مرکز دانلود رایگان مهندسی مالتورزی و مواد
www.Iran-mavad.com
Corrosion Inhibitors for Steel in Concrete
State of the Art Report

Edited by
B. ELSENER

Published for the European Federation of Corrosion
by Maney Publishing on behalf of The Institute of Materials
Preface

In steel-reinforced or prestressed concrete structures adequate corrosion resistance is usually provided by a passive layer on the steel surface resulting from the high alkalinity of the concrete environment. However, as a result of mechanisms which destroy the passive layer, for example, carbonation of the concrete cover or chloride contamination, depassivation can take place. In such cases it is necessary to take measures to prevent corrosion induced damage of the reinforcement or to keep this within tolerable limits during the design lifetime of the structure. To avoid some of the disadvantages of traditional rehabilitation methods various new methods have been developed and successfully applied in recent years. Thus, besides electrochemical techniques — which have been the subject of a previous state of the art report from the EFC Working Party — the use of corrosion inhibitors is continuing to attract attention.

Inhibitors have been successfully applied for preventing corrosion and corrosion damage in many and varied technical fields for very many years. However, the use of inhibitors for reinforced concrete structures is a relatively new field and has so far been limited to their application as admixtures to fresh concrete or repair products. More recently their use as a surface-applied procedure has attracted much attention as it offers a new cost-effective rehabilitation measure for existing structures. Nevertheless, for non-experts it is almost impossible to assess the inhibiting efficiency of the various inhibitive products (inorganic inhibitors, organic inhibitors, inhibitor blends, etc.) that are proposed.

The preparation of a state of the art report in such a rapidly growing field is possible only with direct contacts to ongoing research projects, especially to the European concerted research action COST 521 which started in 1997 and includes 14 different individual projects investigating corrosion inhibitors for steel in concrete. The present state of the art report which has been prepared by Bernhard Elsener with the support of a Task Group* of the EFC Working Party No. 11 on Corrosion of Reinforcement in Concrete has benefitted from such contacts and describes in detail the different commercial inhibitors available for use in concrete and considers their mechanistic action together with experience from laboratory and field tests. The

* The members of the Task Group were as follows:

B. Elsener (Switzerland) — Convenor of the Task Group;

C. Andrade (Spain);
A. Legat (Slovenia);
U. Nürnberg (Germany);
C. Page (UK);
P. Pedeferri (Italy);

R. Polder (The Netherlands);
P. Schiessl (Germany);
J. Trithart (Austria);
J. Vogelsang (Germany).
Preface

report also deals with the possible effects of inhibitors on concrete properties and with their long term efficiency. Furthermore, various test methods for evaluating the behaviour of corrosion inhibitors for steel in concrete are described and critically assessed.

The report will be valuable for research workers as well as practitioners who are working on improvements in the corrosion protection of reinforcing steel or the rehabilitation of steel reinforced concrete structures. Owners, designers and contractors will profit by this overview of the current state of knowledge which should provide a better assessment of not only the possibilities but also the limitations of the use of inhibitors for concrete structures. It is hoped that this report will achieve a large readership both from corrosion specialists and from civil engineers.

J. Miets  Chairman of the EFC WP on Corrosion in Reinforcement in Concrete

B. Elsener  Convenor of the Task Force Editor of the Report
European Federation of Corrosion Publications

Series Introduction

The EFC, incorporated in Belgium, was founded in 1955 with the purpose of promoting European co-operation in the fields of research into corrosion and corrosion prevention.

Membership is based upon participation by corrosion societies and committees in technical Working Parties. Member societies appoint delegates to Working Parties, whose membership is expanded by personal corresponding membership.

The activities of the Working Parties cover corrosion topics associated with inhibition, education, reinforcement in concrete, microbial effects, hot gases and combustion products, environment sensitive fracture, marine environments, surface science, physico-chemical methods of measurement, the nuclear industry, computer based information systems, the oil and gas industry, the petrochemical industry, coatings, automotive engineering and cathodic protection. Working Parties on other topics are established as required.

The Working Parties function in various ways, e.g. by preparing reports, organising symposia, conducting intensive courses and producing instructional material, including films. The activities of the Working Parties are co-ordinated, through a Science and Technology Advisory Committee, by the Scientific Secretary.

The administration of the EFC is handled by three Secretariats: DECHEMA e. V. in Germany, the Société de Chimie Industrielle in France, and The Institute of Materials in the United Kingdom. These three Secretariats meet at the Board of Administrators of the EFC. There is an annual General Assembly at which delegates from all member societies meet to determine and approve EFC policy. News of EFC activities, forthcoming conferences, courses etc. is published in a range of accredited corrosion and certain other journals throughout Europe. More detailed descriptions of activities are given in a Newsletter prepared by the Scientific Secretary.

The output of the EFC takes various forms. Papers on particular topics, for example, reviews or results of experimental work, may be published in scientific and technical journals in one or more countries in Europe. Conference proceedings are often published by the organisation responsible for the conference.

In 1987 the, then, Institute of Metals was appointed as the official EFC publisher. Although the arrangement is non-exclusive and other routes for publication are still available, it is expected that the Working Parties of the EFC will use The Institute of Materials for publication of reports, proceedings etc. wherever possible.

The name of The Institute of Metals was changed to The Institute of Materials with effect from 1 January 1992.

The EFC Series is now published by Maney Publishing on behalf of The Institute of Materials.

A. D. Mercer
EFC Series Editor,
The Institute of Materials, London, UK
EFC Secretariats are located at:

Dr B A Rickinson  
European Federation of Corrosion, The Institute of Materials, 1 Carlton House Terrace, London, SW1Y 5DB, UK

Mr P Berge  
Fédération Européene de la Corrosion, Société de Chimie Industrielle, 28 rue Saint-Dominique, F-75007 Paris, FRANCE

Professor Dr G Kreysa  
Europäische Föderation Korrosion, DEHEMA e. V., Theodor-Heuss-Allee 25, D-60486, Frankfurt, GERMANY
Contents

Series Introduction
Preface

1. Introduction

2. Corrosion Inhibitors for Use in Concrete
   2.1. Mechanism
   2.2. Inhibitors as Repair Strategy

3. Literature Results on Corrosion Inhibitors for Steel in Concrete
   3.1. Nitrites
      3.1.1. Effect of nitrites on concrete properties
      3.1.2. Mechanism of the action of nitrites
      3.1.3. Critical ratio between chloride and nitrite
      3.1.4. Nitrites as curative inhibitors
      3.1.5. Long term efficiency
   3.2. Other Inorganic Inhibitors
      3.2.1. Inhibitors as admixtures to concrete
      3.2.2. Sodium monofluorophosphate (MFP)
   3.3. Alkanolamines and Amines
      3.3.1. Literature studies and patent applications
      3.3.2. Studies with proprietary inhibitor blends based on alkanolamines
   3.4. Other Organic Inhibitors
4. Critical Evaluation of Corrosion Inhibitors
   4.1. Concrete Properties — Environment
   4.2. Concentration Dependence
      4.2.1. Mechanism of inhibition of localised corrosion
      4.2.2. Inhibitors admixed to concrete — new structures
      4.2.3. Surface-applied inhibitors
   4.3. Measurement and Control of Inhibitor Action
   4.4. Field Tests and Applications
   4.5. Durability of the Inhibitor Action

5. Test Methods to Evaluate Corrosion Inhibitors for Steel in Concrete
   5.1. Non-perturbing Tests
   5.2. Open Circuit Potential
   5.3. Polarisation Resistance Measurements
   5.4. Macrocell Tests
   5.5. Test Variables
      5.5.1. Surface preparation of the rebars — Electrical connection
      5.5.2. Pre-passivation
      5.5.3. Method of ponding
   5.6. Polarisation Curves
      5.6.1. Pitting potential
      5.6.2. Influence on cathodic oxygen reduction reaction

6. Ongoing Research Work
   6.1. Migrating Corrosion Inhibitors
   6.2. Surface-applied MFP
   6.3. Testing

7. Concluding Remarks

8. References

9. Abbreviations

Appendix: List of Ongoing Research Projects
1 Introduction

In general, reinforced concrete has proved to be successful in terms of both structural performance and durability because the concrete provides chemical and physical corrosion protection of the rebars. The alkaline pore solution passivates the steel and the concrete cover prevents or at least retards the ingress of corrosion-promoting substances. 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 carbonation. As a result of the corrosion reaction the cross section of the rebars is reduced and rust is formed. This process can cause cracking or spalling of the concrete and dangerous loss of structural stability.

From the point of view of the corrosion protection of the rebars two different situations have to be distinguished:

- on **new structures**, the most effective measure for durability can be achieved in the design stage by using adequate concrete cover and high concrete quality. This will prevent aggressive substances as e.g. chloride ions from deicing salts or sea water, from reaching the rebars within the design life. Additional protective measures can be applied such as admixtures to concrete to decrease its permeability, the use of more corrosion resistant materials for the reinforcement (e.g. stainless, galvanised, or epoxy coated steels), electrochemical protection systems (e.g. preventive cathodic protection) or others.

- on **existing structures** the deterioration process may have reached different stages according to age, exposure condition, concrete cover and quality: for a corrosion risk situation or at the onset of corrosion, preventive measures may be applied, whereas in severely corroding structures repairs have to be conducted.

Inhibitors, which are chemical substances that prevent or retard corrosion by action at the steel/concrete interface, have been proposed (and used) both as preventive measures for new structures and as repair measures for existing reinforced concrete structures. The method of application differs: in new structures inhibitors are admixed in sufficiently high concentrations to the fresh concrete, on existing structures, where the onset of corrosion has to be prevented, inhibitors are applied at the concrete surface; for repair work inhibitors can be present in paints for the reinforcement or in repair mortars.

In this state of the art report a literature survey on inhibitors for steel in concrete, covering laboratory results, field experience and long term
performance, is given. The literature results available are commented upon and critically evaluated with respect to the inhibitor performance and durability. 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.
2 Corrosion Inhibitors for Use in Concrete

There is a general consensus on the definition and requirements of corrosion inhibitive admixtures or repair systems for concrete, which is based on the ISO definition of a corrosion inhibitor and is that: “Corrosion inhibitors are chemical compounds that, when added in adequate (preferably small) amounts to concrete, can prevent or retard corrosion of steel in concrete [1], but do not show adverse effects on the concrete properties (e.g. compressive strength) or adversely affect the nature and microstructure of the hydration products”. Several admixtures — pure compounds or mixtures — have been available as corrosion inhibitors for a long time and are claimed to offer protection for reinforcing steel in concrete against chloride-induced corrosion. These admixtures are used as a preventive measure and are added to fresh concrete or to repair products (paints for reinforcing steel, adhesion bridges and mortar). More recently, new interest has arisen regarding the use of inhibitors as a rehabilitation or curative measure. These compounds are applied onto the concrete surface and should penetrate through the concrete to the steel to stop or retard corrosion. There are conflicting opinions, however, about the effectiveness of these compounds for corrosion protection and several publications obtained from independent research in this field are available.

2.1. Mechanism

The lifetime of a reinforced concrete structure, as described by Tuutti [2] consists of two phases (Fig. 1): the first phase corresponds to the initiation time, $t_i$, taken for chlorides or $CO_2$ to penetrate the concrete cover in sufficient quantities to destroy the passive film (depassivation). The second phase covers the period of active corrosion from $t_0$ to the time at which safety or durability of the structure are affected (loss of load bearing capacity, spalling or delamination). The length of this period is determined by the rate of corrosion (governed by the oxygen availability, relative humidity and temperature) and the ability of the concrete cover to withstand internal stresses. In this general picture of corrosion, ‘inhibitors’ could be substances that affect the rate of ingress of chlorides or $CO_2$ from the environment, the degree of chloride binding, the rate of ingress of dissolved oxygen to sustain the cathodic reaction, the electrical resistance of the concrete etc. This review focuses on ‘inhibitors’ that act at the steel/concrete interface and influence directly the corrosion mechanism. The hydroxyl ions act as the primary inhibitor of steel in concrete, but chloride removal or realkalisation treatments are not included here, as a state of the art report on these has been published recently by the European Federation of Corrosion [3].

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 of the successful use of corrosion inhibitors for many decades. This undoubtedly is true and the overwhelming majority of literature reports on corrosion inhibitors deals with the...
Corrosion Inhibitors for Steel in Concrete — State of the Art Report

Fig. 1 Lifetime of a reinforced concrete structure after Tuutii [2]; a, b, c: decreasing corrosion rate.

Effects of inhibitors on uniform corrosion, e.g. of steel in acidic or neutral solutions, where inhibitors can be classified [4-6] into:

(i) adsorption inhibitors, acting specifically on the anodic or on the cathodic partial reaction of the corrosion process or on both reactions (mixed inhibitor),

(ii) film forming inhibitors blocking the surface more or less completely, and

(iii) passivators favouring the passivation reaction of the steel (e.g. hydroxyl ions).

In the case of the inhibition of corrosion of steel in concrete, a completely different situation has to be considered. Thus, steel in concrete is usually passive, being protected by a thin film of oxy-hydroxides formed spontaneously in the alkaline pore solution (passive film). The mechanistic action of corrosion inhibitors is thus not to counter uniform corrosion (see above) but localised or pitting corrosion of a passive metal arising from the presence of chloride ions or a drop in pH. It is thus obvious that the long and proven track record of inhibitors against general corrosion in acidic or neutral media cannot provide a basis for (tacitly) assuming that similar compounds should work as well for steel in concrete.

Indeed, inhibitors for pitting corrosion (the typical situation for steel in concrete) have been far less studied [7,8]. Chloride ions are responsible for pitting corrosion, with the pitting potential depending on the chloride activity $E_{pit} = C - B \log(a_{Cl^-})$. Inhibitors for pitting corrosion can act

- by a competitive surface adsorption process of inhibitor and chloride ion (reducing the effective chloride content on the passive surface)
Corrosion Inhibitors for Use in Concrete

- by buffering of the pH in the local pit environment
- by competitive migration of inhibitor and chloride ions into the pit so that the low pH and high chloride contents necessary to sustain pit growth cannot develop

Further, it has to be taken into account that commercial inhibitors are frequently blends of several compounds, so that more than one mechanistic action can be involved and difficult to identify. This will lead to major difficulties in the independent evaluation of corrosion inhibitors that are proposed in commercially available concrete repair systems.

