Corrosion inhibitors for steel in concrete – an update
Inibitori di corrosione per l’acciaio nel calcestruzzo - un aggiornamento

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Abstract: 16 years ago a first state of the art report “Corrosion Inhibitors for Steel in Concrete” has been published as EFC publication No. 35. Industry continued to develop and improve admixtures that can be added to the fresh concrete (preventative) or systems that can be used as surface applied inhibitors (curative). This paper presents an update on the state of the art on corrosion inhibitors, with particular emphasis on long-term and especially field studies. There is a general agreement from both laboratory and field studies that mixed-in corrosion inhibitors can delay the onset of chloride-induced corrosion in good quality concrete by a factor of about 2. The reduction of the corrosion rate once corrosion has initiated appears to be much less significant. Surface applied inhibitors can show positive results only at low chloride concentrations and with beginning corrosion.

Keywords: Corrosion, reinforcement, corrosion prevention, admixture, inhibitor, surface applied

Riassunto: 16 anni fa un primo stato dell’ arte “Inibitori di corrosione per il calcestruzzo armato” è stato pubblicato come EFC numero 35. Gli inibitori di corrosione vengono utilizzati maggiormente come tecnica preventive, dunque aggiunti durante l’impasto del calcestruzzo. In questo caso i risultati di prove in laboratorio ed il comportamento in pratica indicano che il tempo di innesco di corrosione viene prolungato da un fattore di circa due. La riduzione della velocità di corrosione invece non è significativo. Inibitori applicati sul calcestruzzo indurito come sistema di ripristino hanno mostrato risultati positivi solamente a tenori di cloruro bassi e quando la corrosione è in fase iniziale.

Parole chiave: corrosione, calcestruzzo armato, inibitori, prevenzione, ripristino

INTRODUCTION

In general, reinforced concrete has proved to be successful in terms of both structural performance and durability. Premature failure of reinforced concrete components (corrosion of the reinforcement) occurs due to the ingress of chloride ions from de-icing salts or seawater or the reaction of the alkaline pore solution with carbon dioxide from the atmosphere (carbonation) [1]. In 2001 a first state of the art report “Corrosion Inhibitors for Steel in Concrete” was published [2]. Since then the use of “corrosion inhibitors” got increasing interest as these substances can be used in reinforced concrete either as preventative measure for new structures (addition to the mixing water) or as surface applied inhibitors for preventative and restorative purpose. Especially the easy application from the concrete surface could be an economically interesting alternative to the traditional restoration methods as it could increase the lifetime of structures that already show some corrosion attack. Most of the results published in literature refer to laboratory studies using solution experiments or relatively small mortar or concrete samples. This paper focuses on long-term field tests that are still rare.

CORROSION INHIBITORS USED AS ADMIXTURES (PREVENTATIVE)

The most frequently used technique is adding of the inhibitors to the mixing water of concrete as admixtures for new structures in order to prevent or at least delay the onset of corrosion (see a recent publication of the authors [3]). A large number of pure substances and commercial inhibitors have been studied in solutions and in mortar or concrete [4, 5]. A critical ratio of inhibitor to chloride concentration around 1 has been reported in order to prevent the onset of corrosion both for calcium nitrite [6] and for a commercial migrating inhibitor blend [7]. Indeed, only 10% of inhibitor blend was able to prevent the onset of corrosion (Figure 1a). For the commercial inhibitor blend both components (identified as dimethylethanolamine and benzoate) have to be present at the steel surface to effectively delay the onset of corrosion [7]. This has been confirmed by XPS and ToF SIMS surface analysis on steel in alkaline solutions [8].

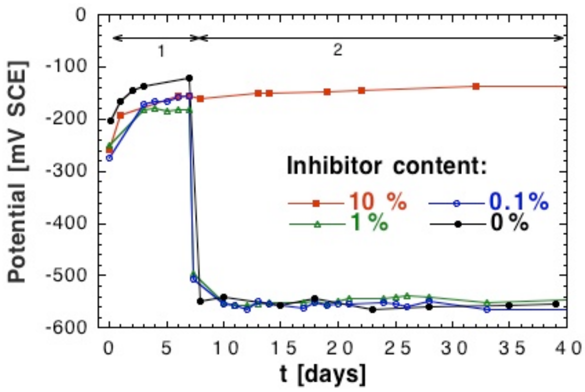

Figure 1: Influence of the inhibitor concentration on corrosion performance of steel in alkaline pore solution pH 13.5. Phase 1: no chlorides, phase 2: 1 M NaCl in the pore solution [7]

