SINTEF Building and Infrastructure   Roar Myrdal

Corrosion Inhibitors
– State of the art

COIN Project report 22 - 2010

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– State of the art

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Preface

This study has been carried out within COIN - Concrete Innovation Centre - one of presently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfil this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our over-all ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 - 20 PhD-students, 5 - 10 MSc-students and a number of international guest researchers, work on presently eight projects in three focus areas:

•   Environmentally friendly concrete
•   Economically competitive construction
•   Aesthetic and technical performance

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approx. 40 %), industrial partners (approx 45 %) and by SINTEF Building and Infrastructure and NTNU (in all approx 15 %).

For more information, see www.coinweb.no

Tor Arne Hammer
Centre Manager

Summary

This state-of-the-art report reviews the history, chemistry/electrochemistry, mode of action and commercial availability of corrosion inhibitors for concrete. Corrosion mitigating substances like hydrophobic materials and pore blockers to inhibit intrusion of chloride salt, are not considered corrosion inhibitors in this review, and consequently, not treated.

A corrosion inhibitor can affect steel reinforcement in concrete in two ways: (1) By delaying the time of depassivation by strengthening the passive film, or (2) by reducing the corrosion rate after depassivation. An inhibitor fit into one of three broad electrochemical classes: (a) anodic, (b) cathodic and (c) mixed, depending on whether it affects the anodic reaction, the cathodic reaction, or both.

Inhibitors for concrete are either mixed into fresh concrete (mixed-in inhibitors) or applied onto the surface of hardened concrete (migrating inhibitors, MCIs) to penetrate the concrete cover.

Sodium nitrite, an anodic inhibitor, was the first inhibitor to be used in concrete (more than 50 years ago). Since then, a lot of chemical substances have been tested, of which nitrates, phosphates, amines, alkanolamines and carboxylic acids are the most investigated. Today, blends of nitrite/nitrate salts (preferably calcium) are among the most common commercial mixed-in inhibitors outside Europe.

Roughly two decades ago, amines and alkanolamines became the most common mixed-in inhibitors on the European market. These are mixed inhibitors suppressing both the anodic and cathodic reactions. In recent years, the research on the inhibiting effect of carboxylic salts and their salts in alkaline media has been intensified. Like amino groups, carboxylate groups have the potential of adsorbing to metal surfaces, thereby forming an organic layer on the entire surface, i.e. acting as a mixed inhibitor. Today, carboxylic compounds are found in commercial mixed-in inhibitors for concrete, typically as ingredients in amine-based products.

Most mixed-in inhibitors show secondary effects on the properties of fresh and hardened concrete. Nitrites/nitrates accelerate setting of fresh concrete, whereas many carboxylic acids tend to retard the cement hydration rate.

Nearly all MCIs on the market are blends of amines/alkanolamines and carboxylic acids, i.e. aminocarboxylates. Reports on MCIs deal mostly with the penetration (or lack of penetration) of the inhibitor in the hardened concrete cover. There is a debate going on whether these products really act as anticipated.

It is recommended to continue the research on carboxylic compounds, as sole admixtures, and blended with other compounds with inhibiting properties, e.g. nitrates and alkanolamines, already known for their inhibiting properties. At the same time, it is important to investigate any secondary, often undesirable, effect of an inhibitor on concrete properties in the fresh and hardened state. One should aim at counteracting undesirable secondary effects of promising inhibitors (e.g. a retarding effect) by smart blending of substances. This may also open for the development of multifunctional admixtures.

"I sometimes think that the construction industry is like the person who seeks the wonder cure: the elixir that will provide eternal life with no effort at all on their part. Wouldn't it be wonderful if by the simple expedient of adding ingredient X all would be solved? There would be no need to worry about cover, compaction, curing or even the concrete itself. Life is not that simple..."   C.D. Pomeroy

(A.M. Vaysburd and P.H. Emmons, Cement & Concrete Composites, 26, 2004, pp 255-263)

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1   Introduction

1.1   Principle objectives and scope

The objective of this state-of-the-art report is to give an overview of chemicals reported to have an inhibiting effect on corrosion of steel in concrete. Although sometimes referred to as 'inhibitors', concrete additives like hydrophobic materials and pore blockers to inhibit intrusion of chloride salts, are not considered corrosion inhibitors in this review. Only inhibitors capable of obstructing or slowing down the electrochemical corrosion process at the steel/concrete interface will be treated.

The mode of action of corrosion inhibitors will be discussed. Their (secondary) effect on the properties of fresh and hardened concrete will be treated only briefly. An overview of commercial inhibitors for concrete is also presented.

1.2   The electrochemistry of corrosion

The mode of action of inhibitors is closely related to either the anodic or the cathodic half-cell reaction of the corrosion process, or both. These reactions are (simplified):

Anodic reaction – oxidation of iron

At anodic sites on the steel surface metallic iron is dissolved, i.e. oxidation of metallic iron (Fe, oxidation state 0) to form ferrous ions (Fe^{2+}, oxidation state +2), leaving behind electrons in the steel:

$$Fe = Fe^{2+} + 2\,e^- \qquad\qquad (1)$$

Cathodic reaction – reduction of oxygen

Liberated electrons from the dissolved iron are consumed by oxygen in the presence of water to form hydroxyl ions (OH^-). In this reaction oxygen is electrochemically reduced from O_2 (oxidation state 0) to OH^- (oxidation state −2):

$$\tfrac{1}{2}\,O_2 + H_2O + 2e^- = 2\,OH^- \qquad\qquad (2)$$

The algebraic sum of these two half-cell reactions makes the total reaction, called the corrosion cell reaction:

$$Fe + \tfrac{1}{2}\,O_2 + H_2O = Fe^{2+} + 2\,OH^- = Fe(OH)_2 \qquad\qquad (3)$$
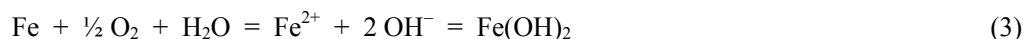
Ferrous hydroxide, $Fe(OH)_2$, a sparingly soluble compound (solubility product $\sim 10^{-16}$), may undergo further oxidation reactions to form different forms of hydroxides and oxides, depending on pH and the availability of oxygen and water, like insoluble ferric hydroxide, $Fe(OH)_3$, or gamma ferric oxide, γ-Fe_2O_3 (solubility product $\sim 10^{-36}$). The ferric species precipitate to form a thin (~a few nanometers thick) and dense layer on the steel surface in the highly alkaline pore solution of the concrete. This surface oxide layer, being a physical barrier separating the metal from the adjacent electrolyte (pore solution), is often called the oxide film, or the passive film [1,2]. The steel is passivated by the high pH in the pore water of sound concrete.

As long as the passive film remains intact, the corrosion current density is very low, probably in the range of 0.01 µA/cm^2. Using Faraday's law, this corresponds to a corrosion rate, or loss of steel bar section, of approximately 0.1 µm/year. Hence, the corrosion rate is depressed to an insignificant low level by the passive film. This low corrosion rate maintains the protective passive film due to a very slight dissolution of the iron oxides that form the passive film.

The passive state persists as long as the concrete pore solution in contact with the reinforcement is sufficiently alkaline and free from 'aggressive' ions like chlorides. The protective passive film is destroyed, a phenomenon called depassivation, if (1) the pore solution in contact with the steel drops to a pH level of about 8-9 (normally as a result of carbonation), and/or (2) the pore solution in contact with the steel contains dissolved chloride ions above a threshold value. After depassivation, the corrosion rate often increases by several orders of magnitude, either locally, typically chloride-induced pitting corrosion, or more evenly across the entire steel surface, typically as a result of carbonation of the concrete. In such cases the structure may suffer from active corrosion, in contrast to the "passive" corrosion maintaining the passive film. A corrosion inhibitor can affect this situation in two ways:

- Delay the time of depassivation by strengthening the passive film

- Reduce the corrosion rate after depassivation

1.3   Definition and classification of corrosion inhibitors

To inhibit, from Latin *inhibere*, literally means to hold back or restrain [3]. Opposite to a catalyst, i.e. a substance which accelerates a reaction, an inhibitor decelerates or slows down a reaction. Chloride is actually a catalyst for the corrosion reaction of steel in concrete, while inhibitors are capable of slowing down the same reaction by affecting the chemistry on the steel surface. Inhibitors are normally consumed in the process, particularly anodic inhibitors capable of passivating the steel surface, while catalysts are not consumed.

According to NACE International a corrosion inhibitor is "*a chemical substance that, when added in small concentration to an environment, effectively decreases the corrosion rate*" [4].

Another definition can be found in ISO 8044 [5]: "*A chemical substance that decreases the corrosion rate when present in the corrosion system at suitable concentration, without significantly changing the concentration of any other corrosion agent*". This definition excludes 'inhibitors' capable of reducing the chloride concentration.

