

INHIBITORS IN CONCRETE STRUCTURES

INHIBITOREN IN BETONKONSTRUKTIONEN

INHIBITEURS DANS LES STRUCTURES EN BETON

Ulf Nürnberger

SUMMARY

By adding inhibitors, for instance calcium nitrite, to fresh concrete in an appropriate dosage, corrosion of reinforcing steel may be prevented. Nevertheless, due to underdosage or local separation of inhibitors, pitting corrosion may occur. In reinforced concrete structures which, on behalf of an insufficient concrete quality and/or concrete cover or, as a result of the formation of cracks in concrete, need an additional protection against corrosion, inhibitors may be washed out under natural environmental conditions. Therefore, and because the properties of fresh and hardened concrete may be modified in an uncontrolled way, users in Germany are against the application of nitrite inhibitors.

ZUSAMMENFASSUNG

Durch eine Zugabe von Inhibitoren zum Frischbeton in geeigneter Dosierung, z.B. in Form von Calciumnitrit, kann eine Bewehrungsstahlkorrosion unterbunden werden. Bei Unterdosierung oder lokaler Entmischung des Inhibitors kann allerdings verstärkt Lochkorrosion auftreten. Stahlbetonkonstruktionen, die aufgrund einer nicht ausreichenden Betongüte und/oder Betondeckung sowie einer Betonrißbildung am ehesten eines zusätzlichen Korrosionsschutzes bedürfen, neigen unter natürlichen Umgebungsverhältnissen zu Auswaschungen der zugegebenen Inhibitoren. Deshalb, und weil die Frisch- und Festbetoneigenschaften in unkontrollierter Weise verändert werden können, ist man in Deutschland z.Z. gegen eine Anwendung von Nitrit-Inhibitoren.

RESUME

L'admixtion d'inhibiteurs, tels que par exemple le nitrite de fer, au béton frais peut, à un dosage approprié, empêcher la corrosion de l'armature. Un sous-dosage ou une ségrégation locale de l'inhibiteur peuvent mener à une corrosion par piqûre prononcée. Les constructions en béton armé qui, pour cause

d'une qualité insuffisante du béton, d'un recouvrement trop faible de l'armature ou de fissuration nécessitent des mesures supplémentaires de protection contre la corrosion, tendent à subir un appauvrissement en inhibiteurs par lessivage sous des conditions d'environnement naturelles. Pour cette raison, et parce que les propriétés du béton frais et durci peuvent être modifiées de façon incontrôlée, les utilisateurs en Allemagne sont actuellement contre l'application d'inhibiteurs à base de nitrites.

KEYWORDS

Inhibitor, Corrosion, Corrosion Protection, Chloride, Reinforcing Steel, Concrete Properties

1 INTRODUCTION

In order to protect metallic materials against corrosion, certain inorganic and/or organic products, called corrosion inhibitors, are added in small concentrations to the attacking medium /1/. The application of inhibitors belongs to the active corrosion-protective measures. That is to say, the inhibitor intervenes directly (actively) into the corrosion process and hinders or prevents an attack.

In building constructions, there exists only a few special fields, such as for instance drinking water-supply and hot-water-heating systems, where inhibitors are used. Very seldom, corrosion-sensitive metals (for instance prestressing steels) were protected by means of so-called vapour-phase-inhibitors against atmospheric corrosion. For instance in the USA and in Russia inhibitors were also used in concrete construction. In some European countries, the use of these products is discussed in connection with the corrosion of reinforcing steel. In Germany, reservations exist against the addition of inhibitors to concrete. For example, in the cooling water of automobile motors, inhibitors frequently protect metal against corrosion for only a few years and may be re-added, whereas in concrete buildings a protective effect of more than 50 years is expected and a later, direct addition to concrete is impossible. Furthermore,

it is frequently not accepted that sometimes inhibitors don't completely prevent corrosion but only retard its beginning and reduce its intensity. The most essential objection made is that the anodic inhibitors used are "dangerous inhibitors" which, under certain conditions, may favour pitting corrosion. Furthermore, the concrete qualities may be modified in an uncontrolled manner.

