Corrosion Inhibitors for Steel in Concrete

B. Elsener, Faculty of Engineering, University of Cagliari (Italy) and Institute of Materials Chemistry and Corrosion, Swiss Federal Institute of Technology, Zürich

Abstract

Corrosion of reinforcing steel represents the most widespread form of deterioration of concrete structures resulting in significant costs for repair and replacement worldwide. Despite the huge demand, a simple, cheap and reliable technique that either protects the steel in concrete from corrosion or at least lowers its corrosion rate is still lacking. The concrete repair industry has developed novel techniques that are claimed to prevent the steel from corrosion and/or to restore the protective character of the cover concrete by introducing corrosion inhibitors into the carbonated or chloride contaminated concrete.

Inhibitors, chemical substances that prevent or retard corrosion, are applied as concrete admixtures or as surface applied liquids both for preventive or for restorative applications. A short review on literature results regarding the performance of the most frequently used inhibitors for steel in concrete in laboratory and in field tests is given, in particular two inorganic inhibitors, calcium nitrite (DCI) and MFP, and several organic inhibitors, the „migrating inhibitors“ (MCI or SIKA) and an organic corrosion-inhibiting admixture (OCI) are addressed. The problem of transport of inhibitors into concrete is discussed. A critical review of corrosion inhibitors to be used on reinforced concrete structures regarding concentration dependence, durability and measurement and control of the inhibitor action is given.

Keywords: inhibitor, admixtures, surface applied, corrosion, adsorption, transport, durability

Introduction

In general, reinforced concrete has proved to be successful in terms of both structural performance and durability. However, there are instances of premature failure of reinforced concrete components due to corrosion of the reinforcement. The two factors provoking corrosion are the ingress of chloride ions from deicing salts or sea water or the reaction of the alkaline pore solution with carbon dioxide from the atmosphere, a process known as carbonatation. Despite of the huge demand, a simple, cheap, and reliable technique which either protects the steel from corrosion or at least lowers its corrosion rate is still lacking. Over the past decade, however, concrete repair industry has developed novel techniques that are claimed to prevent or at least reduce corrosion of steel in concrete. The use of these „corrosion inhibitors“ is of increasing interest as they can be used in reinforced concrete either as preventive measure for new structures (addition to the mixing water) or as surface applied inhibitors for preventive and restorative purpose. Addition to the mixing water does not require any additional working steps and allows a simple handling of the inhibitor, unless it affects the properties of the cement paste adversely. Application from the concrete surface could be a promising technique to protect already existing structures from corrosion or increase the lifetime of structures that already show corrosion attack. The application of inhibitors on the concrete surface requires the transport of the substance to the rebar where it has to reach a sufficiently high concentration to protect steel against corrosion or reduce the rate of the ongoing corrosion.

Very often the long experience with chemicals operating as corrosion inhibitors e.g. in the oil field, gas or petroleum industry is taken as an example for the successful use of corrosion inhibitors, transferring this success also to applications on reinforced concrete. This is a priori not correct because the mechanism of inhibitor action are completely different:

• in the application of oil and gas industry (and most others) the steel to be protected is uniformly corroding in slightly acidic or neutral media. Thus the inhibitors have to protect the bare metal surface, e.g. as adsorption inhibitors acting specifically on the anodic or on the cathodic partial reaction of the corrosion process or as film forming inhibitors blocking the surface more or less
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- Steel in concrete instead is in a highly alkaline environment, the high concentration of hydroxyl ions acts as passivation promoting inhibitor and indeed, steel in concrete is passive, thus protected by a thin oxy-hydroxide layer. This is the starting point for any mechanistic action of inhibitors in concrete.
- Inhibitors for chloride induced pitting corrosion are by far less studied [3]. Inhibitors for pitting corrosion can act by film forming prior to the ingress of chlorides, by buffering the pH in the local pit environment, by competitive surface adsorption processes between inhibitor and chloride ions or by competitive migration of inhibitor and chloride ions into the pit.