FIELD TESTS WITH ADMIXED CORROSION INHIBITORS

Despite a great number of laboratory research works [2, 3] and a widespread application of corrosion inhibiting admixtures, well-documented field studies, especially of long-term duration, are rare. This lack of information about field performance makes it difficult to specify appropriate product requirements. In the following, major field tests are summarized:

Florida department of transportation (FDOT) studies: As part of a ten years study on the efficiency of corrosion inhibitors also field studies with so-called “field columns” were performed [9]. This field specimen configuration had been used for more than 20 years to assess the field performance of reinforced concrete. Three inhibitor blends were compared. After ten years it was concluded that only calcium nitrite (DCI) appeared to provide some performance improvement, ranging from negligible to a factor of 3 in delaying the time to corrosion. The organic inhibitor blends (Ferrogard and Rheocrete) showed no consistent trend and no significant improvement.

Canada, Vachon Bridge: During a period of ten years researchers at the National Research Council Institute (NRC-IRC) studied the effectiveness of different commercially available corrosion-inhibiting systems on the Vachon Bridge in Laval, Québec, Canada [10]. During a major rehabilitation project concrete barrier walls were selected because of their high exposure to de-icing salts and their accessibility to perform measurements. The concrete mix design had a water-cement ratio of 0.36 and a cement content of 450 kg/m3, cement type similar to ASTM Type I, resulting in a 28-day compressive strength exceeding the required 35 MPa. The concrete cover was 75 mm. Organic concrete admixtures (alkanolamines, ethanol-amine and phosphate) as well as inorganic concrete admixtures (calcium nitrite) were added to the fresh concrete by the manufacturers. Measurements included half-cell potential, polarization resistance and corrosion detection by rebar ladders. After 5 years of exposure, the chloride content at a depth of 13 to 25 mm in all test sections significantly exceeded the value of 1.4 kg/m^3 (0.3% by cement weight) that was considered critical. At year 10 (2006) the chloride contents at a depth of 50 to 75 mm in all test sections were near but below the critical value. Based on corrosion current density measurements, it was found that the tested inorganic inhibitor (calcium nitrite) and the organic corrosion inhibitors performed slightly better than the control concrete. From potential measurements, it was apparent that all inhibitors also were able to delay corrosion initiation, however only moderately.

Hawaii harbor field test: A long-term field exposure study was conducted to evaluate corrosion inhibitors in a marine environment (Honolulu Harbor). Twenty-five field panels were constructed (concrete with w/c ratio

0.4), exposed to the tidal zone. The panels were monitored with half-cell potential measurements and by assessing visual appearance. The results after 9 to 10 years of exposure showed that control specimens had negative potentials after 40 month and cracks and or rust after 7 years. Specimens with 20 L/m^3 calcium nitrite (DCI) did not show negative potentials and also no visual appearance of rust or cracks after 10 years. Rheocrete or Ferrogard inhibitors added according to manufacturer dosage showed no improvement with respect to the control panels [11]. These results were confirmed by weight loss analysis at the end of the tests [12].

Field tests in Switzerland: A long-term field trial was initiated in the early 1990s in Switzerland with a proprietary inhibitor formulation based on alkanolamines (Sika FerroGard 901). Reinforced concrete elements were cast with Portland cement concrete (w/c=0.45) with and without inhibitor (reference specimen) and exposed to chlorides (deicing salt splash water) at a road in the Swiss Alps. Inspections were perfomed on a regular basis (intervals of 3 years), which included the determination of chloride content in the cover concrete and measurements of steel potentials, galvanic currents and concrete resistivity. After 18 years of exposure, the reinforcing steel was visually inspected (after removal of the cover concrete) in selected areas [13]. Furthermore, additional electrochemical measurements were performed. It was found that at a cover depth of 15 mm corrosion had initiated after approx. 8-9 years in the concrete without inhibitor. In the sample containing the admixed inhibitor, the steel at the same cover depth was after 18 years still largely free from corrosion. This factor of roughly 2 in delaying corrosion initiation is in agreement with short-term laboratory studies. In contrast to other literature results, however, the prolongation of the initiation period was not attributed solely to a slightly higher chloride threshold value (0.8% by weight of cement instead of 0.7%) but also to a (moderately) lower chloride diffusivity in the inhibitor containing concrete [13].