Corrosion inhibitors for concrete have been grouped in numerous ways [6,7,8,9,10], according to:
- Type of chemical (distinction between inorganic and organic substances)

- Electrochemical mode of action (anodic or cathodic, or both)

- Capability to passivate the steel

- Film-forming property

- The way the inhibitor is applied; either mixed in fresh concrete ('mixed-in inhibitors'), or applied at the surface of hardened concrete ('migrating inhibitors')

This type of grouping is somewhat confusing, and does not form a sound basis for evaluating and comparing different types of inhibitors. For instance, most anodic inhibitors are also passivators, i.e. belonging to two 'groups'.

Based on the electrochemical mechanism of action alone, all inhibitors fit into one of three broad classes: (a) anodic, (b) cathodic and (c) mixed, depending on whether they affect the anodic reaction, the cathodic reaction, or both [11]. However, if one of the reactions (anodic or cathodic) is slowed down, the other is forced to act likewise (due to the fact that the production and consumption rates of electrons in the corrosion process must be equal; electrons cannot exist freely). In his review on the chemistry of corrosion inhibitors, Gaidis [12] did not group mixed inhibitors into a separate class, but included those in the cathodic class, probably due to the tendency of many mixed inhibitors to affect the cathodic reaction more strongly than the anodic reaction. In this state-of-the-art report distinctions are made between all three classes.

1.3.1 Anodic inhibitors

This class consists mainly of oxidizing agents, i.e. substances with the ability to accept electrons in chemical redox reactions (shorthand for reduction-oxidation reactions). An anodic inhibitor oxidizes ferrous ions to ferric ions, leading to the formation of a dense passive film on the surface of the steel, and a subsequent suppression of the anodic part of the corrosion reaction. The precipitated ferric product blocks the transport of ferrous ions into the electrolyte [7]. The effect on the cathodic reaction is negligible. The anodic inhibiting action will give a rise in the electrochemical potential of the anodic reaction. Consequently, the anodic and cathodic curves in the current-potential diagram will intersect at higher corrosion potential and lower corrosion current (see Figure 1).

Figure 1 A schematic current-potential diagram showing the effect of an **anodic inhibitor** on corrosion.
E_{corr} = corrosion potential (mV vs a reference electrode)
i_{corr} = corrosion rate (current density, e.g. $\mu A/cm^2$)
The presence of an anodic inhibitor causes a shift in the corrosion potential and the corrosion rate to E'_{corr} and i'_{corr} respectively. The corrosion rate is reduced, while the corrosion potential shifts towards higher (more positive) values.

Anodic inhibitors, mostly oxidizing anions, are effective only when present in sufficiently high concentrations. The concentration required is often determined by the level of chloride to which the steel will be exposed [11]. Today, the most commonly used anodic inhibitor for concrete is calcium nitrite, $Ca(NO_2)_2$ [7]. The 'relative' of this compound, calcium nitrate, $Ca(NO_3)_2$, shows similar inhibiting properties (see Chapter 2.1). Alkali salts of nitrite, benzoate and chromate have also been used [8].

1.3.2 Cathodic inhibitors

Cathodic inhibitors slow down the oxygen reduction reaction on the steel surface by precipitating salts with poor solubility in water. A surface barrier of precipitated salts reduces the oxygen transport to cathodic sites by covering the steel surface [8]. The effect on the anodic reaction is generally minor. Cathodic inhibitors are strong proton acceptors [11]. The reduction in oxygen supply to the corrosion process will lower both the corrosion potential and the corrosion rate (see Figure 2). Hence, a lowering of the corrosion potential, normally attributed to higher risk of corrosion, in this situation has an opposite meaning.

Cathodic inhibitors may include carbonates, phosphates, polyphosphates and silicates, and the dosage tends to be relatively high because the corrosion suppression effect is inferior to that of the anode type corrosion inhibitor [13,14]. Zinc oxide has also been reported to act as a cathodic inhibitor [15].
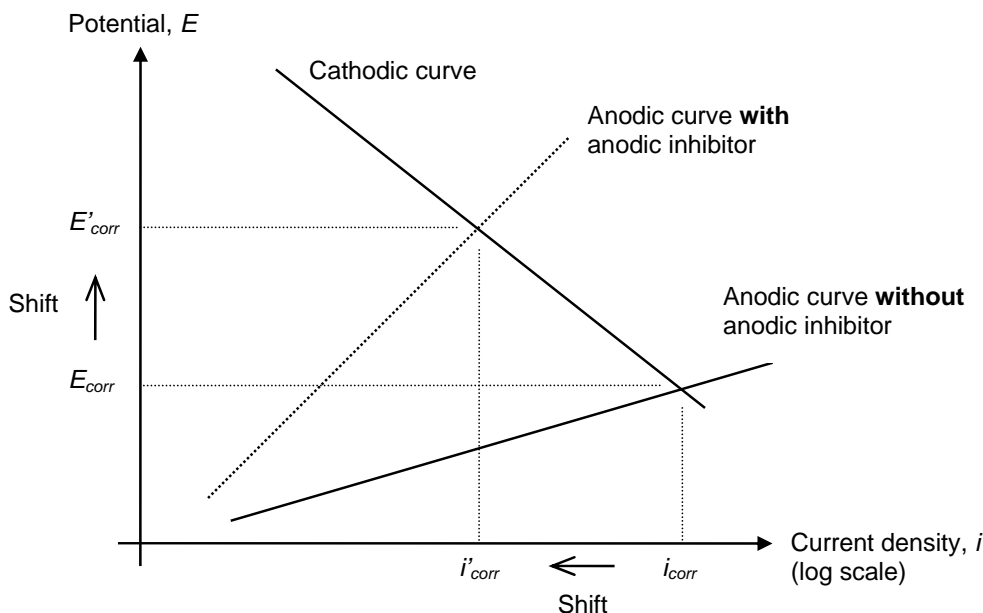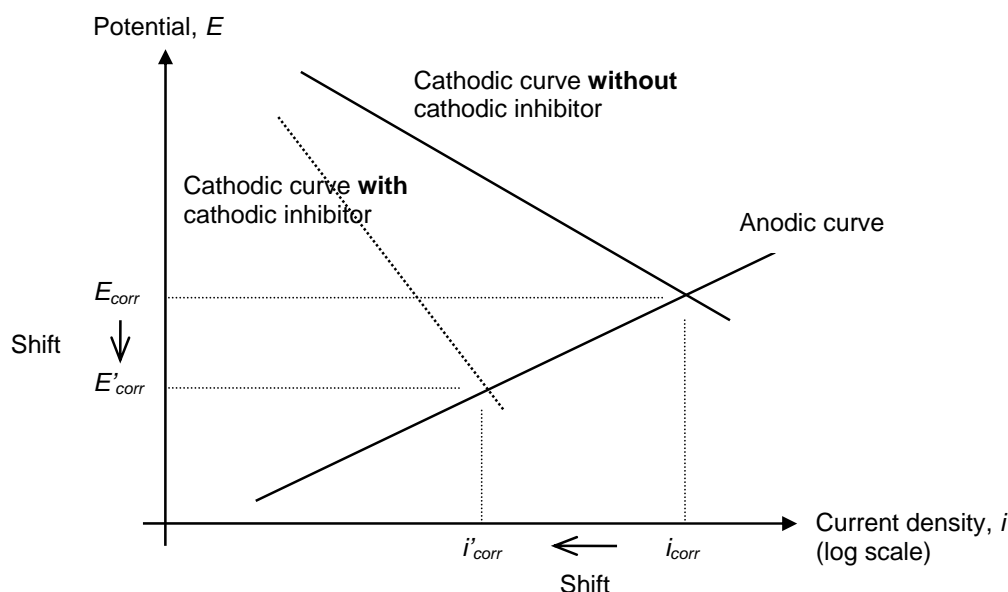

Figure 2 A schematic current-potential diagram showing the effect of a **cathodic inhibitor** on corrosion.
E_{corr} = corrosion potential (mV vs a reference electrode)
i_{corr} = corrosion rate (current density, e.g. $\mu A/cm^2$)
The presence of a cathodic inhibitor causes a shift in the corrosion potential and the corrosion rate to E'_{corr} and i'_{corr} respectively. The corrosion rate is reduced, while the corrosion potential shifts towards lower (more negative) values.

1.3.3 Mixed inhibitors

Mixed inhibitors (not to be mixed up with *mixed-in* inhibitors) suppress both the anodic and cathodic corrosion reactions, generally by adsorption on the entire surface of the steel, consequently forming a thin protecting layer [8]. Therefore, these inhibitors are often referred to as 'adsorption inhibitors' [16], or 'film-forming inhibitors' [7], and they are among the most commonly used inhibitors for concrete today. A mixed inhibitor slows down the corrosion rate without a significant change in the corrosion potential. The corrosion potential may shift somewhat to either the anodic or the cathodic side, depending on which half-cell reaction is most affected, but the total effect on the corrosion potential is generally negligible (see Figure 3).