Another point in the terminology of „inhibitors“ has to be clarified: a corrosion inhibitor can prolong the service life due to chemical / electrochemical interaction with the reinforcement. Any other substances that may prevent the onset of corrosion or reduce ongoing corrosion by surface treatment (e.g. hydrophobation) or by admixtures that reduce porosity of the concrete (e.g. fly ash, silica fume, waterproofing admixtures etc.) are not considered to be corrosion inhibitors.

Most of the results published in literature and reviewed recently [4 – 6] are from laboratory studies using solution experiments or relatively small mortar samples. Long term performance results are available from admixed inhibitors only, especially calcium nitrite [7], results from well documented field tests with surface applied inhibitors instead are rare. There are, however, other difficulties to get unambiguous, conclusive results on the performance of corrosion inhibitors on reinforced concrete structures:
- most of the “inhibitors” available under different trade names are blends of essentially unknown composition that even might be changed without notice. This makes even laboratory experiments difficult.
- sometimes the use of surface applied inhibitors is recommended only in conjunction with other corrosion protection methods as e.g. hydrophobation of the surface and it is difficult to isolate the inhibitor performance.

This paper is based on a recent state of the art report of the author on corrosion inhibitors for steel in concrete [4, 6] and the literature results reviewed therein. In particular calcium nitrite (DCI), the migrating corrosion inhibitors (SIKA or MCI) and MFP (Monofluorophosphate) are addressed. The problem of testing different inhibitors for steel in concrete is addressed and - as far as available results from field tests with inhibitors are presented. Finally a critical evaluation of corrosion inhibitors for steel in concrete is given.

**Corrosion inhibitors to prevent or delay corrosion initiation**

The most frequently used technique is adding of the inhibitors to the mixing water of concrete as admixtures for new structures in order to prevent or at least delay the onset of corrosion. **Calcium nitrite** is the most extensively tested admixed corrosion inhibitor [7] and has - when applied according the specifications together with high quality concrete and sufficient cover - a long and proven track record in the USA, Japan and in the Middle East [7]. It is used in parking, marine and highway structures. Nitrite is acting as a passivator due to its oxidizing properties and stabilizes the passive film [8]. All investigations revealed a critical concentration ratio (threshold value) between inhibitor (nitrite) and chloride of about 0.6 (with some variation from 0.5 to 1) in order to prevent the onset of corrosion.

Another inorganic inhibitor, **sodium mono-fluoro phosphate** Na₂PO₄F (MFP), can be used only as surface applied inhibitor due to adverse chemical reaction with fresh concrete [9]. Laboratory studies of the preventive inhibitor action against chloride induced corrosion showed that by applying several intense flushings before the ingress of chlorides [10], it could prevent the onset of corrosion during the test duration of 90 days even at chloride concentrations as high as 2% by weight of cement. A critical concentration ratio MFP / chlorides greater than 1 had to be achieved, otherwise the reduction in corrosion rate was not significant [10]. In solutions containing Ca(OH)₂ MFP is reported to react...
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with the calcium ion to form insoluble products as calcium phosphate and calcium fluoride [9, 10], thus the active substance, the PO$_3$F$^-$ ion, disappears from the pore solution. The main problem using MFP as surface applied liquid is the penetration to the reinforcement in order to act as inhibitor. In early field tests in Switzerland no sufficient penetration of MFP has been found [11]. This was partly due to a too dense concrete, to cover depth greater than 45 mm or due to an insufficient number of MFP applications on the surface. In more recent field applications [12], e.g. on the Peney Bridge near Geneva [12], concrete buildings and balconies, MFP was applied onto cleaned, dry concrete surfaces in up to 10 passes and the concrete is impregnated to the reinforcement level in a few days or weeks [12]. More recently, the use of a MFP containing gel on the concrete surface could improve the penetration of MFP.