2.2. Inhibitors as Repair Strategy

Inhibitors are one of several possible repair strategies [9,10] and their use on reinforced concrete structures has to be planned with the same care as the construction of new structures. Before any decision to use inhibitors as a rehabilitation method is taken, the following analysis of the situation is recommended to achieve cost-effective and durable repairs [9]:

1 **Structural condition.** A thorough condition assessment of the structure (or part of it) should include a visual survey, the identification of structural cracks, deformations etc. in order to clarify whether and to what extent structural repairs have to be carried out.

2 **Cause of deterioration.** Any condition assessment should be continued as long as necessary to identify clearly the cause(s) of the observed degradation. It is useful to start with non-destructive techniques (e.g. potential mapping [11, 12] to locate corroding zones) before applying destructive techniques (e.g. core drilling for chloride analysis).

3 **Expected service time of the structure.** The owner of the structure has to decide the future use of the structure and to define the desired service time.

Rehabilitation with inhibitors has the advantage of requiring only a minimum of intervention although some local repairs may be necessary because of the presence of cracks, spalling, etc. or for aesthetic reasons. The use of surface-applied corrosion inhibitors as components of proprietary concrete repair systems has therefore increased over the last few years since this approach appears to offer a simple and economical alternative to other available methods. In addition, fewer restrictions apply to the choice of corrosion inhibitive substances for surface-applied inhibitors than for those used as admixtures because the effects on cement hydration kinetics are less relevant. When used to restore deteriorating concrete structures, however, inhibitors must be capable of penetrating cover concrete. There is a clear need for the limitations of corrosion inhibitors to be appreciated by those who are responsible for specifying concrete repairs. Questions frequently asked by engineers who work in this area are set out in a recent paper by Page et al. [13]:

www.iran-mavad.com
مرجع علمي مهندسي مواد
is there evidence that inhibitors can stop, or at least substantially reduce, corrosion rates of steel which has already corroded significantly in carbonated and/or chloride-contaminated concrete?

what concentrations of inhibitor are needed at the level of the reinforcing steel and is it clear that these can be achieved in practice for concretes of different composition if recommended methods of application are used?

how long is the corrosion inhibitor likely to remain in adequate concentration at the level of the embedded steel and can this time be related to a quantifiable extension of service life of the structure concerned?

can the possibility of harmful side effects arising from the use of inhibitors in concrete repair be excluded?
3

Literature Results on Corrosion Inhibitors for Steel in Concrete

The primary 'inhibitor' for steel in concrete is the hydroxide ion (OH⁻) present in high concentration in the pore solution of concrete, promoting the formation of a stable oxide/hydroxide film at the steel surface (passive film). While numerous inhibitors have been suggested, only a small group has been seriously studied: the need to ensure adequate corrosion protection without altering the physical and mechanical properties of concrete and to obtain sufficient solubility in a solution saturated in Ca^{2+} considerably restricts effective choices. In the early book of Nathan [14] on corrosion inhibitors, in the chapter "Inhibitors for use on reinforcing steel in concrete", only a few works are cited, but it is stated that "much additional work would be required before inhibition of reinforcing steel corrosion can be considered practical". Since then numerous studies have been performed and several earlier literature reviews on inhibitors of steel in concrete have been published [15,16]. Older studies on chemical substances that prevent the onset of pitting corrosion have focused mainly on anodic corrosion inhibitors, especially calcium nitrite, sodium nitrite, stannous chloride, sodium benzoate and some other sodium and potassium salts (e.g. chromates) [14]. More recently interest in organic inhibitors for steel in concrete has arisen; these substances are claimed to be able to penetrate (migrate) from the concrete surface to the steel and inhibit or at least reduce corrosion. In contrast to some opinions put forward in the literature [17], in this state of the art report considers only chemical substances that prevent or retard corrosion by action at the interface steel/concrete; other admixtures used to reduce chloride penetration (e.g. hydrophobic materials, silica fume, superplasticisers, etc.) are not treated.

3.1. Nitrites

Nitrite inhibitors have been extensively studied; the first literature reference regarding investigations of nitrite as inhibitors for use in concrete dates back to the late 1950s [18]. In Russia (and probably also in other countries) mixtures of NO₂⁻, NO₃⁻ and CaCl₂ were frequently used as 'antifreeze' admixtures. Since then, numerous investigations have been carried out with different experimental techniques in solutions, in mortar and in concrete, focusing on the inhibitive effect of sodium or calcium nitrite added to the mixing water. Both, carbonation and chloride induced corrosion were investigated. It is not intended to give a historical review but to provide experimental evidence for the main questions concerning inhibition:

- effect on hardening and strength of concrete,
- the mechanism of the inhibitor action,
Corrosion Inhibitors for Steel in Concrete — State of the Art Report

- the critical ratio between chlorides and inhibitor,
- the effectiveness over time
- combination with other inhibitors.

3.1.1. Effect of Nitrites on Concrete Properties

Sodium nitrite (NaNO₂) causes moderate to severe compressive strength loss (20–40%) [19–22] when admixed to concrete in concentrations between 2 and 6%. Similar results were found for potassium chromate and sodium benzoate (Fig. 2) [23]. Sodium nitrite enhances the risk of alkali-aggregate reaction (AAR) problems [21]. For ordinary Portland cement (OPC) with a high cement content of 450 kg m⁻³ an increase in setting time is reported, for other cement types a reduction was found [24]. Calcium nitrite, introduced as a commercially available admixture since 1970, acts as a moderate accelerator and normally requires the addition of a water reducer and retarder in the concrete mixture. It increases the compressive strength of concrete [25] and no susceptibility to AAR is reported [23]. Such an effect has been ascribed to the different effects of the cations in the two salts. Only in one work was deterioration of mortar soaked in a solution containing calcium nitrite reported [26].

![Fig. 2 Effect of inhibitor addition on compressive strength of concrete [23].](www.iran-mavad.com)
3.1.2 Mechanism of the Action of Nitrites

The passive film on steel in concrete formed at high pH values can be destroyed by the action of chlorides or by carbonation. In the dissolution process ferrous ions, Fe(II), are formed. Nitrite is acting as a passivator due to its oxidising properties and stabilises the passive film according to the following reactions [27-29]

\[
\begin{align*}
2 \text{Fe}^{2+} + 2 \text{OH}^- + 2 \text{NO}_2^- & \rightarrow 2 \text{NO} + \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \\
\text{Fe}^{2+} + \text{OH}^- + \text{NO}_2^- & \rightarrow \text{NO} + \gamma\text{FeOOH}
\end{align*}
\]

The effect of nitrite in enhancing passivity is related to its ability to oxidise ferrous ions to ferric ions which are insoluble in aqueous alkaline solutions and block the transport of ferrous ions into the electrolyte. Nitrite is not incorporated into the passive film, but reacts with the anodic corrosion products in an early stage competing with chloride ions. An XPS surface analytical study [30] on the passivation of reinforcing steel in synthetic pore solution with and without calcium nitrite inhibitor showed similar passive film composition, with evidence of Fe(III) in the passive film and no incorporated nitrogen. From the reactions it can be concluded that

(a) nitrites have to be present in sufficient concentration with respect to chloride ions, and

(b) some nitrite is consumed when the passivating action takes place.

3.1.3. Critical Ratio between Chloride and Nitrite

Most of the corrosion studies that have been conducted have shown a critical concentration ratio between inhibitor (nitrite) and chloride, although the exact values differ. In comparing different works care has to be taken to express the ratio in units of chemical concentration, for example in mole L\(^{-1}\). An early study of Rosenberg and Gaidis [27] showed that reinforcing bars immersed in saturated Ca(OH)\(_2\) solution (pH 12.2–12.5) with NaCl and Ca(NO\(_2\))\(_2\) added between 0.1 and 3% (by weight) showed time-dependent corrosion initiation. Thus, after 1 h of immersion negative potentials and rust spots were observed at a level of 0.1% Ca(NO\(_2\))\(_2\) with 1 or 3% NaCl, and after 24 h corrosion was observed also at 0.3% Ca(NO\(_2\))\(_2\) after 92 h even at the level of 1% Ca(NO\(_2\))\(_2\) and 3% NaCl. In molar ratios this indicates that a [Cl\(^-\)]/[NO\(_2\)-] ratio of about 0.8 or lower is required for complete protection. Andrade \textit{et al.} reported values from experiments in solution of [Cl\(^-\)]/[NO\(_2\)-] from 1 to 0.7 [24]. Experiments with mortar or concrete mostly were performed with admixed chlorides [24,29-34] or prepared with sea water [35]. Results of work prior to 1990 are summarised by Berke [25], from which a critical ratio of [Cl\(^-\)]/[NO\(_2\)-] of about 1.5 can be deduced (Fig. 3) which is significantly higher than the results cited above. Calcium and sodium nitrites were tested as inhibitors by pore solution analysis and electrochemical experiments in mortars with admixed NaCl [34]. The free chloride concentration in the pore solution decreased and the OH\(^-\) content increased with time of ageing, the [Cl\(^-\)]/[NO\(_2\)-] ratio remained fairly constant and achieved a value of 0.3 and 0.8 respectively for 0.5 and 1% of admixed NaCl and 1% of sodium or calcium nitrite. At a (admixed) chloride
content of 1% the corrosion of steel could not be inhibited even at a level of 1% Ca(NO₃)₂, in agreement with the critical ratio of [Cl⁻]/[NO₂⁻] being at 0.8. Experiments with NaCl penetrating into concrete with admixed Ca(NO₃)₂ inhibitor showed a (calculated) molar ratio of [Cl⁻]/[NO₂⁻] of 1.5 for lower chloride contents and 1 for high chloride contents [37].

Differences in the critical [Cl⁻]/[NO₂⁻] ratio determined in different experiments might be due to

(a) the way of determining the concentrations of chlorides and nitrites in concrete (free ions, total ions, etc.). It has been shown by pore solution expression that a great part of the admixed nitrites is bound during cement hydration [34,38,39]; on the other hand, it was found that by crushing seven year old concrete from a bridge deck into a fine powder, the original quantity of admixed nitrite could be recovered by water extraction [40].

(b) the different qualities of mortars and concretes used in the experiments. The higher tolerable values reported [25,29,37] were found in mortars or concretes with w/c ratio < 0.5 and high cement contents. In a recent work of Gonzalez et al. [32] it was found that a [Cl⁻]/[NO₂⁻] ratio of 0.66 was more than adequate
to ensure preservation of the passive state in mortar with a correct mix proportion and high cement content, whereas it proved inadequate for low quality-mortar with a cement/sand ratio of 1:6 or 1:8.

Calcium nitrite was included in the tests in a comparative study to evaluate corrosion inhibitors [41,42], but due to an error in the recommended dosage the nitrite concentration was too low and so the inhibitor was effective only for specimens with low chloride concentration. Lower concentrations than the critical resulted — even when no complete inhibition was achieved — in a reduction of the corroded area and of the corrosion rate determined by weight loss or by linear polarisation resistance both in chloride [23,24,32,35,37,43] or carbonation corrosion situations [24,31,47]. Increasing dosage of Ca(NO₂)₂ resulted in a prolongation of the time to depassivation of the rebar exposed to sea water (Fig. 4), but even 4% of Ca(NO₂)₂ could not prevent corrosion initiation [35]. A delay of corrosion initiation was reported for laboratory experiments with concrete using different cements [36]. In the case of cracked reinforcing beams concentrations of nitrites that are too low may have been the cause of the risk of increased corrosion rate as has been found in laboratory studies [21,44,45]. This has been explained by the higher potential difference between passive rebar in concrete and the steel in the cracked area. In contrast to these findings results on macrocell corrosion tests on cracked beams show that Ca(NO₂)₂ additions significantly improved corrosion resistance of the embedded steel at cracks [46] even at low inhibitor dosage. The risk of intensified pitting with inadequate dosages of

![Graph showing the effect of Ca(NO₂)₂ inhibitor on corrosion initiation](image-url)

**Fig. 4** Time to corrosion initiation of steel in mortar samples with admixed Ca(NO₂)₂ inhibitor exposed to sea water [35].

www.iran-mavad.com
مرجع علمي مهندسي مواد
Corrosion Inhibitors for Steel in Concrete — State of the Art Report

Nitrites in the presence of chlorides may depend on several factors related to the quality of the concrete, the initial surface condition of the steel and the exposure conditions. The fact that no such problems have been identified in specific investigations involving only a limited range of these variables should not be taken to imply a blanket assurance that there is no risk of intensified pitting in all circumstances [13]. In this respect it is worth noting that calcium nitrite is marketed only for use in combination with other proper design measures for durability such as cover, concrete quality, etc.

In carbonated concrete nitrites act as corrosion inhibitors as well. Laboratory studies in synthetic pore solutions and in carbonated mortar showed that 3% Ca(NO₂)₂ by weight of cement can protect reinforcements against corrosion. In chloride-contaminated and carbonated concrete only a slight reduction in corrosion rate was reported [47].

3.1.4. Nitrites as Curative Inhibitors

The use of nitrites in repair systems has so far been comparatively limited. Nitrite ions, however, can penetrate into concrete by absorption and diffusion if applied to the surface by spraying or ponding with aqueous solutions, pre-drying is recommended and supplementary doses may be provided in the form of admixtures to mortar or concrete overlays. First tests to impregnate concrete with calcium nitrite involved drying part of a bridge deck and ponding of 15% calcium nitrite solution for 24 h [50]. A column was impregnated by removing delaminated concrete and drilling holes into which a calcium nitrite rich grout was placed and a calcium nitrite rich latex modified concrete applied to the surface of the column [50]. A commercially available repair system of this type based on calcium nitrite has been introduced in the USA [51] and, in Japan, systems based on lithium nitrite have been proposed [52].