Effective mixed inhibitors are found among organic substances with polar groups containing nitrogen (N), sulphur (S) and hydroxy (OH) [13]. Organic compounds such as amines and alkanolamines are commonly used [8,17], both as 'mix-in inhibitors' (Chapter 2) and 'migrating inhibitors' (Chapter 3).

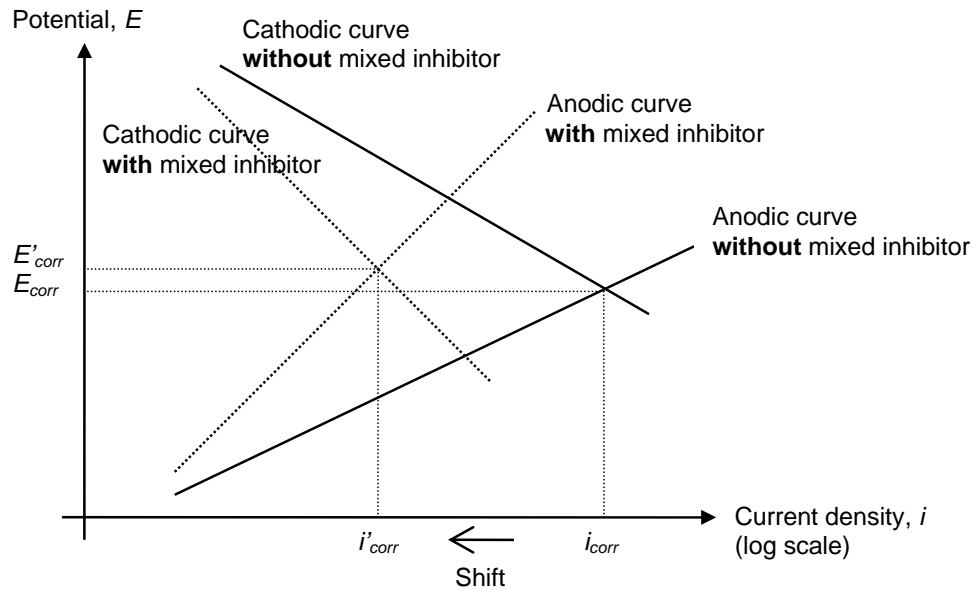**Figure 3** A schematic current-potential diagram showing the effect of a **mixed inhibitor** on corrosion.

E_{corr} = corrosion potential (mV vs a reference electrode)

i_{corr} = corrosion rate (current density, e.g. $\mu A/cm^2$)

The presence of a mixed inhibitor causes a reduction in the corrosion rate (to i'_{corr}), but a negligible shift in the corrosion potential (to E'_{corr}); in this case a slight increase.

2   Mixed-in corrosion inhibitors for concrete

2.1   Nitrites and nitrates

Nitrite (NO_2^-) differs chemically from nitrate (NO_3^-) in the oxidation state of nitrogen; oxidation state +3 and +5 for nitrite and nitrate respectively. Inorganic nitrites and nitrates are anodic inhibitors capable of passivating the steel surface even when chloride is present in the in concrete.
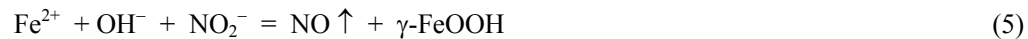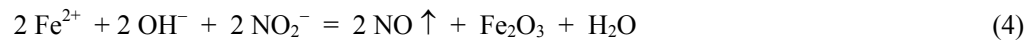
The corrosion inhibiting effect of nitrites has been known for decades. In the late 1950s sodium nitrite was investigated for use in concrete [7]. Due to loss in long-term compressive strength and risk of alkali-aggregate reactions, caused by alkali nitrites, calcium nitrite was introduced in the middle of the 1970s [18,19]. Calcium nitrites have a long and proven track record, especially in the USA, Japan and the Middle East [7,13,20]. It has been stated, however, that commercial calcium nitrite based admixtures, due to their accelerating effect on cement hydration, primarily are used to increase setting and hardening of concrete, rather than to inhibit corrosion [12].

Even before the commercialization of calcium nitrite for concrete in the 1970s (Grace Construction Products, USA), nitrite/nitrate blends had been studied by Russian workers, probably due to the fact that it is easier to produce blends than pure nitrite [12]. Later, Justnes [22] has shown that nitrate has inhibiting properties of its own.

Even though calcium nitrite has proven to be an efficient corrosion inhibitor, and is known as "*the best non-chloride admixture* [accelerator] *to date*" [9], nitrites suffer from one big commercial disadvantage compared to nitrates. Nitrites are toxic and environmentally unfriendly substances, and therefore, highly regulated in Europe [23]. This means that nitrites, at least for future applications, probably will be discouraged due to health and environmental requirements and regulations.

2.1.1   Inhibiting mode of action of nitrites and nitrates

It has been proposed that nitrite ions react with ferrous ions in alkaline environments according to the following redox reactions [12,21,24]:

$$2\,Fe^{2+} + 2\,OH^- + 2\,NO_2^- = 2\,NO\uparrow + Fe_2O_3 + H_2O \tag{4}$$

$$Fe^{2+} + OH^- + NO_2^- = NO\uparrow + \gamma\text{-}FeOOH \tag{5}$$

Ferrous ions (Fe^{2+}) are oxidized to ferric ions (Fe^{3+}), to form a passivating ferric oxide layer on the steel surface, while nitrite (oxidation state +3) is reduced to nitric oxide (oxidation state +2). The arrow ($\uparrow$) indicates that nitric oxide, being a (toxic) gas at ambient temperature and pressure, will evaporate.

The inhibiting property of nitrate may be linked to its ability to be easily reduced to nitrite by ferrous iron in alkaline solutions [22]:

$$2\,Fe(OH)_2 + NO_3^- + H_2O = 2\,Fe(OH)_3 + NO_2^- \tag{6}$$
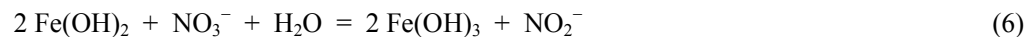
2.1.2   Significance of nitrite/chloride ratio

If chloride salts are present in the concrete pore solution, nitrite ions will compete with chloride ions for ferrous ions at the steel/concrete interface. Hence, the nitrite concentration required is determined by the level of chloride to which the steel will be exposed. In case of insufficient nitrite dosage and the problem of leaching out over the long service life of a structure, leading to a low NO_2^-/Cl^- ratio, increased local corrosion attack may occur [25]. Ramirez et al [26] determined the critical $[NO_2^-]/[Cl^-]$

molar ratio in a $Fe/Ca(OH)_2/Cl^-/NO_2^-$ system and found that the transition from an active state (corrosion) to a passive state started and ended at molar ratios of 0.1 and 1 respectively. Several investigations reported in the literature revealed a critical molar ratio (threshold value) of about 0.6 (with some variation from 0.5 to 1) in order to prevent the onset of corrosion in concrete [25].

It has been reported that too low NO_2^-/Cl^- ratios may cause risk of <u>increased</u> corrosion rate in cracked reinforcing beams (compared to concrete without nitrite) [7]. This can be explained by the increase in potential difference between the passive rebars in the nitrite-containing crack-free concrete and the steel in the cracked area with little or no nitrite, due to the positive shift in potential in the passive region (see Figure 1). In general, if anodic inhibitors protect large parts of a steel surface (cathodic areas), while some parts are unprotected (anodic areas), the driving force of corrosion – the potential difference between the two parts – may increase, leading to the risk of intensified pitting corrosion in the unprotected parts.

2.1.3   Effects of calcium nitrites and nitrates on concrete properties

Mixed-in inhibitors usually do more than just inhibit corrosion. They may influence initial set, strength development and other properties [12]. Calcium salts of nitrites and nitrates are well known accelerating admixtures for concrete [12, 26]. Calcium nitrite has probably been the most popular non-chloride setting accelerator in the USA since late 1960s [27]. Nitrites may even increase the hardening rate of concrete comparable to that obtained with calcium chloride – the classic hardening accelerator [28].

Calcium nitrate acts as an accelerator of setting in cement paste at low concentrations without affecting the strength development [29].

The accelerating effect of nitrites and nitrates may, in some situations, require the addition of a retarder in the concrete mixture to counter unwanted acceleration of the cement hydration.

Calcium nitrites and nitrates do not cause final compressive strength loss as the alkali salts do [7].

Other side effects of calcium nitrites on the fresh and hardened concrete properties are reported to be negligible [8].