In order to prevent corrosion, passivating inhibitors are added to fresh concrete together with cement or dissolved in mixing water. For the use of such corrosion inhibitors in concrete, it has to be taken into consideration that concrete already has an inhibiting action. The high alkalinity of pore water produces a passivation. If it is removed in carbonated areas or eliminated in the presence of chlorides, further additions of inhibitors to concrete may counteract this depassivation if the quantity of inhibitors is in agreement with the "depassivation degree".

2 SUBDIVISION AND EFFECT OF INHIBITORS

Depending on whether an inhibitor hinders the anodic reaction of metal dissolution or the cathodic reaction of reduction of an oxidizing agent, it may be distinguished between anodic and cathodic inhibitors. Besides that, it is more usual to subdivide according to the interaction of an inhibitor with the metal surface to protect; a difference is made between physical and chemical corrosion inhibitors.

2.1 Anodic and cathodic inhibitors

Most of the inhibitors are anodically effective and must be ranged among chemical inhibitors and here especially among passivators and film-forming inhibitors. Especially the physical inhibitors belong to the cathodically effective admixtures.

The anodic and cathodic effectiveness of an inhibitor may be determined by comparing current-density vs. potential curves of metals in non-inhibiting and inhibiting media: an anodic effectiveness may result in a decrease of steepness of the anodic curve and a shift of the corrosion potential to more positive values (transition from A 1 to A 2 in fig. 1, right side). Inhibition may also cause a transition from the active to the passive state. In the presence of depassivating chlorides, an increase of the breakdown-potential may be observed after the addition of inhibitors (pitting inhibitors").

A cathodic effectiveness results in a decrease of steepness of the cathodic curve and a shift of the corrosion potential to more negative values (transition from K2 to K1 in fig. 1, left side).

2.2 Physical (adsorption inhibitors) and chemical inhibitors

Physical inhibitors are bound adsorptively by physical forces to the metal surface, without transforming the surface chemically. They form an adsorption layer composed of a few molecular layers which more or less hinder electrode processes. Organic compounds with extremely polar sulphur or nitrogen combinations tending to adsorption belong to these.

Chemical inhibitors react with the metal surface to protect or components of the corrosive medium and, as a result, develop layers of different thicknesses which hinder the reactivity of anodic and/or cathodic areas. The surface is changed chemically. Chemical inhibitors are used in acid, neutral and alkaline environments.

A difference is made between passivators, film-forming inhibitors and electrochemical inhibitors, where only the two first are important for concrete constructions.

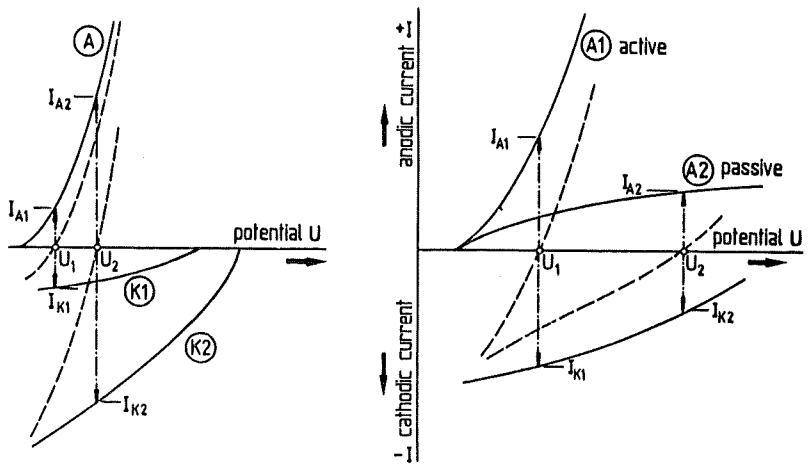


Fig. 1: Current-potential curves with variation of cathodic (left side) and anodic (right side) curves (schematically)