From recent work at Aston University in the UK [13] it was found that when calcium nitrite was introduced into moderately pre-corroded reinforced concrete specimens by means of ponding followed by application of an overlay, in accordance with recommended practices [53], significant reductions in the overall rate of corrosion of bars embedded at depths of 12 mm were achieved, provided that the initial chloride content was relatively low (<0.6% Cl) for non-carbonated concrete and very low for carbonated concrete (Fig. 5). The treatment often fell short of restoring full passivity to the steel. This raised the question of whether the presence of nitrite ions might, in some cases, reduce the overall anodic area but intensify the rate of corrosion locally at unpassivated regions on the metal.

3.1.5. Long Term Efficiency

Some concern exists regarding the leaching-out of nitrites from concrete. In poor quality mortar (cement to sand 1:6 or 1:8) [32] or concrete [45] with admixed chlorides and nitrites both ions were leached out at nearly the same rate, the main influence being the leaching frequency [32]. In contrast, outdoor exposure for two years [37] or results from bridge decks after seven years [40] showed that nearly all nitrite is preserved in the concrete. A study simulating concentration gradients of nitrite in
concrete by admixing different concentrations showed that only marginal diffusion occurred [49]. The acceleration of macrocell corrosion processes between areas without and with a high nitrite content was confirmed when the anodic area (no nitrite) was small, in the case of different nitrite contents (Cl⁻/NO₂⁻ ratio < 2) no corrosion acceleration was found [49].

Leaching of nitrites will not be a problem when the mix design of the concrete, e.g. low water to cement ratios, and good concrete cover meets specified national and international standards for moderate to severe chloride exposure conditions. Indeed, calcium nitrites — when applied according to the specifications together for high quality concrete — have a long and proven track record in the USA, Japan and in the Middle East [48].

In summary, the above results indicate that high nitrite concentrations (up to 30 L m⁻³ of a 30% calcium nitrite solution) have to be admixed to concrete in order to act against chlorides penetrating from the concrete surface in, e.g. bridge deck situations. Calcium nitrite provides a reduction in corrosion rate and in the corroded area of the rebars even when the critical chloride to nitrite ratio is exceeded. The inhibitor is not detrimental to concrete properties. Calcium nitrite has — combined with high quality concrete (w/c ratio < 0.5) — a long and proven track record in the USA, Japan and in the Middle East. However, due to environmental regulations and concern about its toxicity it has found only few applications in Europe so far. This might change after the official approval of DCI (30% calcium nitrite) inhibitor systems in Germany [54].
3.2. Other Inorganic Inhibitors

Although quite a large number of chemical compounds have been studied as inhibitors to be admixed to concrete, only monofluorophosphate (MFP) has been tested and applied in practice as a surface applied inhibitor for preventive and curative treatment of reinforced concrete.

3.2.1. Inhibitors as Admixtures to Concrete

Several alternative inorganic inhibitors such as alkalies, phosphates and chromates, benzoates or metasilicates have been studied for a long time [13,16,55,56]. More recently, molybdate and borates [59] as well as formaldehyde and potassium dichromate [64], acetate and urea [65] and glycerophosphates [66] have been investigated. Sodium borate was included in the comparative study of the Strategic Highways Research Programme (SHRP) project [41,42]. In a recent work, other substances such as zinc oxide, gluconates and urotropin have been studied [32]. None of them resulted in a similar inhibition efficiency to that given by calcium nitrite (Fig. 6).

*Stannous chloride* (SnCl$_2$·2H$_2$O) was tested as inhibitor for chloride-induced corrosion of steel in alkaline solutions [67]. The results showed that stannous chloride did not dissolve well in the pore solution (lime water) and could not protect the steel completely from corrosion. Stannous chloride appeared to be a non-corrosive accelerator that causes concrete to harden faster. Due to the chlorides dissolved from
the ‘inhibitor’ this substance is not used.

**Sodium molybdate** (added to the mixing water at 2.5% by weight of cement) resulted in a more than five-fold decrease in mean corrosion current density compared to the control sample with 2.5% of NaCl after 28 days (Fig. 7). At longer times, 90 and 180 days, the corrosion rate decreased further [59]. This is interpreted as evidence that molybdates are incorporated into the passive film. A combination of calcium nitrite and sodium molybdate (5:1) was found to be more efficient than nitrite alone [60].

**Sodium borate** (added to the mixing water at 2.5% by weight of cement) took a longer time to provide an effective reduction in corrosion rate (Fig. 7). After 180 days a corrosion rate similar to mortar without admixed chlorides was measured [59]. Since borate is a strong set retarder for concrete its potential use as corrosion inhibitor in cement based systems is considered to be not practical. In the SHRP study, borate did not show notable inhibitive effects [42].

**Sodium benzoate** resulted in a decrease in compressive strength when admixed to fresh concrete; the inhibitive properties were moderate [23,56]. Mixtures of sodium benzoate and calcium gluconate have been studied as ecologically compatible inhibitors for steel in chloride solutions [57]. The long-term performance of sodium nitrite and dinitrobenzoic acid used as corrosion inhibiting additives has been studied by electrochemical impedance spectroscopy [58].

![Graph](image.png)

**Fig. 7** Corrosion rate of steel in concrete with 2.5% admixed NaCl with and without different admixed inhibitors [59].
Deicing salts with added corrosion inhibitors, e.g. polyphosphates or calcium-magnesium-acetate (CMA) have been studied in solutions and in concrete [60]. Only pure CMA, an alternative de-icer without chlorides, could avoid corrosion of the reinforcement. Chelating agents have been found to inhibit corrosion of steel in alkaline solutions [61].

Nitrates ($\text{NO}_3^-$) have been studied as corrosion inhibitors by Justnes et al. [62]. Calcium nitrate, $\text{Ca(NO}_3\text{)}_2$, has been found to delay the initiation of chloride-induced corrosion of rebars in concrete similar to calcium nitrite, $\text{Ca(NO}_2\text{)}_2$. The kinetics for the inhibitive nitrate reaction are slower than for nitrite, but this is only relevant for rapid tests since rebar corrosion in practice is a rather slow process. According to theory, calcium nitrate should be an even better inhibitor than calcium nitrite. It is also cheaper, less harmful and more available. Between 2-4% calcium nitrate of cement weight seems sufficient to protect the rebar against initiation of chloride-induced corrosion [63].

### 3.2.2. Sodium Monofluorophosphate (MFP)

MFP ($\text{Na}_2\text{PO}_3\text{F}$) has been studied — as outlined in a recently published paper [68] — in the laboratory as inhibitor in neutral aqueous solutions, then as admixture to de-icing salts based on the results of studies at DOMTAR Inc., and has been patented in Canada [69]. This inhibitor cannot be used as admixture due to chemical reaction with the fresh concrete, so that it has to penetrate from the concrete surface to the steel. Its mechanism and action as inhibitor against chloride-induced corrosion has been tested in the laboratory [70] and on site [68, 75]; an inhibitive action against carbonation-induced corrosion has been studied in the laboratory [72].

#### 3.2.2.1. MFP as inhibitor against chlorides

In the solution tests ($\text{Ca(OH)}_2 + 0.5\text{M NaCl}$), MFP addition increased the pitting potential, but only the addition of 0.5M MFP could avoid the onset of pitting. Immersion tests in the same solutions, where the corrosion potential $E_{\text{corr}}$ and corrosion current density $i_{\text{corr}}$ (determined from linear polarisation resistance measurements) was followed for 30 days, indicated that even at an added concentration of 0.5 mole L$^{-1}$ MFP no pronounced inhibitive effect was found [70]. This fact has been confirmed by immersion tests [71], where the corrosion rate (weight loss) of steel samples immersed in aerated solutions containing $\text{Ca}^{2+}$ ions was clearly higher then in solutions with the same chloride and MFP content but without $\text{Ca}^{2+}$ ions.

Experiments using small mortar samples with 0.5M NaCl and different amounts of MFP added showed (Fig. 8) that only at 0.5 mole L$^{-1}$ MFP was a reduction in corrosion (by about a factor of 3) found. At lower concentrations no enhancement of pitting was noted [70]. Immersion and drying cycles in solutions with NaCl + MFP confirmed these results, thus, a ratio of NaCl to MFP of 1 resulted in low corrosion rates over 80 days but not in complete passivation. On pre-corroded samples (NaCl added during mixing) immersion in 0.1 and 0.5M MFP solutions resulted in an increase of the corrosion potential and a decrease of the corrosion rate which were similar for both MFP concentrations [70]. Due to the lack of a control sample, i.e. immersion, only in water, the MFP effect could not be distinguished from other effects, e.g. lack
of oxygen, etc. An important result from the experiments [70,71] was that a minimum MFP/chloride concentration ratio greater than 1 had to be achieved, otherwise the reduction in corrosion rate was not significant. No complete repassivation has been found after the onset of chloride-induced corrosion. In recent work at Aston University
15% by weight solutions of MFP were applied repeatedly (10 passes with intervening periods of drying) to reinforced concrete specimens of w/c 0.65, and various levels of chloride contamination and steel bars at depth of 12 mm. The embedded bars, which had been allowed to corrode under cyclic wetting and drying conditions for about 5 months prior to the treatment with MFP did not exhibit marked reductions in corrosion rates when wetting and drying cycles were reinstated after the inhibitor treatment (Fig. 9). Only a very slight gradual improvement was perhaps discernible in the specimens with the lowest chloride levels. Analysis of aqueous extracts of samples of the concrete by means of ion chromatography, which allows the concentrations of MFP and its hydrolysis products to be estimated, indicated that very little penetration of either MFP or phosphate had in fact taken place beyond the outermost 4 mm of concrete [13].

Indeed, it has to be noted that in solutions containing Ca(OH)₂ (free Ca²⁺ ions) MFP reacts with the calcium ion to form insoluble products of calcium phosphate and calcium fluoride [70,71] and thus the active substance, the PO₃⁻F⁻ ion, disappears from the pore solution irrespective of the initial concentration. This leads to an enhancement of the concentration of NaOH in the pore solution and improved corrosion inhibition might then largely be due to the increase of the [OH⁻]/[Cl⁻] ratio [13]. In alkaline solutions without Ca²⁺ ions MFP does not react [71]. On old concrete structures the MFP inhibitor was essentially found to be stable and formation of insoluble phosphates was observed only in the near-surface region [77] even four years after impregnation with MFP. It was concluded by the authors [77] that the critical concentration for MFP to be effective as an inhibitor is thus much lower than the molar ratio of 1 found in young mortar samples or in solutions [70].

![Graph showing corrosion rate of steel bars](image-url)  
*Fig. 9* Corrosion rate of steel bars at a cover depth of 12 mm in concrete (w/c 0.65) with various levels of chloride contamination; Na₂PO₃F treatment was applied after 150 days initial exposure, according to Page et al. [13].
3.2.2.2. MFP as inhibitor in carbonated concrete

Electrochemical studies conducted with sodium, potassium and zinc monofluorophosphates have shown that the anion can act mainly as a cathodic inhibitor when added in low concentrations (ca. $10^{-2} \text{M}$) to flowing, aerated solutions of neutral pH [73]. The inhibitive effect of MFP towards corroding reinforcement in carbonated concrete has been studied in the laboratory [74]. Solutions of saturated Ca(OH)$_2$ were carbonated by bubbling CO$_2$ through until pH 7 was reached. Addition of 0.7 mole L$^{-1}$ of MFP delayed the carbonation process indicating either a slight buffering action of the inhibitor or the decomposition of the inhibitor with increase in NaOH concentration — as mentioned above [13]). The drop in corrosion potential, depassivation of the rebars, was delayed in solutions with MFP. After total carbonation of the solution the corrosion potential and corrosion current density were followed during 70 days of immersion. In solutions with MFP added (0.35 or 0.7 mole L$^{-1}$) the corrosion potentials tended to more positive values and the corrosion rates were lower by more than a factor of 10 but still around 1 $\mu$A cm$^{-2}$ [72], and so far from the passive state (Fig. 10). Repeated MFP treatments with drying (50°C) and immersion cycles in 20% MFP solution have been found to be a suitable method to allow penetration of the inhibitor to the steel, although high concentrations and long treatments are needed to reduce significantly ongoing active corrosion. The inhibition mechanism is thought to be similar to phosphates, i.e. hydrolysis of MFP forming H$_2$PO$_4^-$ and HPO$_4^{2-}$ [72]. Bearing in mind the low cover depths (< 10 mm) in these experiments [72], the results do not suggest that it would be easy to apply MFP under realistic site conditions in such a way as to ensure a substantial reduction of the corrosion rates of steel reinforcements suffering active corrosion at normal depths of cover; this has been confirmed by the work of Page et al. [13] where no significant reduction in corrosion rate was noted.

3.2.2.3. Field tests and applications with MFP

Beside the question of the efficiency of MFP as an inhibitor, the main problem in using MFP as a surface-applied liquid is the penetration to the reinforcement so that it can act as an inhibitor. In fresh or even young mortar and concrete, MFP cannot be applied due to the reaction with the calcium ions (see above). In early field tests in Switzerland [74,75] no sufficient penetration of MFP was found. This was partly due to a concrete that was too dense and partly to a cover depth greater than 45 mm, or, to an insufficient number of MFP applications on the surface. On the first site, in the Rofla Gallery*, a reinforced concrete (RC) side wall of 60 m length, various heating systems and temperatures were tested, the amount of surface applied MFP varied between 500 and 2200 g m$^{-2}$. Heating of the concrete surface did not show any beneficial effect for MFP penetration [75], on the contrary, the maximum penetration (25 mm) was found on areas without any heating but with repetitive MFP applications. The results of half-cell potential measurements showed a gradual shift to more negative values with increasing MFP content, both on actively corroding and on passive rebars. The difference compared to untreated areas was about 150 mV [75]. This coincided with a decrease in concrete resistivity measured after MFP application. On the second site, a carbonated parapet on a bridge, no inhibitive

*Near Thusis, on the A13 Alpine Road, Switzerland.
Fig. 10 Change in open circuit potential and corrosion rate of steel in carbonated solutions with addition of different amounts of MFP [72].
effect of MFP was found [75], since insufficient MFP had penetrated to the rebars because they were in a dense, good quality concrete. Only a few mm of penetration were found in a test conducted recently at another site [78]. In other recent field applications [68], e.g. on the Peney Bridge near Geneva [76], concrete buildings and balconies, MFP was applied onto cleaned, dry concrete surfaces in up to 10 passes and the concrete was impregnated down to the reinforcement level, in some cases down to 40–60 mm in a few days or weeks [79]; good penetration was found in carbonated concrete. Increased penetration was obtained when using a gel rather than a solution in the application [79]. Unfortunately, the concrete quality in terms of porosity was not reported. No other tests except the detection of MFP (by analysing the P content by SEM or ion chromatography) were performed, so conclusive results on MFP efficiency as corrosion inhibitor on site cannot be deduced. What constitutes an adequate concentration of inhibitor at the level of the steel bars and how this depends on factors such as the extent of prior corrosion of the steel remains uncertain. In addition, the application of MFP under realistic site conditions in such a way as to ensure adequate reduction of the corrosion rates of steel in concrete suffering active corrosion may not be easy, as can also be concluded from the recent tests conducted at Aston University [13].