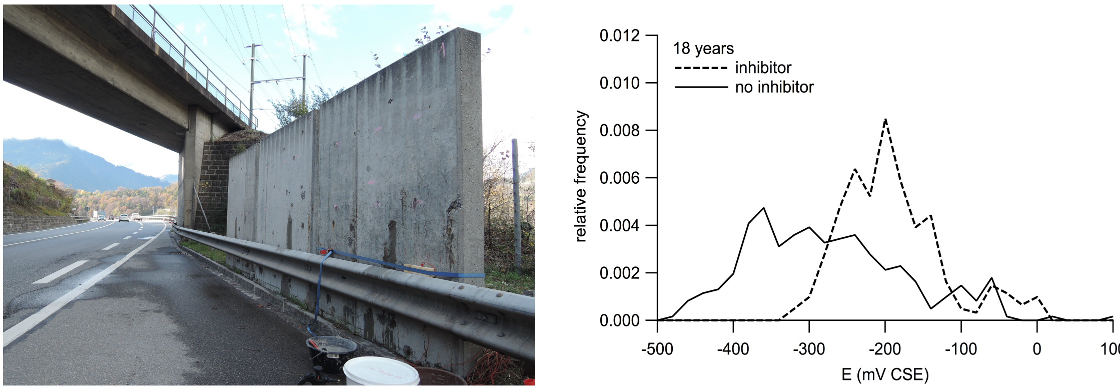

Figure 2: Left: Concrete specimens exposed in Swiss field test. Right: Statistical distribution of half-cell potentials after 18 years of exposure for the concrete with and without admixed inhibitor [13]

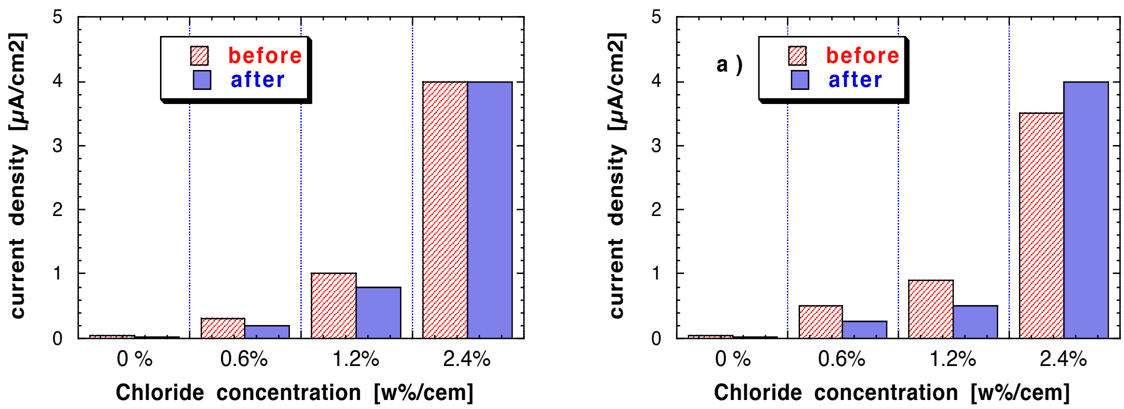

Figure 3: Corrosion rate of rebars in mortar (w/c 0.65) prior and after treatment with inhibitor. Left: MFP, right: proprietary alkanolamine based inhibitor, after Page et al. [5, 14, 15].

SURFACE APPLIED CORROSION INHIBITORS

At the time of the first review [2] only few works dealing with this topic were available, since then several laboratory and field tests have been performed with surface applied inhibitors. For mono-fluorophosphate (MFP) repeated drying and MFP immersion cycles allow the penetration of the inhibitor to the steel. In a research at Aston University [5, 14, 15] 15% by weight solutions of MFP were applied repeatedly to reinforced concrete specimens (w/c 0.65, cover 12 mm) with various levels of chloride contamination. The embedded bars, pre-corroded under cyclic wetting and drying conditions for about 6 months prior to the MFP treatment, did not exhibit marked reductions in corrosion rate (figure 3). Surface application of a commercial migrating inhibitor blend did not result in a reduction of the corrosion rate because only one component of the blend (volatile dimethylethanolamine) reached the steel surface [7].

CONCLUSIONS

Corrosion inhibitors used as admixtures to fresh concrete when used in the correct dosage can delay the onset of chloride-induced corrosion by a factor 2. Once corrosion has started no significant reduction of the corrosion rate has been found.

The performance of surface applied organic and inorganic inhibitors intended to stop or at least reduce ongoing chloride induced corrosion cannot be considered positive. Some success can be expected for low chloride concentrations (< 0.5%) and low corrosion rates.

Engineers and contractors working in the area of concrete maintenance should be aware of the fact that the composition of proprietary corrosion inhibitors marketed under different trade names may change with time and geographical region [3].

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