actively corroding system. The results of the polarization tests, however, clearly show that the corrosion currents of the series with Masterprotect 8500 are by a decade lower compared to series Ref. As the measured potentials in the cell are more positive than in the electrolyte of the measuring cell an influence of the hydrophobing can be excluded. An inhibiting effect of series MP 8500 when using CEM III is also given. Differences due to different electrolyte resistance developments between the series Ref and MP-III cannot be determined due to the applied hydrophobization.

7. Summary

For the test series MP 8500 using CEM I and CEM III a corrosion inhibition could be proven. The influence of the hydrophobic effect on the corrosion inhibition and the reduction of macro element corrosion currents could be observed. The potential increase of the reference series after the drying phase is based on the drying process of the samples. A 100% inhibition of the corrosion processes during the long-term measurement could not be observed, only a delay of the corrosion initiation but with a reduced corrosion rate against the reference series.

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