3.3. Alkanolamines and Amines

In this section, a short review on the earlier literature studies and related patent applications to amines and alkanolamines is given. In the second part, laboratory research results of commercial inhibitor blends based on alkanolamines are presented. The major difficulties associated with the independent evaluation of these organic corrosion inhibitors that are proposed and used in commercially available concrete repair systems is the unknown or, at least, the uncertain composition.

3.3.1. Literature Studies and Patent Applications

Alkanolamines and amines and their salts with organic and inorganic acids have been described and patented for different applications, such as for the protection of steel in cementitious matrices ([80,81] and literature cited therein). These substances originate from the temporary corrosion protection known as vapour phase inhibitors (VPI) or volatile corrosion inhibitors (VCI). A European Patent Application published in 1987 [82] describes the use of one or more hydroxyalkylamines having molecular weights ranging from about 48 to 500 and vapour pressures at 20°C ranging from \(10^{-4}\) to \(10\) mm Hg that are employed as major ingredients of a corrosion inhibitor to be mixed into hydraulic cement slurry. The hydroxyalkylamines provide corrosion protection to iron and steel reinforcing members embedded in concrete and do not substantially affect the air entraining capacity. As typical compounds diethanolamine, dimethylpropanolamine, monoethanolamine and dimethylethanolamine are mentioned. Compressive strength and time of setting are not altered by more than 20%. The influence of ethanolamines on the hydration and mechanical properties of Portland cement has been studied in detail [83]. Monoethanolamine and diethanolamines showed slight retardation effects at low concentrations (0.1%).
whereas at 1% the retardation was significant. The reduction in compressive strength was highest for triethanolamine (27% at 90 d) and lowest for monoethanolamine (5%). Triethanolamine, depending on the cement type and on its concentration, can lead to set acceleration or retardation [83]. Figure 11 shows the corrosion rates obtained in laboratory experiments in presence of different hydroxyalkylamines or their mixtures compared to the control sample [82]. A study on the inhibition of pitting corrosion of mild steel in solutions of NaHCO₃ by mono- and dimethylamines and monoethylamine showed a marked increase of the pitting potential above an inhibitor concentration of 0.1 mole L⁻¹ (Fig. 12) [84]. The concentrations necessary to inhibit pitting increased with higher NaCl content in the solution and with lower pH.

Another patent specification [85] regarding corrosion inhibition in reinforced concrete addresses vapour phase corrosion inhibitors (VPI) or volatile corrosion inhibitors (VCI). As preferred inhibitors for reinforcement, dicyclohexylamine nitrite (DCHN), cyclohexylamine benzoate (CHAB) and cyclohexylamine carbamate (CHC) or mixtures of CHAB and CHC are proposed. The aim of mixing is to get a VPI with a fast initial release and one with a slow vaporisation. It is proposed to bring the VPI into the concrete by drilling holes at suitable places. The spacing of the drill holes depends on the amount of reinforcement, the volatility of the VPI, the porosity of the concrete and the VPI content in the holes. Only short term corrosion tests and no evidence of long term efficiency are given [85]. Further information on vapour phase inhibitors can be found in a review [86] and research papers [87,88].

It is interesting to note that the patent application explicitly reports the advantage of all hydroxyalkylamine compounds being water soluble so that they can demonstrate mobility within concrete structures when water is applied. It is claimed that these inhibitors can be applied to existing reinforced concrete structures and

![Fig. 11 Corrosion rate [µm/year] of steel in concrete with different inhibitors mixed in [82]. A: Control; B: Dimethylaminoethoxyethanol; D: N,N,N’-trimethyl (hydroxyethyl)-1,3-propane diamine; E: N,N,N’-trimethyl (hydroxypropyl)1,3-propane diamine; F: Methyläethanolamine; G: Triethanolamine; H: Monoethanolamine; I: Dimethylthanolamine; J: Dicyclohexylamine.](image-url)
that the corrosion inhibitor will then be carried by water into proximity of the reinforcing steel. The inhibitor could thus be included in hydraulic cement overlays on old concrete structures. Some vapour phase migration of the inhibitors is believed to occur as well as a result of the vapour pressure of the inhibitors.

3.3.2. Studies with Proprietary Inhibitor Blends based on Alkanolamines

Several proprietary blends from different producers (e.g. Cortec VCI-1337 or MCI-2020, Cortec VCI-1609 or MCI-2000, SIKA Armatec 2000 or SIKA Ferrogard 903) are based on the principle of using alkanolamines and amines and their salts with organic and inorganic acids. The Cortec inhibitors are described as [41,42]:

- Cortec VCI 1337 (MCI 2020), a proprietary blend of surfactants and amine salts in a water carrier: a secondary electrolyte inhibitor with appreciable vapour pressure under atmospheric pressure or volatile corrosion inhibitor. The product is designed to migrate in a vapour phase and adsorb on a metallic surface to form a monomolecular film at anodic and cathodic sites. The inhibitor is applied by spraying/rolling on a concrete surface or by injection into the concrete structures. The pH is 7.5, the density 0.99–1.08 g cm$^{-3}$, as it contains 27–30% of non-volatile components [89].

- Cortec VCI-1609 (MCI 2000), proprietary alkanolamines: this product is designed to migrate and inhibit in a manner similar to VCI-1337 with the difference that it is a concrete admixture. The liquid appears colourless to pale and has an ammoniacal odour, pH 11–12, a density of 0.88 g cm$^{-3}$.
and vapour pressure of 4 mmHg (20 deg) containing 1.5% of non volatile products [89].

Laboratory tests in the SHRP project [41,42] showed good inhibitive properties of the surface applied inhibitor: a one day ponding with Cortec VCI-1337 after drying of the concrete showed that at pre-corroded reinforcing bars in concrete (cover 2.5 cm) the corrosion rate (determined from linear polarisation resistance measurements) decreased and the corrosion potential shifted to more positive values (Fig. 13) after 50 days. The inhibitors penetrated from the repair material through to the next layer of steel reinforcement in the parent concrete [41]. It is interesting to note that the Cortec VCI-1337 inhibitor showed the most pronounced reduction in corrosion rate but the most negative potentials. Further, the reduction in corrosion rate for rebars with medium to low corrosion rates prior to treatment (non-dried specimens) was much less pronounced (only about 60%). This was the same reduction as found in a conventional Latex modified concrete (LMC) overlay without any inhibitors.

3.3.2.2. Electrochemical corrosion testing

A recent comparative test of different organic amines [90] used simulated pore water solutions with 1.2% chlorides to test both the effects with admixed inhibitor and

![Graph](https://www.iran-mavad.com)

**Fig. 13** Estimates of corrosion current density after application of different inhibitors; MCI 2020 (0.6 L m⁻²) □; Ca(NO₃)₂ (30 L m⁻²) ■; sodium tetraborate (0.1 m L⁻¹ in mix water) +; and Latex overlay as control, x; and a proprietary organic blend, Alox 91, *, on dried specimens with high initial corrosion rates [41]. ID indicates that the specimens had been dried at 82°C at a depth of 13 mm below the reinforcing steel and ponded with the corrosion inhibitor for 1 day.
remedial work. At a concentration of 1% (by weight) the commercial MCI 2000 inhibitor showed very good corrosion inhibition, pure dimethylethanolamine being practically ineffective. In the remedial situation, where the steel coupons were corroding, the MCI 2000 inhibitor was effective over the whole period of the test (1000 h). Also in these tests, the open circuit potentials of the steel remained at values around -400 mV (SCE) and became more negative after the addition of MCI inhibitor to the solution.

Migrating corrosion inhibitors (MCI 2000 and 2020) have been tested in a two year laboratory study in solution and in mortar samples [91-95] as inhibitors against carbonation or chloride-induced corrosion. In a first series of experiments the inhibitor efficiency of MCI 2000 as admixture for concrete was determined [91,94]. First the critical concentration of MCI 2000 was determined in solutions. Sand blasted rebar samples were immersed for 7 days in chloride-free saturated Ca(OH)₂ solution (pre-passivation) with different contents of inhibitor, then the solution was changed to saturated Ca(OH)₂ with 1m NaCl. As is shown in Fig. 14, it is only with addition of 10% inhibitor that the electrode potentials remained in the passive state after the addition of 1m NaCl. Continuing the experiment shown in Fig. 14, it was found that a few days after opening the cell to air the corrosion potential and the polarisation resistance of samples immersed in solutions with 10% of inhibitor dropped to low values indicating the onset of pitting corrosion [94].

Simple chemical analysis revealed that the inhibitor blend consisted of two main fractions, a volatile amine, mainly dimethylethanolamine (ca. 95%), and a non-volatile part (5%); they were separated by distillation at 30°C. Electrochemical tests were performed with these two main components in alkaline solutions. Potential and linear

![Fig. 14 Effect of MCI 2000 inhibitor concentration on open circuit potential of mild steel in sat. Ca(OH)₂ solutions with 1m NaCl [91,94]. 1: prepassivation in sat. Ca(OH)₂; 2: immersion in sat. Ca(OH)₂ + 1m NaCl.](www.iran-mavad.com)
polarisation resistance (LPR) measurements showed that neither component of the inhibitor, the volatile and the non-volatile component, when present alone in solution could prevent initiation of corrosion (Fig. 15); polarisation resistance values measured in solutions with either of the inhibitor components indicated a reduction in the corrosion rate by a factor of about 2–3 compared to solutions without inhibitor. The volatile part of the inhibitor caused a shift of the corrosion potential to more positive values (Fig. 15); opening the cell after 50 days resulted in a drop of the potential indicating the evaporation of the volatile part of the inhibitor. Electrochemical impedance spectroscopy (EIS) measurements performed after immersion of steel in saturated Ca(OH)₂ solutions without and with 10% of inhibitor clearly revealed a second time constant at high frequencies on the sample immersed in solution with inhibitor (Fig. 16). This indicates some type of film formation on the passive steel surface in presence of the MCI 2000 inhibitor blend.

The effectiveness of the inhibitor in preventing or delaying chloride-induced corrosion was studied using mortar samples (lollipops) with w/c ratio of 0.5 and admixed MCI-2000 contents of 0, 0.015, 0.075 and 0.375% per weight of mortar. After curing for 70 days in 100% RH all samples (6 for each inhibitor concentration) were exposed to cycles, consisting of 1 day immersion in 6% NaCl and 2.5 h drying in air to initiate chloride-induced corrosion. Time to corrosion initiation in presence of the inhibitor was increased (Fig. 17), the first sample of the series with the highest concentration of inhibitor started to corrode after 90 instead of 50 days. On the other hand, no significant reduction in the corrosion rate of samples after the initiation of corrosion was found. A reduction in corrosion rate on already corroding rebars by inhibitor penetration was hardly seen [91,94]. It has been shown by measuring the

![Graph](image-url)

*Fig. 15* Open circuit potential (□ ○ △) and polarisation resistance (■ ● ▲) of mild steel in sat. Ca(OH)₂ solutions with 1M NaCl without inhibitor (△, ▲), with 10% of volatile compound (□ ■) and with 10% of the non-volatile compound of the inhibitor (○ ●)[91,94].
Fig. 16 Impedance spectra (Bode plot) for steel immersed in sat. Ca(OH)$_2$ solution without and with 10% of inhibitor MCI 2000. Immersion 3 h [91,93,94]. — = impedance; - - - = phase.

Fig. 17 Percentage of actively corroding mortar samples during cyclic immersion tests with 2.5 h drying and 1 day immersion in 6% NaCl solution [91,93,94]. Each series with different inhibitor content contained six samples.
amine concentration in airtight compartments that the volatile component of the inhibitor is evaporating from the mortar [94].

Similar experiments were conducted with rebar in mortar exposed to carbonation. Blowing CO₂ into the solution after 1 week passivation of the samples resulted in a drop in pH to 10.7 for 10% inhibitor, to 9.6 for 1% and to 7.3 without inhibitor. Corrosion potentials of samples in solution with 1 and 10% of inhibitor remained in the passive range (ca. -100 mV (SCE)), whereas samples in the solution without inhibitor were activated (-720 mV (SCE)). In carbonated mortar samples the onset of corrosion was more difficult to determine. Weight loss measurements of the embedded rebar after 380 days of exposure to CO₂ showed no significant differences between different inhibitor concentrations [91,94].

The inhibitor efficiency against ongoing corrosion brought about by chloride or carbonation (repair method) was studied [91,95]. Samples were pre-passivated in Ca(OH)₂ solution for one week. Addition of 1M NaCl resulted in a sharp drop of both corrosion potential and polarisation resistance. After 12 days 10% of inhibitor was added to the solution, resulting in a shift of the corrosion potential to more positive values and an increase in the polarisation resistance (Fig. 18). Mortar samples without inhibitor were cured and then exposed to cyclic treatment in chloride solutions in a CO₂ atmosphere. After the onset of corrosion, the samples were immersed in solutions of MCI 2020, where more than the recommended dosage of inhibitor was taken up. As is shown in Fig. 19, the corrosion potential and polarisation resistance remained at low values indicating that pitting corrosion was continuing, despite low cover and quite high porosity. An increase in corrosion potential was

Fig. 18 Corrosion potential and polarisation resistance of steel in sat. Ca(OH)₂. After 7 days prepassivation 1M NaCl was added and corrosion started; 12 days later 10% of inhibitor were added [91,95].
Fig. 19 Corrosion potential and polarisation resistance of steel in mortar. After curing the samples were cyclically immersed in 1 M NaCl solutions until corrosion started (period 1) and then soaked in inhibitor solution. In the period 2 samples were stored at 80% humidity [91,95].

observed only after changing the measurement frequency, longer intervals allowing a better drying out of the mortar samples. A possible explanation of this discrepancy between solution and mortar experiments might be that the inhibitor is a two-component blend and only the volatile compound reached the rebars.