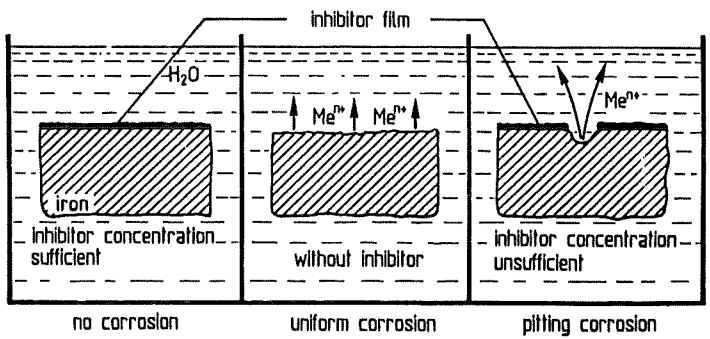


Fig. 2: Effect of anodic inhibitors

Passivators: Passivators support the formation of passive layers (for instance by a high Redox-potential) and may form thin, but even and very dense protective films. These hinder the anodic partial reaction of corrosion. Anions with passivating qualities are the nitrite (NO_2^-), chromate (CrO_4^{2-}) and molybdate (MoO_4^{2-}). Frequently these anions are bound to sodium. Usually passivators already become active in very low concentrations from 10^{-4} to 10^{-5} mol/kg.

Anodic inhibitors, especially the passivators, may show undesired side effects if they are not used in sufficiently high concentrations. For an underdosage (falling below a necessary minimum concentration), especially in the presence of chlorides and/or sulfates, pitting corrosion may appear initiated by cell formation. For a partial blocking of anodic surface areas (fig. 2) anodes are diminished and thus, the ratio of the cathode area vs. the anode area is increased in comparison to the non-inhibited state; in accordance with the regularity for corrosion cells, the density of the cell current is increased. This causes an intensification of pitting corrosion. For this reason, anodic inhibitors are referred to as "dangerous inhibitors"/2/. An optimal use of anodic inhibitors is only convenient if the concentration of inhibitors may be adapted to the prevailing corrosion conditions. The cathodic inhibitors aren't dangerous inhibitors, because an insufficient concentration increases the corrosion velocity, but doesn't produce an increased local corrosion.

Among passivators, especially nitrides are used in concrete constructions. Chromates belong to the most effective inhibitors, but their use has been reduced because of the existing toxicity (for instance as an inhibitor in concrete constructions). Cements have a natural chromate content which, for instance, is important for the use of galvanized reinforcing steels.

Film-forming inhibitors: They react either with the metal surface or with substances in water to insoluble compounds. The layers are thicker, less uniform and less dense than passive layers. Film-forming inhibitors cover anodic

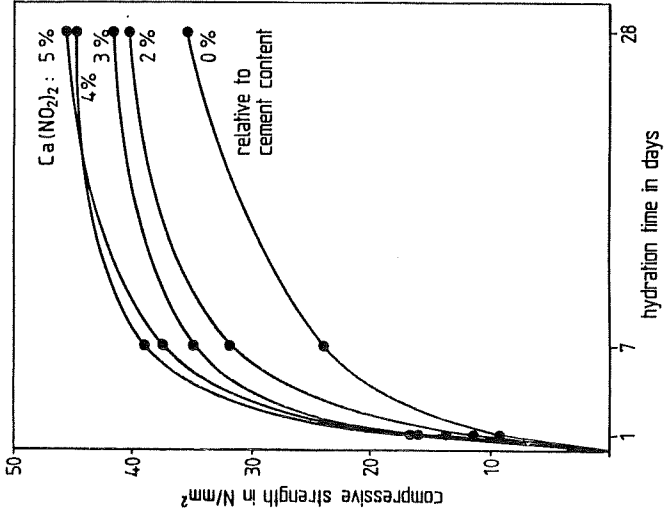


Fig. 4: Compressive strength of concrete in relation to the hydration time and the addition quantity of Ca(NO₂)₂ [4]