2.1.4   Calcium nitrite and long-term inhibiting protection

It is generally agreed that the corrosion-inhibiting effect of calcium nitrite is degenerative in nature, as the unbound nitrite ions diminish in concentration as they stabilize the passivation of the steel reinforcement [30]. Another concern is the leaching of nitrites from concrete. However, it has been claimed that leaching will not be a problem for a low water to cement ratio mix design combined with sufficient concrete cover as specified by standards [7].

Reliable data on long-term in-situ inhibiting protection by calcium nitrite in concrete has not been found.

2.2   Amines and alkanolamines

The inhibiting properties of amines and alkanolamines (organic basic nitrogen compounds) have been described and patented for several decades, also for protection of steel in concrete [7]. Often their salts with organic or inorganic acids are used as inhibitors for concrete [8].

Amines and alkanolamines contain a basic nitrogen atom with an unshared electron pair (:N). They are derivatives of ammonia (NH_3) in which one or more of the hydrogen atoms (H) have been replaced by

a substituent such as alkyl (R) in the case of amines and hydroxyalkyl (R-OH) in the case of alkanolamines. Figure 4 shows examples of the molecular structures of two alkanolamines.
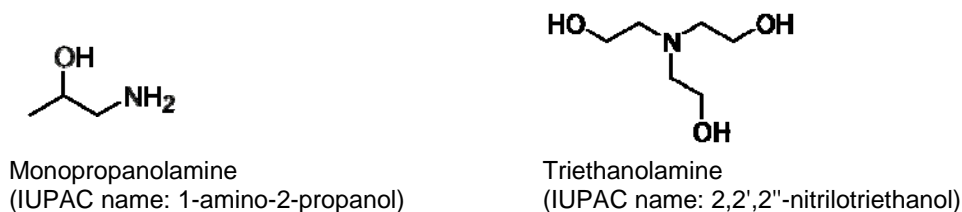
Monopropanolamine
(IUPAC name: 1-amino-2-propanol)

Triethanolamine
(IUPAC name: 2,2',2''-nitrilotriethanol)

Figure 4 Simplified molecular structures of two alkanolamines. Carbon (C) and carbon-hydrogen (C-H) bonds are not shown.

It seems that alkanolamine based inhibitors for concrete are more investigated than the 'alkanol-free' amines. In his review on inhibitors for use in concrete, Gaidis [12] only describes alkanol-type amines. In their recent state-of-the-art report on corrosion inhibitors for steel in concrete, Söylev and Richardson [8] describe both types, amines and alkanolamines, but put emphasis on alkanolamines. Also several commercial inhibitors for concrete contain alkanolamines (see Chapter 4).

2.2.1 Inhibiting mode of action of amines and alkanolamines

The inhibiting properties of amines and alkanolamines are linked to the capability of the amino groups to adsorb on metals and metals oxides by sharing their unshared electron pair of the nitrogen atom with the metal (oxide) substrate, thereby covering the surface (film-forming) [8,12,31], i.e. a mixed inhibitor suppressing both the anodic and the cathodic reactions. However, it has been claimed that alkanolamines probably acts more like cathodic inhibitors, blocking sites where oxygen picks up electrons, but may adsorb at anodic sites as well [12].

Amino groups are able to displace water molecules at the metal surface and form a hydrophobic film which protects against corrosion [32,33]. The mode of action can be explained in this way, exemplified by a tertiary amine [32]:

The nitrogen atom (:N) in the amino group (:NR_3) is an electron acceptor which can bond to a hydrogen atom (H) of a chemisorbed water molecule (H_2O) at the metal surface (M). The water molecule then desorbs and its site will be replaced by another chemisorbed amino group, illustrated by the following reactions:

$$M{:}OH_2 + {:}NR_3 \rightarrow M{:}OH_2{\cdots}NR_3 \rightarrow M + OH_2{\cdots}NR_3 \tag{7}$$

$$M + {:}NR_3 \rightarrow M{:}NR_3 \tag{8}$$
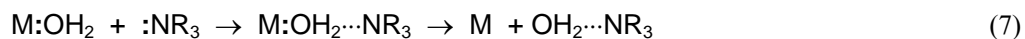
The adsorption behavior of the inhibitor and the accompanying water replacement are considered major factors for its protective properties, and experimental data fit best to the Langmuir–Freundlich adsorption isotherm [33]. Figure 5 shows a schematic illustration of an amine adsorbed at a steel surface.

Figure 5 An amine adsorbed at a steel surface [34].

2.2.2 Ranking of amine and alkanolamine inhibitor efficiency

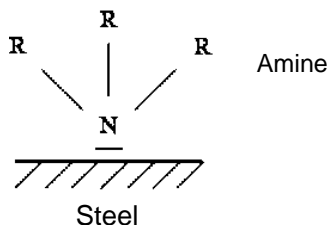One problem of ranking organic inhibitors like amines and alkanolamines is the fact that many scientific reports are based on tests carried out with commercial inhibitors. Such products are mostly made of blends of chemicals. The exact composition of commercial inhibitors is seldom disclosed by the producers. Therefore, a typical identification of a commercial inhibitor in scientific literature can be "*amino-alcohol based mixed corrosion inhibitor*" [9,31,35]. However, there have been attempts to disclose the ingredients found in such products (see Chapter 4).

More than twenty years ago a European patent application [36] compared several amines and alkanolamines having molecular weights ranging from 48 to about 500, and found that methyldiethanolamine, triethanolamine and monoethanolamine were the most efficient inhibitors among those tested. One type of amine that belongs to this group is N,N'-dimethylethanolamine (DMEA), which has been investigated due to the fact that it is used in commercial inhibitors for protection of steel in concrete [37]. Therefore, this alkanolamine can be considered an efficient one.

Monticelli et al [38] investigated more than thirty potential inhibitors of different types, of which three were of the amine/alkanolamine-type: Dicyclohexylamine, triethanolamine and 6-amino-1-hexanol. Their laboratory tests on steel corrosion behavior in saturated calcium hydroxide solution containing 0.1 M chloride ions and in chloride-polluted mortars showed that among the tested substances only sodium nitrite, 5-hexylbenzotriasole, β-glycerophosphate and dicyclohexylamonium nitrite were able to prevent pitting corrosion during the test period [38], i.e. dicyclohexylamonium nitrite seems to be a better inhibitor than dicyclohexylamine.

In their recent work, Ormellese et al [34] investigated different types of chemical substances; among them several amines and alkanolamines with various length and chemical nature of the functional groups (see Table 1). They concluded that these amines and alkanolamines had poor corrosion inhibition effect on steel in chloride containing alkaline solutions, with very scattered results when their volatility increased. They found carboxylates, especially polycarboxylates, to be more efficient substances against chloride-initiated pitting corrosion, making them the most promising candidates among the tested substances (see Chapter 2.3). Note that commercial alkanolamine-based inhibitors often contain carboxylic acids as well (see Chapter 4).

Based on the gravimetric weight loss method, Saraswathy and Song [21] found nitrite-based inhibitors to perform better than mono-, di- and triethanolamine with respect to their ability to protect steel rebars embedded in concrete exposed to 3 % NaCl solution.

Table 1
Various amines and alkanolamines tested by Ormellese et al [34].

Amines	
Methylamine	$CH_3–NH_2$
Dimethylamine	$(CH_3)_2–NH$
Ethylamine	$CH_3CH_2–NH_2$
Propylamine	$CH_3CH_2CH_2–NH_2$
Cyclohexylamine	$C_6H_{11}–NH_2$
Triethylentetramine (TETA)	$NH_2–CH_2CH_2–(NHCH_2CH_2)_2–NH_2$
Hexamethylentetramine (EMTA)	$C_6 H_{12} N_4$
Alkanolamines	
Monoethanolamine (MEA)	$(OH CH_2CH_2)–NH_2$
Triethanolamine (TEA)	$(OH CH_2CH_2)_3–N$
Dimethylethanolamine (DMEA)	$(CH_3)_2(OH CH_2CH_2)–N$
Methyldiethanolamine (MDEA)	$(CH_3)(OH CH_2CH_2)_2–N$

2.3   Carboxylic acids and their salts

Like amino groups, carboxylate groups have the potential of adsorbing to metal surfaces, thereby forming an organic layer on the surface. They cover a variety of organic carboxylate substances, i.e. substances characterized by the presence of one or more proton donating carboxylic groups (-COOH). The carboxylate anion (-COO⁻) is the functional group responsible for the adsorption on the steel surface. Carboxylate adsorption is influenced by the presence of electron-donor or electron-attractor groups, R, bound to the carboxylate ion [34], as illustrated in Figure 6.
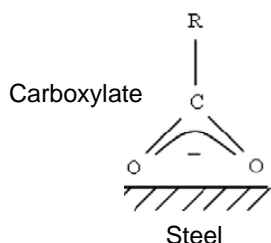
Figure 6 A carboxylate molecule with a functional group (R) adsorbed on a steel surface [34].