Results of tests with proprietary SIKA Ferrogard 901 obtained up to 1996 have been summarised [76]. Electrochemical measurements in solution [97] showed that the inhibitor blend is effective when present prior to the addition of chlorides with an increased concentration showing a more pronounced effect. Cracked beam corrosion tests [76] showed that the inhibitor decreased the current flow by about 60% with reference to the specimen without inhibitor, a similar value to that obtained with calcium nitrite. The pitting after 400 days in reference specimens was larger and slightly deeper than in beams with corrosion inhibitor. The effect on concrete properties of this inhibitor are reported to be negligible with both setting time and compressive strength not being altered when up to 3% of inhibitor was added to concrete [98]. In the same work exposure tests of steel samples in solutions of pH 12 and 10 were performed with 0.006 mole L⁻¹ of NaCl. When adding up to 4.5% of inhibitor (corresponding to about 0.4 mole L⁻¹ of DMEA) corrosion of the steel plates could be prevented (test duration 72 h) [98].

The inhibitor blend was tested as an admixture (3%) in mortar and concrete samples exposed to chlorides [96], exposed both to sea water and to NaCl solution spray. After one year of test on salt sprayed specimens, corrosion had started in specimens with w/c = 0.6, the chloride threshold values in all cases being higher for the inhibitor-containing samples (4–6% Cl⁻ by weight of cement) compared to the control samples (1–3% Cl⁻). Some of the inhibitor-free samples with w/c 0.45 started to corrode at
chloride threshold values of 2–3%, while the specimens containing 3% Ferrogard 901 had not corroded by 15 months [96]. This indicates that the corrosion inhibitor delays the start of chloride-induced pitting corrosion. Specimens submerged in artificial sea water started to corrode after approximately one year, the difference between samples with and without inhibitor was not clear [96]. Concrete specimens with Norwegian HS65 cement, w/c = 0.5, submerged in sea water started to corrode after 15 month of exposure, the chloride threshold was 2.4% ± 0.4% by weight of cement. All of the specimens with 3% of Ferrogard inhibitor blend remained passive [96]. In a recent laboratory study where this inhibitor, known to contain ethanolamine and phosphate components, was applied to chloride-contaminated or carbonated concrete specimens by repeated ponding and drying in accordance with manufacturer’s dosage recommendations only modest reductions in corrosion rates of pre-corroded steel bars embedded at depths of 12 mm in concrete of w/c 0.65 were found. In cases of high chloride contamination the inhibitor blend was apparently ineffective [13] (Fig. 20). The alkanolamine component of the mixture was found to have penetrated to depths of more than 20 mm in the above concrete whereas the phosphate was not detected at depths beyond 4 mm [100].

3.3.2.2. Inhibitor adsorption on steel in alkaline solutions
The interaction of the inhibitor MCI 2000 and of pure 2-dimethylethanolamine (DMEA) solvent with passive iron surfaces has been studied with X-ray photoelectron
spectroscopy (XPS) and with Time of Flight-Specific Ion Mass Spectroscopy (ToF-SIMS) [101]. Mirror-like polished samples were immersed in alkaline solutions simulating the pore solution of concrete for one hour, one day and three days. Solutions studied were blank, with 10% of DMEA and with 10% of inhibitor. After removal from the test solutions and rinsing with distilled water, all samples were mirror-like without deposits or precipitates. Samples from solutions with 10% of inhibitor blend were hydrophobic, the water drops did not wet the surfaces. From the quantitative analysis of the XPS data a thickness of the organic layer on the surface after one hour of immersion in the solution with inhibitor of 6.3 ± 0.2 nm (density assumed 1 g cm⁻³) was calculated whereas only 3.8 ± 0.2 nm were measured in the blank and in DMEA solutions. This indicates a specific adsorption of the inhibitor blend on the surface as has been found by EIS measurements (Fig. 16) [92]. Further immersion for 24 or 96 h did not reveal any significant increase in film thickness. In other work, adsorption of pure DMEA was reported on steel immersed in alkaline solutions [102,103] and the displacement of chloride ions by pure DMEA was claimed.

Highly surface sensitive and molecular fragment specific ToF-SIMS measurements revealed the presence of two prominent lines at negative m/z fragments of 121 and 281, both after deposition of the inhibitor blend (MCI 2000) on gold and after immersion in alkaline solution with 10% of inhibitor on iron [101], thus the inhibitor blend (as mentioned in the patent applications) must contain other chemical substances (e.g. benzoates) in addition to the solvent.

3.3.2.3. Inhibitor migration in concrete
An important property of the class of inhibitors based on amines or alkanolamines is their quite high vapour pressure under atmospheric conditions. The inhibitor is thus claimed to diffuse or migrate into cement-based materials such as mortar and concrete [80, 89, 104-106]. Diffusion experiments were performed in the classical diffusion cell with the concrete sample separating two compartments, one with inhibitor solution (MCI 2020) or air with inhibitor (MCI 2000), the other with saturated Ca(OH)₂ solution [105,106]. Three different concrete mixes were studied. The results of the diffusion experiments showed that the concentration of MCI inhibitor in the compartments with Ca(OH)₂ increases with time up to 0.1 mole L⁻¹ after 20 days, the diffusion coefficients calculated lie within the range of 3 and 0.4 x 10⁻¹² m²s⁻¹, agreeing well with the gas permeability determined for the concrete mixes [105]. A similar slow but steady diffusion of the inhibitor through concrete (w/c ratio 0.6) has been reported [90], after 50 days a concentration of 0.3% with respect to the compartment with inhibitor (aqueous solution of the MCI 2000 inhibitor) being found. Based on the evaporation kinetics of the inhibitor from mortar samples, a diffusion coefficient of 300 x 10⁻¹² m²s⁻¹ has been found [95], which is much higher than other results. This could be due to the fact that the measurements were performed in 80% R.H. and not in immersed conditions. In these studies, the inhibitor content was determined using the ion selective ammonia electrode [80,90,95,105,106]. Amines dissolved in water form ammonia and the potential of the ion selective electrode reflects the concentration of free amine; this technique works both in solution and in air. As has been shown [91,94,101], the inhibitor blend consists of (at least) two fractions and both have to be present on the steel to provide effective corrosion inhibition. In the diffusion tests [90,94,105,106] only the concentration of the volatile
fraction of the inhibitor (the amine) is determined, no information is available about the ingress of the non-volatile fraction of the inhibitor into the mortar or concrete. Further, tests with mortar samples soaked in the inhibitor solution of MCI 2020 showed that the volatile fraction of the inhibitor is diffusing out of the mortar, following the concentration gradient [91,95].

A detailed study on the transport of another proprietary aminoalcohol based inhibitor (SIKA Ferrogard 903) into cement paste and mortar is reported by Tritthart [100,107]. The results showed that both the amount and the rate of inhibitor ingress into alkaline cement paste is higher for the pure aminoalcohol compared to an inhibitor blend containing phosphates (Fig. 21). This discrepancy could be explained by a reaction of the inorganic phosphate component with the calcium ions in the fresh cement paste [107,108] 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 year old, fully carbonated concrete structure, varying the dosage and the way of inhibitor application (Fig. 22). The recommended dosage (500 g m⁻²) 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 m⁻² increased the amino alcohol concentration, but the penetration depth remained low. Only a ponding for 28 or 50 days resulted in a significant inhibitor concentration (both amino alcohol and phosphate) at depths greater than 30 mm [100].

Penetration tests of surface-applied inhibitor using SNMS (secondary neutron mass spectroscopy) indicated that the inhibitor reached up to 7 cm depth after

![Graph](image)

**Fig. 21** Transport of a proprietary aminoalcohol based inhibitor (SIKA Ferrogard 903) into alkaline cement paste, according to Tritthart [100].
3.4. Other Organic Inhibitors

Organic based admixtures to concrete were proposed in a United States Patent [111]. It is marketed as Rheocrete from Master Builders Inc. The admixture comprises a water emulsion, in which 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 emulsion collapses allowing contact between the active agents and the steel reinforcing bars. The mechanism of this organic corrosion inhibitor (OCI) is described as a dual ‘active–passive mechanism’: the active
part of this organic inhibitor is the adsorption of a film-forming amine on the reinforcing steel and the formation of a physical barrier to the action of aggressive agents such as chloride ions [112,113]. Extensive surface analytical studies were performed to get the analytical verification of the film-forming amine mechanism using Fourier transform infrared spectroscopy (FTIR) and FTIR-ATR (attenuated total reflection) spectroscopy, showing that the film-forming amine adsorbs on the steel surface [114]. Electrochemical tests in solution showed polarisation resistance ($R_p$) values of about 1 kΩ cm$^{-2}$ for locally corroding steel in alkaline chloride solutions (0.2 M Cl$^-$), whereas $R_p$ values > 700 kΩ cm$^{-2}$ were measured for inhibited solutions (the inhibitor was present in the alkaline solution before adding the chloride ions) [114]. This is in agreement with results found on another proprietary inhibitor blend [91,94].

The passive part of the mechanism is the reduction in concrete permeability, thus reducing the ingress of chloride ions, moisture and other aggressive chemicals. The waterproofing ester mechanism, forming fatty acids and their calcium salts, results in the formation of a hydrophobic coating within the pores, reducing the ingress of water and chloride ions. This has been demonstrated by measuring the chloride profiles after 1000 days of cyclic ponding, where the OCI-containing samples contained only 50% of the chloride concentration compared to the untreated ones, and also showed a much steeper decrease of the chloride concentration [114].

Corrosion inhibition of steel in concrete by carboxylic acids have been studied [115]. Pore water expression has shown that these substances remain largely soluble after curing. The inhibitor concentration increases with time. All the molecules studied (malonate, formate, acetate and propionate) decreased the mean corrosion current density of steel compared to NaCl solutions without inhibitor [115]. Unfortunately, the most effective compound, malonic acid, has a strong initial retarding effect on the setting of OPC concrete.

Tannin–sugar fractions from vegetables extracts were shown to inhibit corrosion of steel in neutralised concrete with low chloride content [116]. The inhibitor, a mixture of polyalcohols, polyphenols and sugars, is claimed to be incorporated into the protective iron oxide layer.
4
Critical Evaluation of Corrosion Inhibitors

Corrosion inhibitors in new reinforced concrete structures, in concrete repair systems or as surface-applied liquids should prevent or at least delay the depassivation of the steel and/or reduce the corrosion rate of steel in concrete. Several fundamental conditions have to be fulfilled for an efficient and durable inhibitor action:

1. The inhibitor should not adversely affect concrete properties (strength, freeze-thaw* resistance, porosity etc.) and should be environmentally friendly.

2. The inhibitor has to be present at the reinforcing steel at a sufficiently high concentration with respect to aggressive (chloride) ions.

3. The inhibitor concentration should be maintained over a long period of time.

4. The inhibitor action on corrosion of steel in concrete should be measurable.

4.1. Concrete Properties — Environment

Adverse effects of inhibitors on concrete properties (setting time, compressive strength) have been tested in the laboratory. From the results that are available it can be concluded that:

- calcium nitrite is reported to be an accelerator for concrete setting and increases the compressive strength of concrete [25] whereas sodium nitrite causes moderate to severe loss of strength [19–22];

- sodium monofluorophosphate (MFP) strongly retards concrete setting and thus cannot be used as admixture for new structures; on the other hand it has been reported to reduce freeze thaw attack when applied from the concrete surface [74]. Both effects might be due to a hydrolysis of the inhibitor and reaction with free calcium ions to form insoluble calcium phosphate and calcium fluoride [13,70,71,77]; and

- migrating inhibitor blends have been tested with different European cements, both with and without water reducing admixtures [80,81,83], and have shown no significant effect on concrete properties.

*Freeze-thaw resistance is the ability of concrete to withstand spalling and cracking due to cycling: cooling ± 20°C and reheating to room temperature.
Aspects of environmental compatibility of all chemicals used in the construction industry are becoming more and more important both from a legal and financial point of view. Harmful or toxic admixtures have to be replaced because of strict environmental protection regulations. The following should be noted:

- the amine-based migrating inhibitors are alkaline and are classified as irritant products. They should not contaminate water or earth;
- MFP is a non-toxic inorganic substance that is used as a component of tooth cleaning products;
- calcium nitrite when dissolved in water forms NO$_2^-$ ions that are considered quite toxic, because they can oxidise the haemoglobins (in the blood) to methemoglobin (containing Fe(III) ions) that are not able to transport oxygen [117]. On the other hand, nitrites are allowed to a certain extent in meat [117]. In a recent study in Germany, calcium nitrite was not allowed as inhibitor for reinforced concrete (RC) structures in groundwater or water reservoirs because of a significant leaching out of the nitrite ions [118].

More and more concerns are being raised regarding the use of all types of concrete admixtures that are not environmentally friendly because concrete, when demolished at the end of the service life of a structure, may be considered as hazardous waste with very high costs of disposal.

4.2. Concentration Dependence

Text books and the available literature always report a concentration dependence of inhibitor efficiency. In neutral or acidic environments (where uniform corrosion of steel occurs) typical inhibitor concentrations are in the range of $10^{-4}$ M to $10^{-2}$ mol L$^{-1}$ [4,5]. In contrast to these low concentrations found in inhibition of uniform corrosion, application of inhibitors against localised corrosion — also present in the case of steel in concrete — requires much higher concentrations, the necessary dosage increasing with increasing chloride concentration as has been found for nitrite, MFP and aminoalcohols.