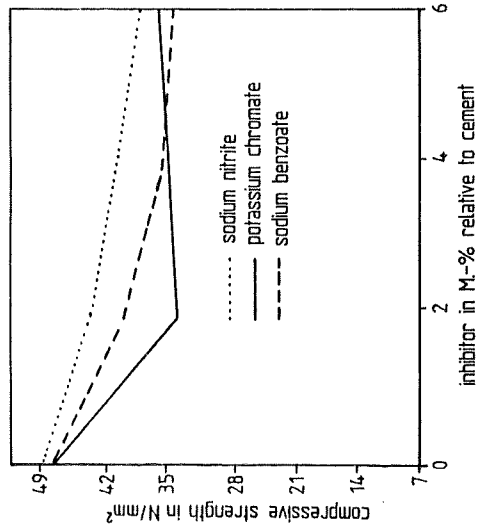


Fig. 3: Effect of some corrosion-inhibitors upon the compressive strength of concrete [3]

and/or cathodic partial surfaces and reduce the corrosion current. Phosphates, phosphonates and benzoates for example belong to the film-forming inhibitors. In concrete constructions, only benzoates (rarely) were used up to now. Their effect may be explained by the formation of thin layers of complex compounds of their anions with the trivalent iron. Benzoate is frequently used in combination with other inhibitors, especially if a protection against pitting-corrosion is required. Benzoate is also an alkalizing inhibitor.

3 INFLUENCE OF INHIBITORS ON CONCRETE QUALITIES

By adding inhibitors to concrete, it is possible to influence the qualities of fresh and hardened concrete, but until now the changes of qualities have only been insufficiently investigated. For instance in /3/, it has been noticed that, after addition of sodium nitrite, sodium benzoate and calcium chromate the concrete strength decreases by 20 to 40 % (fig. 3). As NaNO_3 increases the alkalinity of hardened cement paste, there may also be problems with the use of admixtures sensitive to alkalis.

For the aforementioned reasons, $\text{Ca}(\text{NO}_2)_2$ is nowadays increasingly used instead of NaNO_3 /4-6/. This inhibitor also acts as an accelerator and increases the compressive strength (fig. 4). Furthermore $\text{Ca}(\text{NO}_2)_2$ is compatible with concrete admixtures (i.e. instance fly ash) and is also offered by industry in combination with concrete admixtures (for instance the effect of nitrite on the acceleration of solidification may be compensated by the addition of a retarder) /5/.

4 INFLUENCE OF INHIBITORS ON REINFORCING STEEL CORROSION

4.1 Carbonated concrete /7-10/

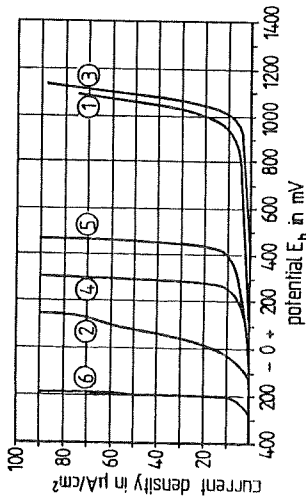
By electrochemical investigations (anodic current vs. potential) it has been determined that it is possible to reduce corrosion in carbonated concrete by addition of at least 1 % by mass of NaNO_2 to the cement, (fig. 5 and fig. 6).

For elements exposed outdoors, a permanent protection effect cannot be expected, as water-soluble inhibitors tend to be washed out (see below)/8/. In the case of an underdosage, the behaviour can be more unfavorable than without inhibitors.

4.1.1 Chloride-containing concrete

The corrosion-protective effect of sodium nitrite /7, 10-12/, calcium nitrite /4-6/, mixtures of calcium nitrite and calcium nitrate as well as chromates and benzoates /11/ in concrete containing chlorides was shown by current vs. potential curves. An important argument against inhibitors based on nitrates is that these produce stress corrosion on reinforcing steels. For this reason, nitrates shouldn't be used as admixture for concrete when reinforcing steels sensitive to stress corrosion are used. Among the quoted inhibitors, NaNO_2 has the best corrosion-protective effect. Because of a possible negative influence on concrete hardening (fig. 3), essentially calcium nitrite, which is also very active in concrete containing chlorides, is offered on market at the moment.