2.3.1   Sodium benzoate – the classic

The sodium salt of benzoic acid, C_6H_5COOH (Figure 7), is the classic carboxylic acid inhibitor used for decades to protect metals in a variety of environments. One example is the sodium benzoate + nitrite inhibitor for automobile radiators [39]. Benzoate is usually classed among the anodic inhibitors [8,14], but benzoate is not an oxidizer [39].
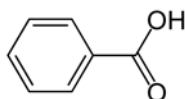
Figure 7 The molecular structure of benzoic acid, C_6H_5COOH, the simplest aromatic carboxylic acid.

Among the carboxylic acids, salts of benzoic acid are probably the most widely researched for protection of steel in concrete [40]. As early as 1970 Gouda and Halaka [14] found sodium benzoate to effectively arrest corrosion of steel in chloride contaminated concrete, provided the concentration of the inhibitor was above a critical concentration. However, they also showed that sodium nitrite could protect at a much lower critical concentration.

In his review from 2004 on inhibitors for use in concrete, Gaidis [12] hardly mentions carboxylic acids and their salts, except benzoate. He states that the inhibiting effect of benzoate, especially at high pH, is probably by adsorbing on active sites [12], i.e. an anodic inhibitor.

On the other hand, Hansson et al [6] reported that the corrosion resistance against chlorides remained unchanged when using sodium benzoate as a corrosion inhibitor.

Andreev et al [41] investigated the corrosion inhibiting effect of salts of substituted benzoic acids in chloride-containing calcium hydroxide solutions, and found that such salts inhibit steel depassivation, elevating the potential of pit formation and extended its induction period. The inhibiting efficiency, however, depends on the hydrophilic/hydrophobic nature of the substituents. The efficiency decreases when both hydrophilic and hydrophobic substituents are introduced in the aromatic benzoic nucleus [41].

In their electrochemical study on steel behavior in synthetic carbonated concrete pore solutions, Trabanelli et al [42] reported that the sodium salts of benzoic acid, and particularly 2-amino benzoic acid, showed some evidence of inhibitive effect towards the rebar corrosion process.

Soeda and Ichimura [13] reported that phthalic acid (benzoic acid molecule with an extra carboxylic group, i.e. a dicarboxylic acid, see Figure 8), was a more efficient corrosion inhibitor than nitrite for Japanese rapid hardening "eco-cement" (made of ash from incinerated wastes, containing high amount of chloro calcium aluminate).
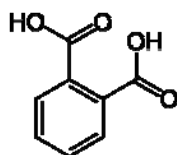
Figure 8 The molecular structure of phthalic acid, $C_6H_4(COOH)_2$.
IUPAC name: Benzene-1,2-dicarboxylic acid.

Kern [33] compared plain benzoic acid with another benzoic-like carboxylic acid, ω-benzoyl alkanoic acid (see Figure 9), both neutralized with the amine base *N*-ethyl-morpholine, and found a noticeable higher adsorption constant for the benzoyl alkanoic acid on iron surfaces in near neutral solutions.
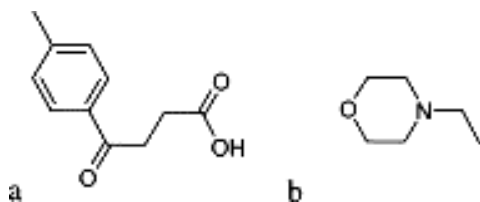
Figure 9 Molecular structures of (a) ω-benzoyl alkanoic acid and (b) *N*-ethyl-morpholine.

2.3.2 Novel carboxylic inhibitors

In 1993, Sagoe-Crentsil et al [40] investigated alkali and earth alkali salts of alternative acids (see Table 2). They found malonic acid (i.e. the sodium salt), a dicarboxylic acid, to be a very effective corrosion inhibitor in mortar even in the presence of 2.5 wt % chloride, and declared that corrosion inhibitors based on dicarboxylic acids remain a fruitful field of investigation. The inhibiting efficiency of malonate is probably linked to its molecular structure, where the presence of two relatively closely-spaced terminal carboxylate groups enables it to complex both ferrous and ferric species in competition with chloride and, possibly, bond strongly to the steel [40]. This suggests the malonate anion to be a mixed inhibitor, forming a film on both anodic and cathodic sites.

Unfortunately, malonic acid has an initial retarding effect on the set of Portland cement [40]. Although not mentioned by Sagoe-Crentsil et al [40], one should investigate the possibility to counteract the retarding effect by using a malonate salt where the counter ion has both an inhibiting and an accelerating effect, e.g. alkanolamine. This is an evident approach when formulating commercial inhibitors.

Table 2
Salts of carboxylic acids tested as corrosion inhibitor in mortar by Sagoe-Crentsil et al [40].

Type of acid	Name	Formula	Salt of acid (carboxylate)	Fomula
Monocarboxylic	Formic	HCOOH	Calcium formate	$(HCOO)_2Ca$
	Acetic	CH_3COOH	Calcium acetate	$(CH_3COO)_2Ca$
	Propionic	CH_3CH_2COOH	Calcium propionate	$(CH_3CH_2COO)_2\,Ca$
Dicarboxylic	Malonic	$CH_2(COOH)_2$	Sodium malonate	$CH_2(COONa)_2$

In their comparative study on several types of inhibitors, Monticelli et al [38] tested different dicarboxylic and hydroxycarboxylic acids or their salts in chloride contaminated alkaline solutions and mortars:

- Sodium gluconate
- D-Saccharic acid, monopotassium salt
- Calcium α-D Eptagluconate
- Phthalic acid, monopotassium salt
- Lactic acid
- Maleic acid
- Suberic acid
- Adipic acid
- Sodium benzoate

Surprisingly, this test did not include malonic acid, the promising dicarboxylic acid reported by Sagoe-Crentsil et al [40]. Instead, Monticelli et al [38] found *maleic* (not *malonic*) acid to be efficient in terms of increasing the pitting potential (E_{pit}) of steel in chloride contaminated alkaline solutions. Normally, one would expect that the higher the pitting potential is, or rather the higher the $E_{pit} - E_{corr}$ value is (E_{corr} is the corrosion potential), the more resistant the material is with respect to pitting corrosion. In this study, however, it was found that all the acids tested, also maleic acid, failed to hinder the corrosion process during longer exposures in mortars, while sodium nitrite at the same dosage did [38].

Note: *Maleic* acid should not be confused with *malonic* acid. Even a third "mal"-acid, *malic* acid, has corrosion inhibiting properties towards steel (see discussion below). All are dicarboxylic acids. Malic

acid has also been studied due to its retarding effect on cement hydration [43]. In order clarify the differences between these acids, their IUPAC names and molecular structures are shown in Figure 10.
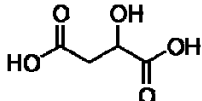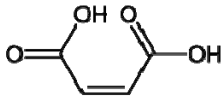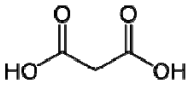
Trivial name (acid):	Malic acid	Maleic acid	Malonic acid
Trivial name (salt)	Malate	Maleate	Malonate
IUPAC name: acid	Hydroxybutanedioic acid	(Z)-Butenedioic acid	Hydroxybutanedioic
Molecular structure:			

Figure 10 IUPAC names and molecular structures of three dicarboxylic acids easy to mix up due to quite similar trivial names.

Goodwin et al [44] carried out corrosion testing that consisted of periodically wetting (with salt solution) and drying cycles applied to steel reinforced concrete slabs. They found that alkali metal and ammonium salts of alkenyl-substituted succinic acid (butanedioic acid) produced significant improvements in corrosion protection compared with the control concrete and with two commercial inhibitors. The commercial inhibitors for concrete were characterized as "a calcium nitrite based chemical" and "an organic based chemical consisting of esters and amines" [44].

Muralidharan et al [45,46] conducted weight loss and electrochemical measurements on steel exposed to synthetic chloride-containing alkaline solutions and extracts from fresh ordinary portland cement (OPC) and OPC/fly ash pastes with high water/binder ratios. They found sodium citrate to be an efficient inhibitor, even at 3 wt % chloride level in the solutions, and stated that the mechanism of action of corrosion inhibition by citrate is due to the formation of stable complex film through the process of chemisorption on the metal surface [45,46], i.e. a mixed inhibitor covering both the anodic and cathodic parts of the steel surface. It is believed that calcium plays a part in the formation of the surface layer [45]. Citrate blended with stannate ($Sn(OH)_6^{2-}$), an inorganic complex-forming species, formed an even more efficient inhibitor in these solutions and extracts [46].