4.2.1 Mechanism of Inhibition of Localised Corrosion

Inhibitors for pitting corrosion (the typical situation for steel in concrete) are not often studied [7,8]. Chloride ions are responsible for pitting corrosion, the pitting potential depends on the chloride activity $a_{Cl^-}$ with $E_{pit} = C - B \log(a_{Cl^-})$. This may become important when chloride-containing mortar or concrete is drying out, water is evaporating and the activities of the ions in the pore solution change.

The observed dependence of the inhibitor concentration necessary to prevent pitting corrosion on the chloride activity (concentration) found for nitrite, MFP and also aminoalcohol type inhibitors can be explained by various mechanisms [7]:

www.iran-mavad.com
Critical Evaluation of Corrosion Inhibitors

- by a competitive surface adsorption process of inhibitor and chloride ion, reducing the effective chloride content on the passive surface and thus reducing the number of pit initiation processes. This effect has been known for a long time for stainless steels [150] where increasing sulfate concentration leads to higher pitting potentials and has recently been confirmed by ex situ XPS analysis for pitting corrosion of stainless steels [151].

- by buffering of the pH in the local pit environment, reducing the acidification due to the hydrolysis of metal ions in the pit. This would reduce the aggressivity of the pit electrolyte and slow down pit growth rates.

- by competitive migration of inhibitor and chloride ions into the pit, so low pH and high chloride contents necessary to sustain pit growth cannot develop. All negatively charged ions (especially OH−) can act in this way. Usually high levels relative to chloride concentration are required.

- inhibitors may also act by adsorption on the passive surface, reducing the rate of cathodic oxygen reduction and thus the corrosion rate.

4.2.2. Inhibitors Admixed to Concrete — New Structures

The goal of inhibitor admixture with new concrete structures is to increase the durability of the structure and to prolong the service life, thus inhibitors should prevent or at least delay the onset of (mainly chloride-induced) corrosion. All the available literature data report a concentration dependent effect of inhibitors, e.g. a critical ratio inhibitor/chloride that has to be exceeded to prevent depassivation of the steel in the case of chloride-induced corrosion. This implies:

- that the expected chloride concentration at the level of the rebars has to be specified; this will be based on experience with similar structures (concrete quality) and exposure conditions or by assumption;

- a need to be on the safe side of the inhibitor action and to take into account maxima in the chloride content (some overdosage will be necessary); and

- that the inhibitor concentration is assumed to remain constant over (long) time, thus no inhibitor leaching, washing out, consumption or evaporation should occur.

For calcium nitrite the Cl−/NO2− ratio should be in the range of 0.7 to a maximum of 1 [24,25,27] to prevent the onset of corrosion at chloride concentrations up to 4%. Some tests have been performed with admixed chlorides [24,29–34], and thus do not represent a real field situation. The critical Cl−/NO2− ratio for penetrating NaCl in such cases was found to be higher (see also section 3.1.3).

For alkanol- and amine-based inhibitors high inhibitor concentrations (10% of inhibitor at 1M NaCl) were reported to be necessary to prevent the onset of pitting
corrosion [91–94]. This corresponds to a molar ratio of chloride to inhibitor of ca. 1 when the molecular weight of the main component (DMEA 89 g mol$^{-1}$) is considered.

### 4.2.3. Surface-applied Inhibitors

Inhibitors applied to the surface of existing structures (surface-applied inhibitors) may face great difficulties in reaching the expected effectiveness in delaying the onset of corrosion or reducing the corrosion rate. This might be due to several factors:

- Chloride contamination or carbonation may vary strongly along the concrete surface, as e.g on a typical sidewall or concrete elements in tunnels exposed to splash water, where high chloride concentrations are found at the bottom near the pavement [119–121]). Thus the necessary inhibitor concentration varies, and in order to get a protective action on the whole surface an overdosage in the less critical zones will result.

- Cover depth and permeability of the concrete may also vary, thus the maximum penetration depth of the inhibitor and the time necessary for it to reach the rebars may vary greatly. As field tests with MFP have shown, the necessary concentration of inhibitor might not be reached [68,74,75,78] and special application procedures may be necessary [79].

- The inhibitor may react with other ions in the pore solution, especially calcium ions, as has been found in the laboratory for MFP [70,71] or for the MCI migrating inhibitors, which form precipitates of calcium-benzoate after 14 days [91,94,95]. Also, for the SIKA Ferrogard 903, a precipitation of the phosphate component has been reported [100].

- The inhibitor might be leached out or evaporate. Leaching-out has been reported for nitrites in poor quality concrete [44,45] and in concrete permanently exposed to water [118] and evaporation has been reported for MCI migrating inhibitors [95]. Indeed, a high diffusion rate (which is claimed to be necessary for a rapid ingress of the inhibitor into concrete) does not depend on the diffusion direction and evaporation will result [95].

In the application notes for surface-applied inhibitors not only an average weight of inhibitor solution to be applied per square metre of concrete should be specified (or alternatively the number of applications) but also the critical concentration to be achieved at the rebar level. This is usually omitted, partly due to the lack of analytical methods to measure the inhibitor concentration.

### 4.3. Measurement and Control of Inhibitor Action

One of the main difficulties in evaluating the performance of inhibitors is assessing the inhibitor action on rebar corrosion 'on site'. This is in part a result of the lack of reliable measurement techniques (see Chapter 5), but also because of the great
variation of the corrosion rate of steel in concrete with temperature, humidity etc.; so that, without careful statistical analysis, it might be difficult to prove in a short time that the inhibitor treatment was effective.

- The application of half cell potential measurements to control repair or restoration work has been discussed recently [122]. In the case of inhibitors the interpretation may present difficulties because of changes in the concrete resistivity [68,75,123,124] introduced by the inhibitor application. Further, a reduction of corrosion rate due to an inhibitor action may not be reflected in a straightforward manner to the half-cell potential since 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 also occur due to the wetting and drying of the concrete [122,123].

- Results of corrosion rate measurements on site depend on the type of device used for the measurements and, so far, can be interpreted only by specialists [11,125,126] (for more details on polarisation resistance measurements, see section 5.1.2). Beside the great variation in current spreadout found when using instruments without a guard ring, the main problems are the daily and seasonal changes of the corrosion rate with temperature and concrete humidity [127,128] which make it difficult to evaluate inhibitor action without a careful statistical data treatment. Small scale field trials using two proprietary vapour phase inhibitors (VPI) that compared treated and untreated fields of (supposed) similar concrete quality and exposure reported a modest but statistically significant reduction in corrosion rate [129] when this was measured with a commercial LPR meter with guard ring.

- Macrocac current measurements between electrically isolated anodes (located and instrumented before inhibitor application) and the surrounding cathode are a simple way to control the effectiveness of inhibitors on site. This has been used on a building where MFP was used as a surface-applied inhibitor [136] and in a field test with MFP and a migrating inhibitor in Switzerland [121,134].

All measurement techniques present some difficulties either in the interpretation or in the application. The most direct answer can be expected from corrosion rate measurements and these are most reliable when applied at the same time to a treated and to a control area. As a rule the penetration depth of the inhibitors and their concentration at the level of the rebars should be checked prior to corrosion rate measurements, since if the inhibitor does not reach the rebars no reduction in corrosion rate can be expected.

### 4.4. Field Tests and Applications

Despite several site jobs and increasing applications of inhibitors on building and structures, conclusive field tests on surface applied inhibitors such as MFP or organic
Corrosion inhibitors are very rarely reported in literature. The available field data are often poor and lack essential information for a conclusive interpretation (see the case histories in e.g., [79,130,131,137]) and provide no clear evidence of the amount of inhibitor applied, whether it reached the rebar and reduced corrosion rates or extended time to cracking [132] — and thus are unfortunately of little or no value.

The Strategic Highway Research Program in the USA undertook field trials of two inhibitor applications on bridge decks and substructures [50], both with calcium nitrite inhibitor. Some ongoing field trials lack well defined condition assessment prior to the inhibitor application, and on others corroding areas were repaired conventionally prior to the inhibitor application.

In Switzerland a comparative field test with surface-applied inhibitors (including MFP and SIKA Ferrogard) [121] on a chloride-contaminated prefabricated cover panel (thickness 50 mm) on the side wall in a tunnel was started in 1997 with a thorough characterisation of the test sites, using chloride analysis and half-cell potential mapping. At the lower part of the panels (< 2 m) chloride contents higher then 1% by weight of cement were found. The test and reference fields were instrumented with macrocells and combined chloride/resistance sensors at different depths [133] in addition to temperature and R.H. sensors. The inhibitors (MFP and FerroGard-903) were applied after washing of the test fields with water by the suppliers of the inhibitors. The results obtained after two years showed that no differences were revealed in half-cell potential measurements performed before and after application for both the inorganic and organic inhibitor. This is confirmed by the macrocell current measurements where no clear current decrease after the inhibitor application was found [121,134]. Thus, these field tests were considered unsuccessful.

Results of long term monitoring of corrosion inhibitors applied to corroding reinforced concrete structures are reported from the USA and the UK [132,135]. Aminoalcohol-based inhibitors were applied down holes drilled in the concrete and in repair patches in concrete support structures for insulators in an electrical substation with more then 1% of chloride by weight in cement cast into the concrete as calcium chloride set accelerator. This trial on over 60 structures showed a slight reduction in corrosion rate but the onset of cracking of the treated structures was at about the same time as untreated controls and so the treatment was not considered successful.

Surface-applied inhibitors were used in a restoration trial on chloride-contaminated (up to 0.8% by weight of cement at the depth of the rebars) and corroding parking decks at Reykjavik [138]. The results of corrosion rate measurements 2.5 years after the inhibitor application did not show any statistical difference between inhibitor-treated and untreated control areas.

4.5. Durability of the Inhibitor Action

On concrete structures exposed to splash water or rain the inhibitors may be washed out (at least at the concrete surface) and the critical inhibitor/chloride concentration ratio may not be maintained over time. Calcium nitrite as a passivating inhibitor reacts to a small extent with iron(II) ions to form a protective film; however, repetitive pit initiation processes can lead to a reduction in the nitrite content near the rebar and the protective action may then be lost. Calcium nitrites, in combination with low
w/c ratios and high cover depth of the concrete, are the only admixed inhibitors with a long and proven track record in the USA, Japan and Middle East [48]. The requirement of good quality concrete and high cover when using calcium nitrite indicates that nitrite in concrete prolongs the time to corrosion initiation when chloride ions have reached the rebars [35,36,140]. In order to be efficient the dosage of the calcium nitrite inhibitor has to be proportional to the expected chloride content at the rebars during service life [140,149].

Other admixed inhibitors have been used only for about the last 10 years and to a much lesser extent than calcium nitrite, and so long term experience is not yet established. From the laboratory results summarised in this review it can be concluded that organic inhibitors based on blends with aminoalcohols can also prolong the initiation time of corrosion provided a correct dosage (proportional to the expected chloride content) of inhibitor has been admixed [91,94].

Inhibitors admixed to repair mortars or surface-applied inhibitors have been promoted and used for only a few years. Some are claimed to migrate (also in the gas phase) through the concrete to reach the rebars. The results of laboratory and field tests summarised in this review do not support a widespread use of these inhibitors: since the penetration into concrete may be very slow or even not achieved [13,74,75,100]. In situations with ongoing chloride-induced corrosion both in the laboratory [13,70,95] and in field tests [121,134] no reduction in corrosion rate has been reported. In situations with a risk of corrosion due to carbonation these inhibitors might delay the onset of corrosion as a result of a buffering action of the aminoalcohol; but no reduction in corrosion rate was found when corrosion due to carbonation was already active [13,95]. The durability of the inhibitor action will be affected by evaporation of at least the volatile compounds of the inhibitor blends and this has been reported [91,93,94]; the necessary concentration for protection may then not be maintained for long or, more probably, the inhibitor application will have to be repeated after several years.

Two additional points should be mentioned:

- Firstly, the construction industry usually uses complete repair and protection systems available from different producers. These systems include corrosion protection and adhesion paints for the rebars, repair mortars (with and without inhibitors) and surface treatments such as hydrophobic impregnation or painting of the concrete surface also after inhibitor application. It is obvious that it is nearly impossible to assess the action of the inhibitors whose recommended use depends on the performance of other components of the repair systems.

- Secondly, the repair industry claims to be continuously improving the inhibitor blends on the market and the way of application. This makes the independent assessment of the effectiveness and durability of the inhibitor action even more difficult because the composition of the inhibitor blends on the market may change without notice and experience from the past (as documented in this review) cannot be used to predict future behaviour.
5 Test Methods to Evaluate Corrosion Inhibitors for Steel in Concrete

Prior to use in practice, newly developed corrosion inhibitors for steel in concrete have to be tested in the laboratory, both in solutions (screening tests) and in mortar and concrete. Preferably, an accelerated test should be used to allow rapid evaluation of the inhibitor performance and to define the necessary dosage. On the other hand, information on the long term performance of the inhibitor should also be available. The gap between these two requirements can be bridged only when the mechanistic action of the inhibitor is clearly understood. As pointed out already, this is particularly difficult when testing commercial inhibitor blends with uncertain composition.

In this chapter, test methods used to study inhibitors for steel in concrete in literature are briefly presented and discussed. The methods include:

- non-perturbing tests (immersion or exposure tests) where visual inspection and/or half-cell potential measurements are performed, macrocell-tests, polarisation resistance or impedance measurements at the open circuit potential, and

- perturbing electrochemical tests such as polarisation curves and potentiostatic or galvanostatic polarisation.

Finally, some parameters such as surface preparation of the sample, principles of mounting and electrical connection of the rebar in mortar or concrete etc. will be discussed.

5.1. Non-perturbing Tests

The simplest way to study inhibitor efficiency is by immersion tests in solutions simulating the pore solution of mortar or concrete, where aggressive (chlorides) and inhibitive substances can be added in different proportions. Such tests can be performed in beakers or Petri dishes with visual inspection of the samples over the immersion time and mass loss at the end of the test. Care has to be taken with the aeration of the solutions (usually open to air), with avoiding crevice corrosion when placing the samples on the bottom of the glass beakers, with progressive carbonation of unbuffered alkaline solutions resulting in a pH drop and with a reproducible surface preparation (see below). At least three samples should be run in parallel.

The time of appearance of corrosion products ('time of corrosion initiation'), the mass loss at the end of the test and visual observation of the form of corrosion should be obtained.