Organic inhibitors, especially alkanolamines and amines and their salts with organic and inorganic acids are used as components in corrosion inhibitor blends of usually complex formulations [13]. These blends often are not sufficiently well described so most of the published work has been undertaken with commercially available systems. A comparative test of different organic amines in alkaline solutions [14] showed very good corrosion inhibition of the commercial inhibitor blend at high concentration, pure dimethylethanolamine instead being practically ineffective. Recent research work at ETH Zurich investigating a commercial migrating inhibitor blend has shown that the blend can be fractionated into a volatile (dimethylethanolamine) and a non-volatile (benzoate) component [15]. For a complete prevention of corrosion initiation in sat. Ca(OH)$_2$ solution with 1 M NaCl added the presence of both components at the steel surface in a concentration ratio of inhibitor / chloride ca. 1 was necessary (figure 1). Modern surface analytical techniques such as XPS [16] have shown that for the formation of a significantly thicker organic film on iron in alkaline solutions both components of the commercial inhibitor blend have to be present. This might be significant for the mechanism of the inhibitor action. The inhibitor in the recommended dosage could delay the average time to corrosion initiation of passive steel in mortar by a factor of 3 (figure 2).

![Figure 1: Corrosion potentials and polarization resistance of rebar samples in solutions containing the two components of the inhibitor: ■ no inhibitor, ○ volatile constituent, △ non-volatile constituent [15](left)](image)

![Figure 2: Percentage of corroding rebars in mortar vs time of cyclic chloride treatment [15](right)](image)

Experiments with a commercial migrating inhibitor blend [15] have shown that the polarization resistance measured after the onset of corrosion in solution increases with the inhibitor concentration (table 1), both the volatile and the non-volatile fraction could reduce the corrosion rate slightly compared to the non-inhibited solution [4, 15]. In mortar experiments with cyclic ponding in 6% chloride solution instead the polarization resistance after the onset of corrosion did not change with inhibitor concentration and was similar to the mortar without inhibitor (table 2) [15]. Thus a delay in the onset of corrosion is obtained but no reduction in the corrosion propagation rate.
Table 1: Average polarization resistance of three rebar samples after the addition of 1 M NaCl to sat. Ca(OH)\(_2\) solution with inhibitor [15]

<table>
<thead>
<tr>
<th>Inhibitor (wt %)</th>
<th>Rp k(\Omega) cm(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>490 ± 80</td>
</tr>
<tr>
<td>1</td>
<td>11 ± 3</td>
</tr>
<tr>
<td>0.1</td>
<td>2 ± 1</td>
</tr>
<tr>
<td>0</td>
<td>3 ± 1</td>
</tr>
</tbody>
</table>

Table 2: Average polarization resistance of rebar samples in mortar with different inhibitor concentration after 343 days cyclic treatment in chloride solutions (see fig. 1b)

<table>
<thead>
<tr>
<th>Series</th>
<th>Inhibitor (wt%)</th>
<th>Rp k(\Omega)cm(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>5.2 ± 2.2</td>
</tr>
<tr>
<td>2</td>
<td>0.015</td>
<td>6.0 ± 1.4</td>
</tr>
<tr>
<td>3</td>
<td>0.075</td>
<td>5.6 ± 1.6</td>
</tr>
<tr>
<td>4</td>
<td>0.375</td>
<td>6.2 ± 0.9</td>
</tr>
</tbody>
</table>

Another alkanolamine based commercial inhibitor blend was tested as admixture in mortar and concrete samples exposed to chlorides [17]. After one year of the tests corrosion had started in specimens with w/c = 0.6, the chloride threshold values for the inhibitor containing samples are in all cases higher (4 - 6% Cl\(^-\) by weight of cement) compared to the control samples (1 - 3% Cl\(^-\)).

Prevention or at least prolongation of the onset of corrosion has been reported also for an organic corrosion-inhibiting admixture (OCI) proposed in a United States Patent [18]. The admixture comprises an oil / water emulsion, wherein the oil phase comprises an unsaturated fatty acid ester of an aliphatic carboxylic acid with a mono-, di- or trihydric alcohol and the water phase comprises a saturated fatty acid, an amphoteric compound, a glycol and a soap. The admixture is added to concrete prior to placement. Upon contact with the high pH environment of concrete the waterproofing ester component becomes hydrolyzed, forming carboxylic anions that are precipitated in the presence of calcium ions as hydrophobic coating within the pore system reducing ingress of water and chlorides into the concrete [19, 20].