In their recent comprehensive screening test to rank the inhibition effectiveness of 80 (!) different organic substances, Ormelese et al [34] found carboxylates, especially polycarboxylates, to be efficient substances against chloride-initiated pitting corrosion on steel. All tests were carried out in chloride-containing alkaline solutions by use of electrochemical potentiodynamic polarisation measurements to give $E - \log i$ curves. The carboxylates tested in their work are shown in Table 3. Note that both malic and malonic acid were tested. The idea was to verify the influence of electron-donor and electron-attractor groups, carbon-chain length and functional groups. Most of the carboxylates gave an increase of pitting potential [34], thereby lowering the risk of corrosion. Figure 11 summarizes their results in a Pedeferri's type diagram comparing carboxylates with amines/alkanolamines and amino acids that were investigated in the same study [34]. It is seen that amines/alkanolamines had only moderate effectiveness, while carboxylates showed the best behavior, i.e. the largest increase in pitting potential compared to the reference solution without inhibitor. At low and moderate chloride levels, carboxylates even showed better inhibiting properties than a commercial sodium nitrite inhibitor (see Figure 11).

Note that carboxylic groups also have a strong affinity to calcium, so testing in alkaline solutions without calcium may not mimic a cement system where the carboxylic acid or salt might adsorb onto cement grains rather than on steel. This is a potential generic problem of testing corrosion inhibitors for concrete in alkaline solution and will also apply in particular for phosphates (section 2.4).

Table 3
Mono-carboxylates (R–COO⁻) and poly-carboxylates (⁻COO–R–COO⁻)
tested by Ormellese et al [34].

Mono-carboxylates	
Acetate	CH_3–COOH
Trifluoroacetate	CF_3–COOH
Trichloroacetate	CCl_3–COOH
Pivalate	$(CH_3)_3$C–COOH
Cyclohexancarboxylate	C_6H_{11}–COOH
2–Methylbutyrate	$CH_3CH_2CH(CH_3)$–COOH
Benzoate	C_6H_5–COOH
Poly-carboxylates	
Oxalate	HOOC–COOH
Malonate (salt of malonic acid)	HOOC–CH_2–COOH
Succinate	HOOC–$(CH_2)_2$–COOH
Glutarate	HOOC–$(CH_2)_3$–COOH
Suberate	HOOC–$(CH_2)_6$–COOH
Azelate	HOOC–$(CH_2)_7$–COOH
Malate (salt of malic acid)	HOOC–CH (OH) CH_2–COOH
Tartrate	HOOC–$(CHOH)_2$–COOH
Citrate	HOOC–COOH–$(CH_2COOH)_2$
Fumarate	HOOC–CH=CH–COOH
EDTA	$(HOOC)_2$–N–CH_2–N–$(COOH)_2$

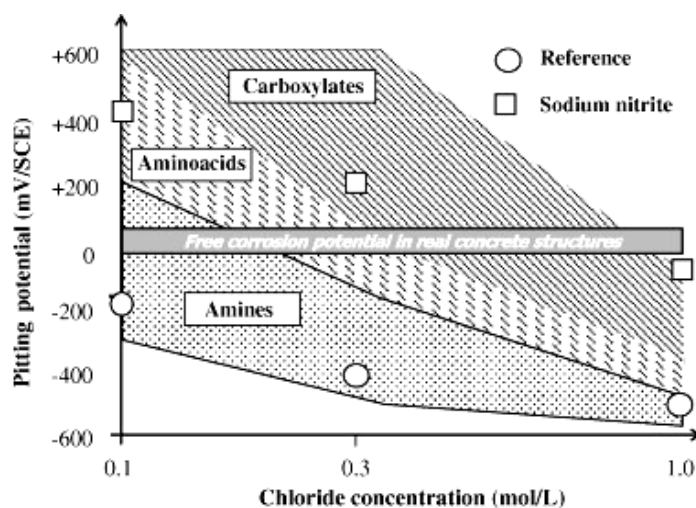**Figure 11** A Pedeferri's type diagram showing the pitting potential range obtained for amines
(including alkanolamines), amino acids and carboxylates with increasing chloride
concentration. Open circles show the pitting potential of the reference solution without
inhibitor for three different chloride levels. Open squares show the pitting potential, at the
same chloride levels, with a commercial sodium nitrite inhibitor [34].

In their extensive screening of organic inhibitors, Ormelese et al ranked the different carboxylates in this way [34]:

Mono/poly-carboxylate comparison

- Polycarboxylate showed the best inhibitive effectiveness

Effect of substituent nature

- The presence of electron-donor groups (e.g. pivalate, see Table 3) increased pitting potential and accordingly the inhibition effectiveness
- A beneficial steric affect was found as the pitting potential increased in the series: acetate, 2-methylbutyrate, pivalate and cyclohexancarboxylate

Effect of chain length

- For polycarboxylates of the series $^-COO–(CH_2)_n–COO^-$ the pitting potential reached a maximum for n=3 (glutarate)

Note that all the tests of Ormelese et al [34] were conducted in solutions only, and they pointed out that a confirmation of promising carboxylate candidates in concrete specimens is required to check compatibility with concrete and long-term effectiveness.

2.4 Phosphorous compounds

Phosphorous compounds, showing corrosion inhibiting properties, can be divided into two major classes: (1) phosphates and (2) sodium monofluorophosphates. Monofluorophosphates are not used as mixed-in inhibitors because these compounds induce a strong retardation of the concrete setting and can be transformed into insoluble compounds [7,38]. Instead, they are used as migrating inhibitors (see Chapter 3). Phosphates, which have been tested as mixed-in inhibitors [14,47], may also strongly retard setting of concrete. Probably, this side-effect of phosphates is one reason for the lack of recent reports on this inhibitor. Actually, several commercial set retarders on the market today contains phosphate [48].

Phosphates and polyphosphates (phosphate polymers, e.g. sodium triphosphate, $Na_5P_3O_{10}$) have been characterized as cathodic inhibitors [8]. However it seems that the mode of action depends on the inhibitor to chloride ion ratio in the electrolyte. One study showed that sodium phosphate acted as a cathodic inhibitor at low inhibitor to chloride ion ratios, whereas at higher ratios, it became a mixed inhibitor [47].

As early as 1970 it was reported that disodium hydrogenphosphate, Na_2HPO_4, is able to arrest chloride-initiated corrosion of steel in concrete, provided the phosphate content is above a critical concentration that depends on several factors: concentration of chloride present in the concrete, type of cement used, and the surface condition of the steel [14]. Yet, the same study found sodium nitrite to be more efficient at lower concentrations.

Later, one study reported that sodium β-glycerophosphate is a promising corrosion inhibitor for steel when tested in alkaline chloride solutions [38].

Recently, a study showed that a pre-treatment of the steel, by immersion in a sodium phosphate solution prior to chloride exposure, is more effective for the rebar protection than adding sodium phosphate to a simulated pore solution already containing chloride [49].

Obviously, the inhibiting mechanism of action of phosphates is not clear. Some put phosphates into the cathodic inhibitor group [8], while others suggest that phosphates are capable of making an anodic

formation of a passive layer on the steel surface consisting of ferric oxides and $FePO_4 \cdot H_2O$ [50], i.e. an anodic inhibitor.

Reports on phosphonic acids and their salts as inhibitors for concrete are scarce. The molecular difference between a phosphoric and a phosphonic acid is shown in Figure 12. Phosphonic acids are compounds in which one of the hydroxyl groups of the phosphoric acid molecule is replaced by an organic group (alkyl) linked to the phosphor atom.
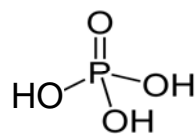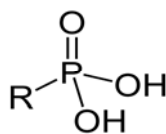
Phosphoric acid   Phosphonic acid with one alkyl group (R)

Figure 12 Molecular structures of phosphoric acid (left) phosphonic acid (right).

In their recent state-of-the-art report on corrosion inhibitors for steel in concrete, Söylev and Richardson [8] did not mention phosphonates, but these compounds seem to be promising candidates. One study [51] has shown that nitrilotris(methylenephosphonic acid) has the potential of inhibiting the cathodic reaction on steel in saturated $Ca(OH)_2$ solutions. It is suggested that this compound adsorbs on cathodic sites on the steel surface, blocking the sites for oxygen reduction [51]. Today, phosphonate inhibitors are typically used in cooling water technology [52]. Within concrete technology it seems that phosphonic acids and their salts, so far, is restricted to be used as set retarding admixtures [48].

2.5   Miscellaneous inhibitors

The most studied, and even commercialized, mixed-in inhibitors for concrete are those described above. Other mixed-in substances with corrosion inhibiting properties in concrete or simulated concrete pore solution, are listed below:

Chromates
Chromate salts, particularly sodium and potassium chromate, have long been known for their inhibiting properties [14]. Even recently, chromate-based inhibitors have been studied in concrete [53]. Chromates are oxidizing agents, consequently anodic inhibitors [8]. Due to its toxicity, water soluble chromate is discouraged today as a chemical admixture for concrete.