Corrosion tests on rebar samples embedded in mortar or concrete are a more
realistic approach compared to synthetic pore solutions, nevertheless the sample preparation ('lollipops', small blocks etc.) is not too expensive so parameter studies (inhibitor dosage, w/c ratio etc.) are still feasible. The inhibitors should be added to the mixing water according to the manufacturer’s specification and chloride ions should be introduced into and penetrate into the concrete by ponding, repeated ponding and drying cycles etc. Tests with admixed chlorides will give only limited information on the performance of the admixed inhibitors.

5.2. Open Circuit Potential

When electrochemical cells are used in the tests, the open circuit potential of the sample immersed in a solution or embedded in mortar or concrete can be measured vs a suitable reference electrode (frequently calomel, Ag/AgCl or HgO electrodes are used). For mortar or concrete samples, the reference electrode (mostly Ag/AgCl or Mn/MnO₂) can be embedded in the mortar or concrete; these embedded electrodes should be checked periodically against an external reference electrode. Reference electrodes that are put on the surface of the mortar or concrete only for the time of measurement are more frequently used. Care has to be taken that the potential readings are stable, and usually a wet sponge or a conductive gel are used to establish a good electrolytic contact to the mortar or concrete. This might alter the humidity content of the mortar especially for samples kept in relatively dry environments.

This type of test has been used by different research groups to study the inhibitive action of nitrites [24,27,35], sodium monofluorophosphate [70–72] or organic alkanolamine type inhibitor blends [90,91–94,97] against chloride- or carbonation-induced corrosion. Typical potential/time curves are shown in Figs 10 and 14. By measuring the open circuit potential over time, the passivation, depassivation and eventually repassivation of the steel can be followed. The type of experimental arrangement used allows the time to depassivation of the steel when chlorides penetrate or when the alkaline solution/concrete has been carbonated to be determined as a function of e.g. the inhibitor concentration present from the beginning, the w/c ratio, etc. In solution experiments (with a known chloride concentration) the critical concentration ratio of chloride to inhibitor to prevent the onset of corrosion can be calculated.

It is good practice always to run a number of control experiments with the same chloride concentration in solution or chloride penetration situation in mortar or concrete in order to be able to assess at least a relative efficiency of the inhibitor. Experience documented in the literature has shown that the results — due to the stochastic nature of localised corrosion of steel in alkaline solutions or concrete — give quite large scatter in the data. e.g. of corrosion initiation time [139] and also several identical tests have to be performed. The data should be presented in a suitable statistical representation (e.g. cumulative probability or Weibull probability curve for the depassivation time — see Figs 4 and 17) or — when a Gaussian distribution is applicable — at least by mean value and standard deviation. An alternative way is a bar graph on the time axis, indicating the time of depassivation of the first and the last sample of the series [140].

www.iran-mavad.com
مرجع علمي مهندسي مواد
5.3. Polarisation Resistance Measurements

Frequently the OCP measurements are combined with polarisation resistance measurements (linear polarisation resistance [11,125,141], impedance spectroscopy [11,58,66,114,125,141,142] or galvanostatic pulse measurements [11,125,126,143]). The linear polarisation resistance (LPR) type of test has been introduced and extensively used by Andrade et al. [141,24,31] and also by other research groups in the study of nitrites [13,30,36], sodium mono-fluoro-phosphate [13,70,72] and organic alkanolamine type inhibitors [13,97,114]. Impedance measurements have been used in the study of inhibitors for a long time [58,91–94,140]; due to the long measurement time involved (typically more than an hour) they are not used very frequently. Galvanostatic pulse measurements [11,126,143] are very rapid, and within 10 s the corrosion potential, the ohmic resistance and the (extrapolated) polarisation resistance can be determined [11,126]; in the study of inhibitors these types of measurement have been used mainly on mortar samples [91–95].

All the polarisation resistance measurements are essentially non-destructive and non-disturbing (performed within ± 10 mV around the open circuit potential), so that the system under test is not altered. Resistance polarisation ($R_p$) measurements using the various techniques can be performed at any time during the test period for samples in solution or rebars in mortar or concrete. $R_p$ measurements of rebars in mortar in concrete can be performed with the counter electrode (CE) embedded or placed on the concrete surface. In both cases a uniform current distribution should be achieved by using e.g. plane parallel [70,72,141] or cylindrical arrangement [91–95] of rebar and CE. Materials for embedded CE should be inert and non-corroding in concrete, e.g. graphite rods, stainless steel bars or grids are used.

When the CE is applied only during the measurement care has to be taken to achieve a good electrolytic contact by using wet sponges. This might introduce water in the surface layer of the mortar/concrete and alter the humidity of the sample under test. Decreasing the measurement frequency may result in changes of the open circuit potential as a result of a better drying out of the samples [94,95].

Polarisation resistance measured on rebars embedded in mortar or concrete always contain the contribution of the ohmic resistance $R_Ω$ between rebar (position of the reference electrode) and counter electrode. The ohmic resistance has to be subtracted from the measured $R_p$ values before further calculations or interpretations are performed.

More critical is the correct interpretation of $R_p$ measurements. In the original paper of Stern [144] several limitations for the application of $R_p$ measurements were defined (linearity, steady state) that might not always be respected. For uniform corrosion situations the polarisation resistance $R_p$ can be converted with the Stern-Geary equation [125,126,141,144,145] to the instantaneous corrosion rate $i_{corr}$. The proportionality constant $B = b_a \times b_c / (b_a + b_c)$ contains $b_a$ and $b_c$ the anodic and cathodic Tafel slopes respectively. The value of $B$ has been established by comparison with mass loss measurements to be 26 mV for actively corroding steel in concrete and 52 mV for passive steel [141]. Due to the product/sum function errors in the $B$ value are within a factor of two — the accuracy that was given in the original paper.

In the frequent case of localised corrosion of steel in chloride-containing alkaline solutions, no meaningful ‘corrosion rate’ or localised penetration rate can be calculated.
in this way [126,148]. Using the geometrical surface of the sample under test, a geometrical corrosion rate $I_{corr}$ with units of $\mu$A cm$^{-2}$ or a geometrical polarisation resistance $R_p$ ($\Omega$ cm$^2$) can be calculated. Both approaches neglect the occurrence of localised corrosion in an otherwise passive rebar. For comparison purposes, or to show the corrosion behaviour vs time during immersion experiments (see e.g. Fig. 15), it seems preferable to use the $R_p$ values. This also avoids uncertainties in the choice of the constant $B$ in the Stern-Geary equation when calculating the geometrical corrosion rate. Even in this case care has to be taken in the interpretation of $R_p$ data: since because of the unknown anode area (pit, localised corrosion), an increase of the experimentally measured $R_p$ value ($\Omega$) is not automatically related to a decrease in the local corrosion rate, for example, the same result can be obtained from a reduction in the effective anode area as observed in the case of passivating inhibitors, e.g. nitrites [44,45].

A true local corrosion rate (penetration rate) can be calculated from $R_p$ measurements only in the very rare cases where the anode area (localised corrosion) has been determined experimentally, e.g. by visual inspection at the end of the test [140,147]. A very instructive example has been published recently [140]: $R_p$ values were determined from impedance measurements and the corrosion rate calculated for the entire exposed steel surface (62.7 cm$^2$), resulting in values of 5–10 $\mu$m/year. A subsequent visual inspection however revealed that the corrosion was usually confined to an area slightly greater than 1 cm$^2$ and never exceeded 4 cm$^2$. Therefore, the actual local corrosion rates were 15 to 100 times higher, lying in the range 0.1–1 mm/year [140] in agreement with results from structures [126].

From polarisation resistance data obtained by LPR or galvanostatic pulse measurements no mechanistic information on the action of the inhibitor can be obtained. AC impedance spectroscopy (EIS) is more advantageous, as it allows film formation due to inhibitor adsorption [93–95] to be identified, i.e. when an additional time constant is revealed at high frequencies (e.g. Fig. 16).

### 5.4. Macrocell Tests

The macrocell type of test is used frequently to test the inhibitive or corrosive properties of admixtures to be used in concrete. This test is standardised by the American Society for Testing and Materials as ASTM G109-02 “Standard Test Method for Determining the Effects of Chemical Admixtures on the Corrosion of Embedded Steel Reinforcement in Concrete Exposed to Chloride Environments”. Briefly summarised, in a concrete beam of ca. $28 \times 15 \times 11$ cm three rebars are embedded, one on the top part of the beam and two at the bottom part. The cover depth of the top bar can be 19 or 25 mm. Cycles of two weeks ponding of 3% NaCl solution on the top of the beam followed by a two weeks dry period are applied on the beams. The voltage over a 100 $\Omega$ resistor connected between the top bar (anode) and the two bottom bars (cathodes) and the open circuit potential of the bars is measured putting the reference electrode in the ponding solution. The macrocell current flowing is obtained from the measured voltage over the 100 $\Omega$ resistor (measured at least once at the beginning of the second week of ponding). The test ends when the average macrocell current of the control specimens exceeds 10 $\mu$A (the 95% limit of test
duration is ca. 6 months). The total integrated currents of control and test specimens are calculated and the bars are examined visually.

This test originally was designed for concrete with 350 kg m\(^{-3}\) cement and a w/c ratio of 0.5. It frequently has been modified in order to test different cover depth or concrete qualities.

The test measures the macrocell current flowing between the top bar (anode) and the two bars at the bottom (cathode). The macrocell current does not include the self corrosion of the anode, thus the measured macrocell currents will underestimate the corrosion rate of the top bar.

5.5. Test Variables

Apart from the ASTM G 109 macrocell test there exist no particular standards for testing the efficiency of inhibitors for steel in concrete, so different research groups apply different testing procedures. The main parameters that influence the test results (apart from planned variations in inhibitor concentration and concrete cover and quality) are:

- surface preparation of the rebars and electrical connection;
- time and environment of the passivation period of the rebars; and
- method of penetration of the aggressive chloride ions.

5.5.1. Surface Preparation of the Rebars — Electrical Connection

The surface preparation of rebar samples when testing inhibitors in alkaline solutions or mortar is not standardised, different methods, such as mechanical polishing, grinding, sand blasting, pickling in acids are used or the rebars are embedded 'as-received' with or without degreasing. From localised corrosion of stainless steels or Fe/Cr alloys it is however well known that a good surface finish of the steel surfaces will reduce the risk of pitting corrosion [152]. Reinforcing steel in synthetic pore solutions have shown much lower pitting potentials after a coarse grinding (SiC 180) compared to fine grinding (SiC 4000), probably due to a reduction in asperities and surface inhomogeneities [153,154].

Additional problems are presented by the mounting and the electrical connection of the steel rebars in mortar or concrete, and particularly the elimination of crevice corrosion. Crevice corrosion occurs at much lower chloride contents than localised corrosion on an open surface and thus can adversely affect inhibitor testing. Several preparation techniques have been tested, but all except one showed crevice corrosion under the sealants and coatings applied for limiting the exposed steel surface and for electrical isolation [155]. Good results without occurrence of crevice corrosion and sound electrical connection have been obtained with a sample mounting technique that completely avoids any sealants and coatings (Fig. 23) [94,95,139,147].
5.5.2. Pre-passivation

The passive film on steel in alkaline media (solution, mortar or concrete) has to form on the steel surface. This implies a complex dissolution/formation process involving especially the oxide layer present on the steel surface before immersion into the alkaline media or embedding in concrete. There is a general agreement that longer pre-passivation times improve the passive film stability as shown e.g. by the increase of pitting potential with prolonged passivation (Fig. 24) [156]. The longer the time of the passive state until depassivation, the more resistant the steel will become towards chloride-induced corrosion — thus the time that chlorides need to penetrate to the steel (governed by cover depth, porosity, ponding regime, etc.) may indirectly influence the results of inhibitor tests in mortar or concrete.

5.5.3. Method of Ponding

The method to ensure penetration of the aggressive chloride ions is not standardised. Ponding, cyclic ponding and drying, cyclic immersion in chloride-containing solutions and drying and acceleration of chloride ingress by applying a d.c. voltage (electromigration, etc.) are used. A comparative test on the method of chloride penetration is reported by Andrade et al. [157]. The authors used small scale laboratory samples (mortar w/c 0.5, c/s 1/3) with two rebars and a graphite bar as counter electrode embedded [141]. The chloride penetration was performed using two methods:

(a) ponding of 0.5M NaCl solution on the surface followed by wetting (100% R.H.) and drying (50% R.H.) cycles, and

(b) solid NaCl salt put on the mortar surface and water applied periodically by spraying, the samples remained at 50% R.H. Afterwards the samples were stored at 100 % R.H.
Test Methods to Evaluate Corrosion Inhibitors for Steel in Concrete

Fig. 24 Influence of the pre-passivation time (ageing of the passive film) on mild steel in synthetic pore solution on the anodic polarisation curves and on the pitting potential \(E_p\) (synthetic pore solution pH 13.5, chloride concentration 1 mol L\(^{-1}\)) [156].

Preliminary results showed that the geometrical corrosion rates (obtained from \(R_p\) measurements) after the depassivation were different: samples with inhibitor depassivated with the ponding method (a) tended to repassivate whereas those depassivated with method (b) showed high corrosion rates despite practically identical chloride contents in the mortar.

5.6. Polarisation Curves

As mentioned above, open circuit potential or \(R_p\) measurements do not allow mechanistic information on the inhibitor action to be deduced. Polarisation curves can, in principle, give this information, but for commercial inhibitor blends with unknown composition it might be difficult in any case to deduce information on the inhibition mechanism. Because of the wide potential scan applied in obtaining polarisation curves — especially in the anodic direction — the sample can be greatly altered (e.g. by passivation or pitting corrosion can be induced), and thus the method cannot be considered as non-perturbating.
5.6.1. Pitting Potential

Polarisation curves are frequently used to determine changes of pitting potential values for different concentrations of chloride ions and inhibitor. The main experimental variables — apart from the surface preparation and pre-passivation time of the sample (Fig. 24) — are the starting potential and the sweep rate of the potential scan. In general, the pitting potential that is determined increases with increasing scan rate, and to achieve pseudo-stationary values a scan rate of < 1 mV s⁻¹ should be chosen. The pitting potential of steel in chloride-containing alkaline solution has been determined for calcium nitrites, MFP [70,72], and organic inhibitors [81,84,96].