The quantity of inhibitors needed in addition to concrete depends on the type of inhibitors and the chloride content /4, 6, 7, 11/: higher chloride contents require higher amounts of inhibitors (fig. 7). The chloride-depending quantities of inhibitor should be chosen such that a $\text{Cl}^-/\text{NO}_2^-$ -ratio of 1.5 to 2.0 is not exceeded. But every inhibitor needs a critical concentration in order to suppress corrosion for a given chloride content. For the inhibitor $\text{Ca}(\text{NO}_2)_2$ commonly



- 1 alkaline concrete + 0.2% chloride
- 2 alkaline concrete + 0.5% chloride
- 3 alkaline concrete + 0.5% chloride + 1% NaNO₂
- 4 alkaline concrete + 2% chloride + 1% NaNO₂
- 5 alkaline concrete + 2% chloride + 2% NaNO₂
- 6 carbonated concrete + 0.5% chloride + 1% NaNO₂

Fig. 7: Influence of sodium nitrite upon the anodic polarisation of steel in chloride-containing concrete after 7 days [7]

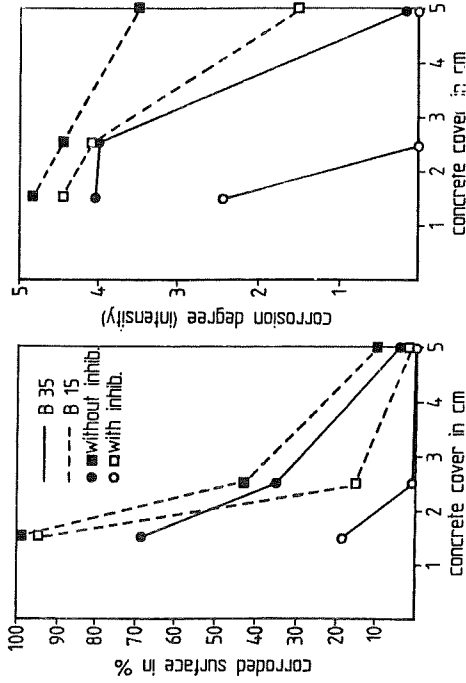


Fig. 8: Corrosion of reinforcing steel in cracked concrete (crack width $w=0.1$ to 0.45 mm) after 2.5-years exposure to sea water analog to splash zone; concrete with and without inhibitor (3M-% Ca(NO₂)₂ [13])

used at the moment, a content of 2 % by mass (in relation to the cement content) is required for the case of an external chloride attack. In the case of carbonation and simultaneous presence of chloride ions in the concrete, higher inhibitor contents are necessary for suppressing corrosion, compared with carbonation of concrete only or concrete containing only chlorides /7, 9, 10/.

Even for reinforced concrete elements submitted to chlorides it may be assumed that the effectivity of inhibitors decreases with decreasing concrete quality and concrete cover, as the inhibitors diluted in the pore water may be washed out from concrete more easily with increasing porosity of the hardened cement paste and increasing proximity of the inhibitors to the concrete surface. Fig. 8 shows the influence of concrete quality and cover upon the corrosion behaviour of steels in concrete elements with and without inhibitors (3 % $\text{Ca}(\text{NO}_2)_2$) after 2.5 years exposure to sea water. For B15 and a concrete cover of 1.5 cm no influence of the addition of an inhibitor upon corrosion has been observed. Even for the high-quality B 35, corrosion could not be completely eliminated for low concrete covers. For a poor concrete quality and a low concrete cover, the effect of the inhibitor may be permanently neglected. It is therefore recommended in /5, 6/ to use inhibitors containing nitrite only if the water-cement-ratio is low ($\text{W/C} < 0.50$), the cement content is high ($> 300 \text{ kg/m}^3$) and the concrete cover is high too ($> 3 \text{ cm}$). However, under these conditions, a concrete without inhibitors has a high protective effect too.