Silicates
Sodium silicate (water glass) has been used for the inhibition of steel for more than 80 years, typically inside water pipes [54]. In concrete a water soluble silicate may act as a cathodic inhibitor by forming a film of precipitated calcium silicate on the cathodic sites at the surface of the steel reinforcement [13].

Zinc oxide
ZnO, nearly insoluble in water, has been under study to try to replace nitrite, either partly or totally, as a mixed-in inhibitor for concrete. It seems that the best inhibiting effect is obtained by mixing ZnO and nitrite in equal concentrations [15,21]. It has been suggested that ZnO reacts with alkaline concrete to form calcium zincate, $CaZn(OH)_4$, causing passivation of the steel reinforcement [55].

Uracil

Uracil is a common and naturally occurring pyrimidine derivative, see Figure 13. Nakayama and Obuchi [56] found 5-aminouracil (a derivative of uracil with three nitrogen atoms in the aromatic ring) to be an efficient cathodic inhibitor for steel in saturated $Ca(OH)_2$ solutions.
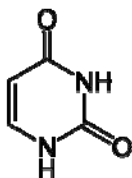
Figure 13 The structural formula of uracil.

Stannate

Muralidharan et al [45,46] tested sodium stannate in extracted pore solution of hardened ordinary cement and fly ash blended cement, and found stannate ($Sn(OH)_6^{2-}$, a complexing agent) to effectively maintain the passivity of steel even in the presence of 30 000 ppm of chloride. They reported that the inhibiting mechanism of action is due to the formation of a stable complex film through the process of chemisorption on the metal surface

Thiosemicarbazide

Gurten et al [57] found that thiosemicarbazide, a simple molecule containing nitrogen and sulphur, see Figure 14, had promising corrosion inhibiting properties in alkaline chloride solution.
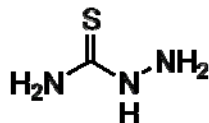
Figure 14 The structural formula of thiosemicarbazide.

Benzotriazole

In 1995 a patent described benzotriazole, a heterocyclic compound (see Figure 15) well known to inhibit corrosion of copper and stainless steel, as a minor constituent in a corrosion inhibitor for steel in concrete (carboxylic acid being the major component) [58]. Recently, Mennucci et al [59] reported that benzotriazole improves the corrosion resistance of steel in chloride-contaminated concrete pore solution, and they claim that the inhibiting effect is superior to that obtained with nitrite.
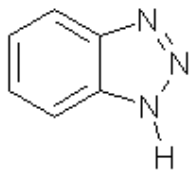
Figure 15 The structural formula of benzotriazole.

3 Migrating corrosion inhibitors for concrete

3.1 Organic MCIs

The 'Migrating Corrosion Inhibitor' (MCI®) technology was introduced by the American company Cortec Corporation in the mid 1980s [60].

A MCI is applied to the external surface of hardened concrete, and the inhibiting compound should penetrate the concrete cover and reach the steel reinforcement in a sufficiently high concentration to protect the steel against corrosion [61]. The inventor of the technology (Cortec Corporation) claims that MCI products migrate in three different ways simultaneously [60]:

- Capillary action – concrete acts like a sponge, drawing the liquid inhibitor inside.

- Vapor phase – MCI molecules move as a vapor from areas of high concentration to areas of low concentration until they reach equilibrium.

- Ionic attraction – MCI molecules adsorb onto metal surfaces forming a protective layer.

MCIs are typically commercial products made of proprietary blends of chemicals, mostly organic compounds. They usually contain an amine or an alkanolamine and a component (normally a carboxylic acid) forming a salt with the alkanolamine [8,9,60,62,63,64,65,66]. Organic MCIs act to suppress both the anodic and cathodic reactions by forming a monolayer film at the steel-concrete interface [64,67]. Hence, organic MCIs are mixed inhibitors.

Most of the chemical substances found in these products are probably the same as those found among mixed-in inhibitors (described above). Generally, the investigations conducted on these inhibitors are more related to the way the products are applied, and less focused on the electrochemical interactions between the inhibitor and the steel.

The development of organic MCIs for concrete is based on the older 'vapor phase inhibitor' technology used for decades to protect steel machinery and components, particularly for shipment and storage [65,66]. Amine/alkanolamine is the main volatile component of the MCI and is transported mainly by gas diffusion inside the concrete pores, whereas the carboxylic parts (at least some types) may react with calcium hydroxide, precipitates, and blocks the pores of the concrete. This pore-blocking property is said to be a secondary protection mechanism against reinforcement corrosion [12,62,65,66,68]. According to the definition of a corrosion inhibitor given in this report (see Chapter 1.3), pore-blocking substances are not inhibitors in the true sense. However, as discussed in Chapter 2.3, carboxylic acids have corrosion inhibiting properties in the electrochemical sense. According to Cortec Corporation, the 'MCI molecule' adsorbs onto the metal surface, forming a protective molecular layer, where the nitrogen (amine) part is responsible for its strong bond with the metal surface, while the hydrocarbon (carboxylate) tail of the 'MCI molecule' creates at hydrophobic layer that helps repel moisture away from the steel [60].

MCIs have been the subject of much debate; many claim the MCI technology works and some states it does not work. This debate is not so much about the electrochemical corrosion inhibiting properties of the chemical components, but more about the penetration (or lack of penetration) in the hardened concrete cover. It is fairly evident that, if these products can reach the steel, they do provide protection against corrosion. The issue on poor performance relates mainly to the ability of a surface applied volatile liquid to migrate through the concrete cover to the steel [64,69]. Bavarian and Reiner [70] tested several MCIs according to the ASTM G109 method and concluded that all inhibitors tested significantly reduced the corrosion rate. On the other hand, Ormelese et al [71] found that migration does occur only if the concrete matrix is sufficiently porous.

3.2 Inorganic MCIs

Research on inorganic MCI technology has been carried out mainly on sodium monofluorophosphate (MFP) [38,72,73]. It is said that this compound has been widely applied in the field (for more than 20 years) to prevent the onset of corrosion or to reduce the corrosion rate [38].

MFP is applied at the concrete surface in the form of an aqueous solution with a mass percentage ranging between 10 % and 20 % [73]. However, Ngala et al [72] point out a problem related to this compound: The PO_3F^{2-} ions, which perform the inhibiting action on the steel surface, will not be present in sufficient concentration in sound, non-carbonated concrete, because PO_3F^{2-} will react with Ca^{2+} present in the pore water and precipitate and accumulate in the porous network. Thus, even though the electrochemical mode of action on the steel surface is hindered, MFP may indirectly protect the steel by blocking the penetration of aggressive species. This has later been confirmed by other researchers [73]. Due to low concentration of dissolved Ca^{2+} in the pore water of carbonated cementitious materials, MFP may penetrate these materials and, thus, act as an inhibitor [73]. The inhibiting properties of phosphorous compounds in general is discussed in Chapter 2.4.

4   Commercial corrosion inhibitors for concrete

4.1   Commercial mixed-in inhibitors

The most commonly used mixed-in inhibitors for steel in concrete are said to be calcium nitrite and amines/alkanolamines [8]. This is a general statement, and no comprehensive report has been found documenting market shares of different types of corrosion inhibitors.

With few exceptions, manufacturers and suppliers of corrosion inhibitors seldom disclose the exact composition of their inhibitors, neither in their open technical documents, nor in their responses to direct inquiries. The Technical Data Sheet (TDS) of the product sometimes gives some information on the main chemical ingredient(s). Due to health and safety regulations more information is often found in the Material Safety Data Sheet (MSDS) of the product. Yet, one should take into consideration that information on chemical ingredients can sometimes differ from a supplier in one country to a supplier in another, even when the brand names of the products are identical. An example is given below.

Table 4 gives information on ingredients found in a selection of well known commercial mixed-in inhibitors on the market. As the information in most cases is based on MSDSs only, one should bear in mind that additional ingredients may be present in the products, e.g. ingredients not disclosed either due to lack of demand in regulations for that particular chemical, or other reasons. The examination of these commercial inhibitors showed that (see Table 4):

- Commercial mixed-in inhibitors are often blends of different chemical compounds.

- The main (disclosed) ingredients in most commercial mixed-in inhibitors for concrete are either calcium nitrite/calcium nitrate blends or alkanolamines.

- The information on chemical ingredients can be contradictory when MSDSs for a product with a given brand name, supplied from two different countries, are compared (e.g. FerroGard 901).

- The information on type and amount of carboxylic acids is not disclosed; only general information is given (e.g. Rheocrete 222+).

- No commercial cathodic inhibitors for concrete (e.g. phosphates) were found among the suppliers listed in Table 4.