A better distinction between different solutions than is given by the potential $E_n$ at which the first pitting occurs (identified by a sharp increase in current density) is provided by a reverse scan polarisation curve which allows a potential $E_p$ to be determined above which pitting is possible. This potential is identified by the potential at which the reverse current becomes equal to the passive current density; this potential $E_p$ is independent of scan rate.

5.6.2. Influence on Cathodic Oxygen Reduction Reaction

Cathodic polarisation curves can be used to assess the possible influence of inhibitors on the rate of oxygen reduction in alcoholic solutions or mortar [156]. A lower cathodic current density could reduce the macrocell activity of steel in concrete and thus the corrosion rate. Only a few studies on the effect of inhibitors on cathodic polarisation curves have been reported in the literature [66,91]: organic inhibitor blends (MCI) did not influence the limiting current for oxygen reduction although a decrease in the cathodic reduction current in the charge transfer region was reported [91]. It is interesting to note that the volatile component alone (DMEA) did not show any decrease in the cathodic reduction current [91].
6

Ongoing Research Work

In this chapter the ongoing research projects — as far as known to the author — are briefly described (see Appendix for titles of projects). The information is derived from the European COST 521 research network ("Corrosion of Steel in Reinforced Concrete Structures") and personal contacts. The results presented are preliminary and will be published more fully later by the respective authors.

6.1. Migrating Corrosion Inhibitors

In several countries research programs are ongoing that are investigating migrating corrosion inhibitors based on amines and alkanolamines. The transport of corrosion inhibitors in cement paste and concrete is being studied by Tritthart [Project A1]. The chemical equilibrium between the Ferrogard 903 inhibitor blend and the cement paste is studied by expression of pore water after admixture and curing. It is planned to study the adsorption behaviour of this type of inhibitor with surface analytical methods as XPS and ToF-SIMS [A2], both on steel in alkaline solutions as well as on cement pastes.

The effectiveness of new organic inhibitors both in admixtures and applied by surface impregnation is being studied on mortar samples of OPC and slag cement [A3]. Setting time, strength and workability have already been investigated. Corrosion had been initiated by adding chlorides to the mixing water and, in this case, whatever the inhibitor type, dosage and the chloride concentration, the steels from inhibitor-containing concrete were more corroded than the reference steels (without inhibitor). Surface applied inhibitors will be studied on concrete beams in which corrosion has been initiated by chloride ponding.

Two penetrating organic inhibitors have been applied to large chloride contaminated parts of bridge decks that had experienced corrosion damage. Various concrete compositions and stages of reinforcement corrosion resulting in chloride penetration or carbonation were studied [A4]. Measurements of steel potential and corrosion rate have not shown any effect of the inhibitors up to four months after application. The scatter due to seasonal and other incidental factors was larger than any differences between treated and control samples. Measurements will continue in order to get results on any possible reduction in corrosion rate at longer times after treatment.

The performance of commercial organic inhibitors based on alkanolamines used as admixtures to concrete has been studied in alkaline solutions with different chloride additions by open circuit potential, linear polarisation resistance and impedance measurements [A5]. Tests in mortar with admixed chlorides will be performed with different inhibitor dosages, the evaluation using the same techniques as in solution. Finally, tests on concrete prisms are planned according to the ASTM G109 macrocell test.
The time to depassivation and long term behaviour of inhibitors in concrete is being studied in alkaline solutions by electrochemical noise, a.c. impedance and open circuit potential measurements [A6]. The tests in synthetic pore water have shown some reduction in corrosion rate. On the other hand, reliable assessment of the effectiveness of the inhibitors in the concrete was difficult; the corrosion rate could be measured by electrochemical methods but the differences in instantaneous corrosion activity between the different stages of wetting and drying was found to be much higher than any possible influence of the inhibitors studied. The investigations on concrete specimens will be continued with corrosion being also monitored by galvanic current and an electrical resistance probe. Corrosion monitoring of two bridges which were rehabilitated by patch repair and the application of inhibitors will be continued.

The UK Transport Research Laboratory has set up laboratory tests on a range of inhibitors available in the UK. They are also conducting field tests on bridge bents on the Midland Links Motorway near Birmingham for the Highways Agency [A13].

The UK Building and Research Establishment (BRE) has started a fundamental and applied study on corrosion inhibitors for steel in concrete, using localised impedance spectrocopy in solutions [A14].

A research work involving different mixed-in and surface applied inhibitors for steel in concrete has been conducted in the last two years at the Politecnico di Milano, and the results are currently being prepared for publication [A15].

Field studies on the effectiveness of the MCI corrosion inhibitor have been performed in a collaboration between Cortec Corporation (USA) and the University of Zagreb [A16].

6.2. Surface-applied MFP

The effectiveness of monofluorophosphate as surface applied corrosion inhibitor is being studied [A7] on large test slabs naturally aged for years; the steel corrosion rate will be measured before and after impregnation with inhibitor. In this project, analytical methods to determine the inhibitor concentration in concrete will be developed and minimum concentration of MFP at the rebar level defined. The short and medium term efficiency of MFP on corrosion is being evaluated on a carbonated structure [A8] as a function of concrete quality and changes in humidity.

6.3. Testing

So far, apart from the ASTM G109 macrocell test, an accepted and standardised test does not exist. Since 1988 possible test procedures have been discussed in CEN TC 104/SC3/WG3, and drafts on a potentiostatic test, galvanostatic test and polarisation resistance test have been produced, mainly with the objective of testing the harmlessness of admixtures to concrete. In a joint project [A9] several types of test procedures to ascertain the effectiveness of corrosion inhibitors in the laboratory in a short time are planned to be evaluated in a cooperative test programme.

A project within the COST 521 action deals with accelerated tests of inhibitor action.
on quite large specimens, representing real parts of a bridge deck [A10]. An activated titanium net is embedded at the bottom of the slabs, the upper surface being equipped with a tank containing chloride solution and another titanium net. A current density of 9 $\mu$A cm$^{-2}$ is applied between the nets so that the chloride ingress can be strongly accelerated (i.e., by a factor of 4). The type of corrosion monitoring has to be established.

Macrocell corrosion testing of the effect of inhibitors admixed to concrete will be performed with chlorides penetrating concrete placed in a salt spray chamber [A11]. At the end of the test the integrated macrocell currents will be compared to mass loss.

The Japanese standard test method JIS A 6205-1993 “Corrosion inhibitor for reinforcing steel in concrete” is being applied to the testing of different commercial inhibitors [A12]. The test procedure comprises two parts: (1) a salt water immersion test, and (2) an accelerating corrosion test in an autoclave ($180^\circ$C, 1 MPa for at least 5 h).

After the test the samples are split and the corroding area is measured, the inhibition efficiency is calculated based on the relative difference in corroded areas. Most of the inhibitors tested have shown a reduction in the corroded area by a factor of 4 to 8.
Concluding Remarks

Inhibitor technology could in principle offer a cost effective way in the rehabilitation of reinforced concrete structures, and would also avoid pollution and inconvenience to owners and users of structures needing repair. Several inhibitors have been tested in the laboratory and are commercially available today both as admixtures for fresh mortar or concrete or as surface-applied liquids. This review has presented a critical state of the art report summarising the documented results from independent laboratory studies and field tests.

The main difficulty and drawback in the numerous research papers and ongoing projects is that — apart from the ASTM G109 macrocell test — no standardised test procedures and no generally accepted definition for the effectiveness of inhibitors for steel in concrete exists. Thus, every research group is working with its own sample preparation, chloride penetration method and (electrochemical) testing method although it is well known that the surface preparation of the rebars, the time of pre-passivation in alkaline media or concrete (curing) and the way chlorides arrive at the steel greatly affect the test results — and make a direct comparison of test results of different laboratories practically impossible.

A test procedure should simulate as closely as possible real conditions of steel corrosion in concrete, and this means the following:

- only open-circuit conditions and measurement techniques (potential, polarisation resistance, impedance, electrochemical noise,...) should be used because polarisation may change the adsorption behaviour of the inhibitor;

- in testing admixed inhibitors, chlorides should not be admixed to the concrete but should penetrate from the concrete surface (e.g. by cyclic ponding);

- in testing surface-applied inhibitors, corrosion of the steel should be initiated by cyclic ponding with chloride solutions or by carbonation. Afterwards the inhibitor treatment should be conducted according to the specifications. Cyclic ponding with chlorides or carbonation may or may not continue; and

- a verification on a field test with inhibitors that showed positive results in the laboratory should conclude the tests.

This review has shown the great difference in knowledge and experience between admixed inhibitors (mainly calcium nitrites) and the more recent surface-applied inorganic or organic inhibitor blends. Calcium nitrite as an admixture — in combination with good quality concrete and cover — has a long and proven track record whereas the use of corrosion inhibitors in concrete repair systems is far less well established and several important questions are still not adequately resolved. If
corrosion inhibitors are to be used effectively as repair strategy in the future, it is important:

- to specify the concentrations that are needed at the reinforcement level instead of the required dosage at the concrete surface;

- to propose and develop suitable means for demonstrating that such conditions are actually achieved and maintained for long times taking into account diffusion, leaching, etc.; and

- to demonstrate on-site that inhibitors prevent or at least delay the onset of corrosion or reduce the corrosion rate.

Engineers and specifiers who work in the area of concrete maintenance and repair need to be aware of the critical questions raised in this review when assessing the claims and counterclaims made in trade literature on behalf of proprietary inhibitors. A proper independent assessment of the effectiveness of proprietary corrosion inhibitors, whose detailed compositions are matters of commercial secrecy and can change, and whose recommended uses depend on the performance of other components of repair and protection systems, is difficult to carry out. Laboratory studies indicate that the newly marketed organic inhibitor blends may prolong the time to corrosion initiation when admixed to the concrete whereas laboratory and field tests indicate so far that the same products are not effective in combating ongoing chloride-induced corrosion.
References

2. K. Tuutti, Corrosion of Steel in Concrete, CBI forskning 4/82, Cement och Betonginstituet, Stockholm.
15. D. F. Griffin, Corrosion inhibitors for reinforced concrete, in Corrosion of Metals in Concrete, ACI SP-49. American Concrete Institute, 1975, p. 95.
20. D. Briesemann, “Corrosion Inhibitors for Steel in Concrete”, Civil Engineering Departement, Munich Technical University, Munich (D), 1971.
References

54. Approval of DCI in Germany, private communication by B. Isecke, BAM Berlin.

www.iran-mavad.com
مرجع علمي مهندسي مواد
69. US Patent No. 5314755, Methods to reduce scaling due to freezing and thawing in concrete; US Patent No. 5071579 and No. 5127954, Corrosion inhibiting systems, products containing residual amounts of such systems and methods therefor.
88. B. A. Miksik, Use of vapor phase corrosion inhibitors for corrosion protection of metal products, in *Reviews on Corrosion Inhibitor Science and Technology* (A. Raman and P. Labine, eds), NACE, Houston, Tx, 1993, pp.11-16.
89. Cortec Company, Product information sheet.
References


110. A. Eydelnant, A. Ostrowski and A. Demidov, Analysis of diffusion rate of migrating corrosion inhibitor MCI2000 in concrete using radioactive isotope tagging techniques; see ref. [80].


<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAR</td>
<td>Alkali-aggregate reaction</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>CE</td>
<td>Counter electrode</td>
</tr>
<tr>
<td>CEN</td>
<td>European Committee for Standardisation</td>
</tr>
<tr>
<td>CHAB</td>
<td>Cyclohexylamine benzoate</td>
</tr>
<tr>
<td>CHC</td>
<td>Cyclohexylamine carbamate</td>
</tr>
<tr>
<td>CMA</td>
<td>Calcium magnesium acetate</td>
</tr>
<tr>
<td>COST</td>
<td>Cooperation européenne dans la domaine de la recherche scientifique et technique</td>
</tr>
<tr>
<td>c/s</td>
<td>cement/sand</td>
</tr>
<tr>
<td>DCHN</td>
<td>Dicyclohexylamine nitrite</td>
</tr>
<tr>
<td>DMEA</td>
<td>2-dimethyl ethanolamine</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy — ATR attenuated total reflection</td>
</tr>
<tr>
<td>FWHA</td>
<td>Federal Highways Administration</td>
</tr>
<tr>
<td>LMC</td>
<td>Latex modified concrete</td>
</tr>
<tr>
<td>LPR</td>
<td>Linear polarisation resistance</td>
</tr>
<tr>
<td>MFP</td>
<td>(sodium) monofluorophosphate</td>
</tr>
<tr>
<td>OCI</td>
<td>Organic corrosion inhibitor</td>
</tr>
<tr>
<td>OCP</td>
<td>Open circuit potential</td>
</tr>
<tr>
<td>OPC</td>
<td>Ordinary Portland cement</td>
</tr>
<tr>
<td>R.H.</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>SC</td>
<td>Sub-committee</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SHRP</td>
<td>Strategic Highways Research Program</td>
</tr>
<tr>
<td>TC</td>
<td>Technical committee</td>
</tr>
<tr>
<td>ToF-SIMS</td>
<td>Time of Flight-Specific Ion Mass Spectroscopy</td>
</tr>
</tbody>
</table>
VCI  Volatile corrosion inhibitor
VPI  Vapour phase (corrosion) inhibitor

W/C  water/cement
WG  Working Group

XPS  X-ray photoelectron spectroscopy
Appendix
List of Ongoing Research Projects

Research projects within the European Research Network COST 521 “Corrosion of Reinforcement in Concrete Structures”

A8. E. Brühwiler, Verification of in situ corrosion inhibition of MFP by means of corrosion rate measurements.
A10. R. Cigna, Accelerated testing to ascertain the effectiveness of corrosion inhibitors.

Other Research Projects

A13. according to Broomfield [132].
A14. personal communication of Dr J. R. Morlidge, BRE.

A15. personal communication, P. Pedeferri, Politecnico di Milano.

A16. personal communication of D. Bjegovic, University of Zagreb, Croatia.