Summarizing, to prevent or strongly delay the onset of pitting corrosion on passive steel in alkaline solutions or mortar, all investigations – independant on the type of inhibitor – seem to indicate that a critical ratio inhibitor / chloride of about 1 has to be exeeded. This implicates that quite high inhibitor concentrations have to be present in the pore water of concrete in order to act against chlorides penetrating from the concrete surface. To avoid chloride ingress and thus the use of excessively high inhibitor concentrations the use of admixed inhibitors is recommended only together with high quality concrete [7]. Too low concentrations of certain inhibitors may cause the risk of increased corrosion rate as has been found in laboratory studies with nitrites on cracked reinforcing beams [21].

**Corrosion inhibitors to reduce the propagation rate of corrosion**

The most interesting application of inhibitors would be a surface treatment with subsequent transport of the inhibitor to the corroding steel with the goal to stop or at least reduce ongoing corrosion. Several laboratory and field tests have been performed to investigate this particular situation.

For monofluorophosphate repeated drying and MFP-immersion cycles have been found a suitable method to allow the penetration of the inhibitor to the steel, but high concentrations and long treatments are needed to significantly reduce active corrosion due to carbonation [22]. In recent research [5] at Aston University, 15% by weight solutions of MFP were applied repeatedly to reinforced concrete specimens (w/c 0.65, cover 12 mm) with various levels of chloride contamination. The embedded bars, precorroded under cyclic wetting and drying conditions for about 6 months prior
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to the MFP treatment, did not exhibit marked reductions in corrosion rate [2] (figure 3). In comparative field tests on chloride contaminated side walls in a tunnel MFP was found to be virtually ineffective at chloride concentrations of 1 – 2% by weight of cement [23].

Figure 3: Corrosion rate of rebars in mortar (w/c 0.65) prior and after treatment with inhibitor. Left: MFP, right: proprietary alkanolamine based inhibitor, after Page et al. [2].

Alkanolamine based inhibitors have been tested in similar conditions, for ongoing chloride induced corrosion with a chloride level of ca. 1 – 2% nor in the laboratory [5] nor in the field [23] a reduction in corrosion rate was found (figure 3). Only at low chloride concentrations a slight reduction was found. The effect of another proprietary migrating inhibitor blend for surface application was tested in solution, after the addition of the inhibitor an increase of the polarization resistance by a factor 3 to values of ca. $4 \pm 1 \, \text{k}\Omega \text{cm}^2$ was found [24]. In contrast to this result precorroded rebars in mortar (w/c 0.75, cover 25 mm) did not show any increase in polarization resistance after inhibitor treatment despite low cover and porous mortar [24].

Other field tests with proprietary vapor phase inhibitors [25] in a parking garage with chloride contaminated precast slabs did not show encouraging results. Corrosion rate measurements showed a reduction of 60% in areas with initially intense corrosion but also an increase in areas with low corrosion rates. On structures from 1960 with admixed chloride content > 1% showing featuring already patch repairs, a three years corrosion rate survey showed lower corrosion rates in the treated areas compared to untreated ones but cracking and spalling increased also in the treated areas [26].

**Transport of the inhibitor into mortar or concrete**

It is claimed for several inorganic and organic inhibitor blends that these inhibitors can be applied to existing reinforced concrete structures and the corrosion inhibitor will be carried by water or by vapor phase migration into proximity of the reinforcing steel [9, 13]. Several diffusion experiments showed that especially alkanolamine-based inhibitors can diffuse through the concrete although great discrepancies in the measured diffusion rates exist. This might partially be due to the different experimental setup (humidity) and measuring techniques used. In addition, it is difficult to determine the diffusion rate of an inhibitor blend of unknown composition.

A detailed study on the transport of a proprietary amino alcohol based inhibitor into cement paste and mortar is reported by Tritthardt [27]. The results showed that both, the amount and the rate of inhibitor ingress into alkaline cement paste is higher for the pure amino alcohol compared to the inhibitor blend containing also phosphates (figure 4a). This discrepancy could be explained by a reaction of the inorganic phosphate component with the calcium ions in the fresh cement paste blocking the further ingress of the inhibitor. To avoid a reaction with calcium ions, the transport of the inhibitor was studied on cores taken from a 100 years old, fully carbonated concrete structure, varying the dosage and the way of inhibitor application (figure 4b). The recommended dosage (500 g/m²) and way of application (several brushings) showed only a moderate concentration of the amino alcohol in the first 15 mm. An increase in the dosage to 1500 g/m² increased the amino alcohol concentration, but the penetratoin
depth remained low. Only a ponding for 28 or 50 days resulted in a significant inhibitor concentration (both amino alcohol and phosphate) at depths higher then 30 mm [27].