- Two different mixed-in inhibitors (different brand names) from Grace show identical type and amount of ingredients according to the MSDSs.

The contradictory information on ingredients in Sika FerroGard 901 was investigated a bit further. It turned out that the Norwegian TDSs on this inhibitor, originating from 1999 [74] and 2006 [75] respectively, gave different information on ingredients. The one from 1999 disclosed a carboxylic acid (benzoic acid) which is not mentioned in the newest data sheet. This does not necessarily mean that benzoic acid is no longer an ingredient, but can be a result of change in policy regarding which chemicals to be disclosed. In his study on a commercial organic inhibitor, Elsener [76] found that the inhibitor consisted to more than 90 % of dimethylathanolamine (DMEA), while the rest was composed of carboxylic acids (mainly benzoic acid). Although not clearly stated by Elsener, it is reasonable to believe that he reported results from an investigation on Sika FerroGard 901. Finely, a Sika patent from 2000 claims [77]:

- "*Advantageous corrosion inhibitors for the present invention comprise, and preferably are the products of, the at least partially performed acid-base neutralisation reaction between amino compounds and acids*"

- "*Preferred amino compounds are N,N-dimethylethanolamine, N-methyldiethanolamine as well as mono-, di- and Triethanolamine*"

- "*Preferred acids are phosphonic acids, benzoic acids, lactic acid, gluconic acid, glucoheptonic acid, enanthic (heptanoic) acid and caprylic acid*"

From all this information it is fairly obvious that Sika FeroGard 901 consists of dimethylethanolamine (DMEA) partly neutralized by benzoic acid. This is in line with the TDS [75] stating that Sika FerroGard 901 has a pH of about 10. Molecular structures of DMEA and benzoic acid are shown in Figure 16. Besides, it is interesting to note that the Sika patent [77] mention phosphonic acid, a promising phosphorous compound with inhibiting properties (see Chapter 2.4).

N,N-dimethylethanolamine (DMEA)   Benzoic acid
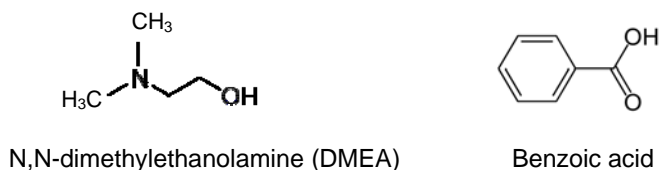
Figure 16 Molecular structures of the compounds likely to be found in Sika FerroGard 901.

Table 4
A selection of commercial **mixed-in** corrosion inhibitors for concrete.

Supplier	Name of product	Chemical ingredients disclosed in the MSDS[*]	
		Type of ingredient	% by weight
BASF	Rheocrete CNI [78]	Calcium nitrite	30 – 60
		Calcium nitrate	3 – 7
	Rheocrete 222+, USA [79]	Monoethanolamine	10 – 30
	Rheocrete 222+, Singapore [80]	Mixture of amines and esters	Not given
	Rheocrete 222+, UK [81]	Polycarboxylic acids, polycarboxylates and alkanolamine	Not given
Sika	FerroGard 901, Norway [74,75]	2-dimethylaminoethanol (DMEA)	5 – 10
		Organic/inorganic nitrogen compounds [**]	Not given
	FerroGard 901, Canada [82]	Salt of alkanolamine	15 – 40
W. R. Grace	DCI [83]	Calcium nitrite	25 – 50
		Calcium nitrate	1 – 10
	DCI-S [84]	Calcium nitrite	25 – 50
		Calcium nitrate	1 – 10
Euclid Chemical	Eucon BcN [85]	Calcium nitrite	30 – 60
	Eucon CIA [86]	Calcium nitrite	30 – 60
		Calcium nitrate	5 – 10
Axim	Catexol CN-CI [87]	Calcium nitrite	30 – 40
		Calcium nitrate	< 5

[*] MSDS = Material Safety Data Sheet (available at suppliers web page, August 2010)
[**] General information on type of ingredient given in the Technical Data Sheet [75]

4.2 Commercial MCIs

As discussed in Chapter 3, it seems that most MCIs are 'organic type' inhibitors containing amine/alkanolamines and a carboxylic part. An examination of data sheets from suppliers of commercial MCIs showed that (see Table 5):

- Commercial MCIs are made of organic compounds.

- Alkanolamines and aminocarboxylates are the main (disclosed) ingredients in most commercial MCIs.

- The information on chemical ingredients can be contradictory when MSDSs for a product with a given brand name, supplied from two different countries, are compared (e.g. FerroGard 903).

- Although it has been claimed that sodium monofluorophosphate is widely applied as MCI [38], no commercial product was found.

Table 5
A selection of commercial **migrating** corrosion inhibitors (MCIs) for concrete.

Supplier	Name of product	Chemical ingredients disclosed in the MSDS[*]	
		Type of ingredient	**% by weight**
Cortec	MCI 2021 & 2022 [88]	Aminocarboxylates [**]	Not given
BASF	MCI-2006NS [89]	Sodium salt of oxycarboxylic acid	30 – 60
		Aminocarboxylates	< 30
	MCI-2020 [90]	3-aminopropyltriethoxysilane	< 10
		2-amino-2-methylpropanol	< 10
		Sodium salt of oxycarboxylic acid	< 10
		Aminocarboxylates	< 10
Sika	FerroGard 903, Norway [91]	2-aminoethanol	5 – 10
	FerroGard 903, Canada [92]	Alkanolamine	10 – 30
		Ethyl alcohol	1 – 5

[*] MSDS = Material Safety Data Sheet (available at suppliers web page, August 2010)
[**] MSDS is not available on supplier's web page due to restricted access. General information on recent MICs is given in a technical paper [88].

5 Conclusions and further research

This state-of-the-art report has reviewed several aspects of corrosion inhibitors for steel in concrete. The following conclusions can be drawn on history of inhibitors, types and chemistry of inhibitors, and commercial availability of inhibitors (as of August 2010):

- Inhibitors for concrete are either mixed into fresh concrete (mixed-in inhibitors) or applied onto the surface of hardened concrete (migrating inhibitors, MCIs) to penetrate the concrete cover.

- From an electrochemical point of view, an inhibitor falls into one of three broad classes: Anodic, cathodic or mixed, depending on whether it affects the anodic reaction, the cathodic reaction, or both.

- The first inhibitor reported for concrete applications was sodium nitrite (more than 50 years ago). Nitrite and nitrate are anodic inhibitors.

- Today, blends of nitrite/nitrate salts (preferably calcium) are among the most common commercial mixed-in inhibitors world-wide.

- Roughly two decades ago, amines and alkanolamines became the most common mixed-in inhibitors on the European market. These are mixed inhibitors suppressing both the anodic and cathodic reactions.

- In recent years, the research on the inhibiting effect of carboxylic salts and their salts in alkaline media has been intensified.

- Like amino groups, carboxylate groups have the potential of adsorbing to metal surfaces, thereby forming an organic layer on the entire surface, i.e. acting as a mixed inhibitor.

- Today, carboxylic compounds are found in commercial mixed-in inhibitors for concrete, typically as ingredients in amine-based products.

- Phosphate salts, considered to be cathodic inhibitors, are not found among commercial inhibitors today.

- Most inhibitors show secondary effects on the properties of fresh and hardened concrete. Nitrites/nitrates accelerate setting of fresh concrete, whereas many carboxylic acids tend to retard the cement hydration rate.

- Reports on MCIs deal mostly with the penetration (or lack of penetration) of the inhibitor in the hardened concrete cover. There is a debate going on whether these products really act as anticipated.

- Nearly all MCIs on the market are blends of amines/alkanolamines and carboxylic acids, i.e. amino-carboxylates.

Based on information presented in this report, a continuation of today's research on corrosion inhibitors for concrete will include both the electrochemical behavior of chemical substances at the steel/electrolyte interface, and the transport of inhibitors in hardened concrete (in the case of MCIs).

If COIN decides to start research on inhibitors, it is recommended to concentrate on mixed-in inhibitors only, in close cooperation with the COIN activities in focus area 'binders/admixtures'.

Prospective COIN research on inhibitors should emphasize:

- Further research on calcium nitrate, a multifunctional admixture already known for its inhibiting properties.

- Continuation of research on carboxylic compounds, as sole admixtures, and blended with other compounds with inhibiting properties.

- Development of multifunctional admixtures.

- Investigate the effect of inhibitors on concrete properties in fresh and hardened state.

- Try to counteract undesirable secondary effects of promising inhibitors (e.g. retarding effect) by smart blending of substances.

- One example of smart blending of admixtures could be: An inhibitor with retarding effect mixed with an inhibitor with accelerating effect, e.g. malonic acid (retarder) and nitrate (accelerator) or an accelerating alkanolamine.

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