4.2 Cracks in concrete /8, 13/

From the point of view of corrosion, cracks in concrete are very important because they accelerate a carbonation of concrete and facilitate the penetration of corrosive agents (especially chlorides). By field tests with cracked concrete elements it has been observed that nitrites in carbonated cracks temporarily have a certain protective effect. A complete and durable elimination of corrosion was not possible because the concentration of the inhibitor decreases after a certain time. In a cracked concrete exposed to temporary attacks by sea wa-

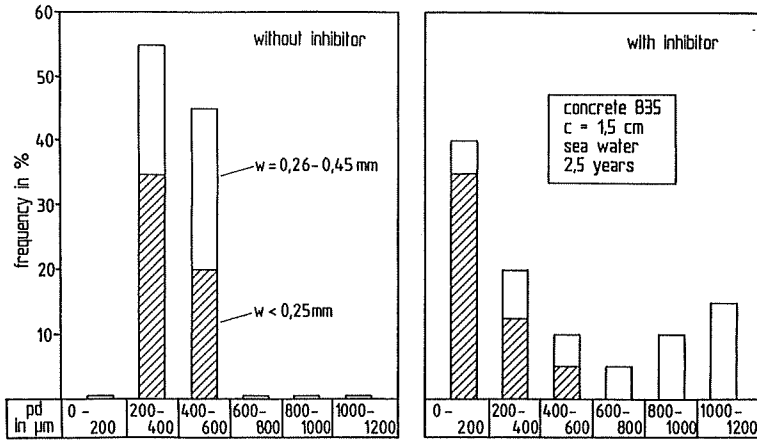
ter and permanent weathering, the corrosion-protecting effect of inhibitor. $\text{Ca}(\text{NO}_2)_2$ in the concrete crack was limited to less than one year if the concrete crack width was >0.2 mm. In the wider cracks, the inhibitors were leached out within a few months.

4.3 Formation of electrochemical cells

Using anodic inhibitors, especially passivators, corrosion cells may develop for instance in the case of underdosage or segregation. The uniform corrosion (loss of mass) is rather diminished, but pitting corrosion may be increased (chap. 2). In concrete constructions, the quoted phenomena especially appear in concrete cracks and while using passivators ("dangerous inhibitors"). Fig. 9 shows the evaluations: the frequency of a maximum pitting depth NT in concrete cracks is indicated in relation to the crack width w and an addition of inhibitors after an outdoor storage of cracked reinforced elements over a period of 2.5 years and occasional exposure to sea water. It is noticed that, owing to the addition of an inhibitor to concrete, the intensity of pitting corrosion decreases within the area of the more narrow cracks ($w < 0.25$ mm) and on the contrary, increases in the wider cracks ($w = 0.26 - 0.45$ mm). In the inhibitor-free concrete the pit depth was always < 0.6 mm; in the concrete containing inhibitors, 30 % of the pits had depths between 0.6 and 1.2 mm.

Because of the relations described, it may be concluded that anodic inhibitors in concrete may only reliably protect against corrosion if the concrete is of high quality, and doesn't have a too low concrete cover. Segregation of inhibitor may produce locally increased corrosion.

An attempt has been made to alternatively fight against corrosion in concrete with cathodic inhibitors. They decrease the presence of dissolved oxygen on the surface of the metal and thus, reduce corrosion attack. They don't protect as well as anodic inhibitors, but they prevent local attacks such as pitting corrosion and wide pitting. Unfortunately, inhibitors suitable for the pH-area



Depth of pitting pd in concrete cracks of different width w; concrete with and without inhibitor (c = concrete cover)