More often only one – the most volatile – component of the inhibitor blend can be analysed as in the case of a proprietary migrating corrosion inhibitor [15, 28]. Using the amine electrode the diffusion of the volatile part of the inhibitor through a mortar disk could be measured [15, 28], no information of the diffusion of the non-volatile part could be obtained so it can be assumed reasonably that only the volatile compound is diffusing. The fact that both components of an inhibitor blend are needed at the steel surface to get an inhibiting effect (fig. 1) but only one component easily diffuses through the porous concrete may explain the discrepancy between solution experiments and mortar or field tests [4, 15, 24]. A high diffusion rate – logically – does not depend on the diffusion direction; so it has been found that the volatile component of organic inhibitor blends evaporates [15, 24].

Critical evaluation of corrosion inhibitors

Assuming that the inhibitor action in laboratory experiments has been established, there remain two critical points for an application on reinforced concrete structures:
- The inhibitor has to be present at the reinforcing steel in sufficiently high concentration with respect to the aggressive (chloride) ions over a long period of time
- The inhibitor action on corrosion of steel in concrete should be measurable

Concentration dependance: The available literature report a concentration dependant effect of inhibitors, a critical ratio inhibitor / chloride has to be exceeded (see above). For new structures the inhibitor dosage thus has to be specified with respect to the expected chloride level for the design life of the structure. Surface applied inhibitors on existing structures may present even more difficulties in achieving the necessary concentration at the rebar level. First, because chloride contamination or carbonation may vary strongly along the surface, second because the cover and permeability of the concrete may vary as well and third because the inhibitor may react with pore solution components. It is crucial to specify the critical concentration to be achieved at the rebar level and not – as in the application notes of surface applied inhibitors - an average weight of inhibitor solution to be applied per m² concrete. This is usually omitted, in part due to the lack of analytical methods to measure the inhibitor concentration. Regarding long term durability it has to be taken into account that inhibitors may be washed out from the concrete or evaporate.

Measurement and control of inhibitor action: One of the main difficulties in evaluating the performance of inhibitors is to assess the inhibitor action on rebar corrosion "on site". The interpretation of half cell potential measurements may present difficulties due to changes in the concrete resistivity. Further, a reduction of corrosion rate due to an inhibitor action may not be reflected straight-forward in
the half cell potential: potentials may become more negative or more positive after inhibitor application, depending on the mechanism of the inhibitor action. Shifts in the half cell potential may occur also due to the wetting and drying of the concrete [29]. Results of corrosion rate measurements on site depend on the type of device used for the measurements and can be interpreted so far only by specialists. The main problems are the daily and seasonal changes of the corrosion rate with temperature and concrete humidity making it difficult to evaluate inhibitor action. Macocell current measurements between isolated anodes (located and instrumented before inhibitor application) and the surrounding cathode may give the most indicative results [23] but can be installed only on test sites.

Concluding Remarks

The use of corrosion inhibitors could be a promising technique in restoring reinforced concrete structures offering benefits as reduced costs and inconvenience of repairs. It has however to be taken into account that the use of corrosion inhibitors in repair systems is far less well-established then their applications as admixtures in new structures.

As stated in this paper the overall performance of surface applied organic and inorganic corrosion inhibitors intended to stop or at least reduce ongoing chloride induced corrosion can not be considered positive, for the case of corrosion due to carbonation there remain at least some doubts.

The concrete repair industry should specify the required inhibitor concentration at the reinforcement and define methods to measure this concentration.

Engineers and contractors working in the area of concrete maintenance should be aware of the fact that the performance of proprietary corrosion inhibitors in repair systems marketed under different trade names is not yet documented by independant research work.

References


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