Fig. 9: Pit depth NT within the area of concrete cracks with different crack width after a 2.5-years outdoor storage and occasional exposure to splash water; concrete without and with inhibitor $\text{Ca}(\text{NO}_2)_2$ [13]

of concrete hardly exist. In [14] the effect of hydroxyphosphono-acetic-acid (HPE), hydroxyphosphono-tetracarboxy butane (PBTC) and sodium molybdate upon corrosion of steel in alkaline concrete containing chlorides and carbonated concrete was investigated, for a cathodic effectivity of these inhibitors had been assumed. The concentration of inhibitors, chosen in accordance with the solubility of calcium salts (for HPE and PBTC), was 0.05 % by mass (HPE, PBTC) or 2 % by mass (sodium molybdate) in the alkaline solutions and 0.25 % or 10 % by mass in the carbonated solutions. No inhibition of cathodic reaction of oxygen reduction could be observed for the investigated substances. PBTC has a pitting-inhibiting effect in alkaline environments; HPE, PBTC and molybdate have a passivating effect in carbonated electrolytes.

5 REFERENCES

- [1] Autorenkollektiv:
Korrosionsinhibitoren; Hrsg. D. Kuron, Verlag Irene Kuron, Bonn 1994
- [2] U.R. Evans:
Korrosion, Passivität und Oberflächenschutz von Metallen. Springer-Verlag, Berlin 1939 und London 1948.
- [3] R.J. Craig, L.E. Wood:
Effectiveness of corrosion inhibitors and their influence on the physical properties of portland cement mortars. Highway Research Record 328 (1979) 77-88.
- [4] A.M. Rosenberg, J.M. Gaidis, T.G. Kossivas, R.W. Previte:
A corrosion inhibitor formulated with calcium nitrite for use in reinforced concrete, S. 88-99; in "D.E. Tonini, S.W. Dean: Chloride corrosion of steel in concrete". STP 629, ASTM, Philadelphia 1976.
- [5] N.S. Berke:
Corrosion inhibitors in concrete. Corrosion 89, Symposium on "Corrosion of Metals in Concrete", NACE, Houston 1989.
- [6] B.El.-Jazairi, N.S. Berke:
The use of calcium nitrite as a corrosion inhibiting admixture to steel reinforcement in concrete, S. 571-585; in "C.L. Page, K.W.J. Treadaway, P.M. Bamforth: Corrosion of reinforcement in concrete". Elsevier Applied Science, London - New York 1990.

- [7] G. Rehm, A. Rauen:
Electrochemical studies on corrosion inhibitors of steel in concrete.
RILEM-Symposium "Durability of Concrete", Prag 1969.
- [8] D. Briesemann:
Korrosion-Inhibitoren für den Stahl in Beton. Zement - Kalk - Gips 2
(1973) 88-91.
- [9] C. Alonso, C. Andrade:
The effect of nitrite as corrosion inhibitor in carbonated mortar containing
or not chlorides. RILEM J. (1988).
- [10] J.A. Gonzales, S. Algaba, C. Andrade:
Corrosion of reinforcing bars in carbonated concrete. Brit. Corros. J. 15
(1989) 135-139.
- [11] K. Gouda:
Anodic polarisation measurements of corrosion and corrosion inhibition
of steel in concrete. Brit. Corros. J. 1 (1966) 138-142.
- [12] N. S. Berke, K. M. Sundberg:
The effect of admixtures and concrete mix designs on longterm concrete
durability in chloride environments. Corrosion 89, Symposium on
"Corrosion of Metals in Concrete" NACE, Houston 1989.
- [13] U. Nürnberger, W. Beul:
Einfluß einer Feuerverzinkung und PVC-Beschichtung von
Bewehrungsstählen und von Inhibitoren auf die Korrosion von Stahl in
gerissenem Beton. Werkstoffe und Korrosion 42 (1991) 537-546.

- [14] U. Nürnberger, K. Menzel, W. Beul, G. Onuseit, F. Schulze:
Korrosionsschutz in Beton. Forschungsvorhaben 11F6121 im Auftrag des
Bundesministeriums für Forschung und Technologie. Forschungs- und
Materialprüfungsanstalt, Baden-Württemberg, Stuttgart 30.8.93 und
Werkstoffe und Korrosion 44 (1993) 154-155.