

# Organic Corrosion Inhibitors for Steel in Concrete

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## ABSTRACT

The efficiency of an organic corrosion inhibitor blend in preventing and stopping ongoing chloride-induced corrosion of mild steel has been investigated in saturated,  $\text{Ca}(\text{OH})_2$  solutions and in ordinary Portland cement (OPC) mortar. The results show that only high concentrations of the inhibitor ( $\approx 10\%$ ) allow the inhibition of pit initiation in solution. However, the inhibiting properties can be lost either by evaporation of the volatile constituent of the inhibitor or by the precipitation of the non-volatile fraction of the inhibitor in presence of calcium ions. The addition of the inhibitor blend to mortar yielded no inhibiting effect except the retardation of the corrosion initiation in the case of chloride-induced corrosion. Once corrosion had started the polarisation resistance values were similar for samples with and without inhibitor. On already corroding steel samples in chloride-containing saturated  $\text{Ca}(\text{OH})_2$  solutions a slight increase (*ca.* 3–4 $\times$ ) of the polarisation resistance was found after adding 10% inhibitor to the solutions. No significant increase of the polarisation resistance was observed after applying the inhibitor on chloride-containing mortar samples with corroding steel. Field tests on chloride-contaminated structures also showed that virtually no effect of the surface applied organic inhibitor blend on half cell potentials or a reduction of macrocell currents were found.

## 1. Introduction

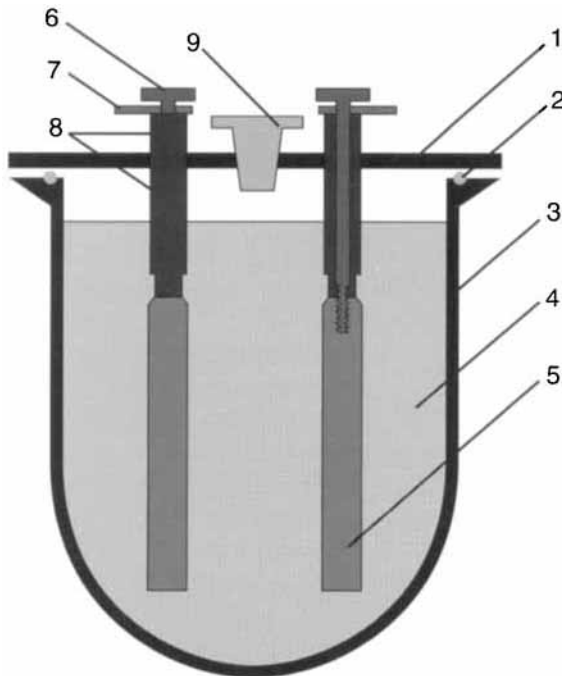
Corrosion of reinforcing steel due to chloride ingress from de-icing salts or carbonation represents the most widespread form of deterioration of concrete structures. Despite the huge demand, a simple, cheap, and reliable technique which either protects the steel from corrosion or at least lowers its corrosion rate is still lacking. Over the past decade, however, the concrete repair industry has developed novel techniques that are claimed to prevent or at least reduce corrosion of steel in concrete. These ‘corrosion inhibitors’ can be used in reinforced concrete as preventive measure for new structures (as addition to the mixing water) or as surface applied inhibitors for repair purpose. The application from the concrete surface could be an especially promising technique to protect already existing structures or increase lifetime of structures that are already showing corrosion. The published knowledge is summarised in a recent state of the art report on corrosion inhibitors for steel in concrete [1]. Regarding organic corrosion inhibitors, a broad variety of compounds can inhibit corrosion of steel in neutral and alkaline environments [2,3]. The published results for organic inhibitors in concrete

repair systems mostly concern commercially available systems and are conflicting: hydroxyalkylamine based blends are reported to exhibit inhibiting properties against chloride-induced pitting corrosion in laboratory and field tests [4–6] but on the other hand insignificant inhibiting properties of a dimethylethanolamine in concrete have been reported [7]. This might in be due to the rather limited information regarding the detailed composition of these products and to a shortage of publications from independent research in this field [8].

The aim of this investigation is the evaluation of the efficiency of various organic inhibitor blends [4–6]. The inhibiting properties were determined (a) in solution, in order to determine the critical concentration of the inhibitor, and (b) with mortar samples, to characterise the behaviour under more realistic conditions for preventive and repair application.

## 2. Experimental

The cell used for immersion experiments is shown in Fig. 1. Three rebars (sand blasted and degreased in acetone and ethanol) were mounted in the cell. Saturated  $\text{Ca}(\text{OH})_2$  solution (pH 12.5) was used to simulate the alkaline pore solution of concrete and 0.1, 1 and 10% of an organic inhibitor blend was added. The cell was closed with a plug in order to avoid evaporation of the volatile part of the inhibitor and only opened



*Fig. 1 Experimental set-up for immersion experiments with simultaneous monitoring of the corrosion potential and the polarisation resistance: 1. PMMA-cover; 2. O-ring; 3. glass vessel; 4. solution; 5. rebar; 6. stainless steel screw; 7. electrical contact; 8. PVC-pipe; 9. plug.*

for short time intervals to provide oxygen in the gas phase. After prepassivation for 7 days, allowing the formation of a stable passive film, the solution was replaced by with saturated  $\text{Ca}(\text{OH})_2$  containing 1M NaCl.

The corrosion potential (SCE) and the polarisation resistance (measured at  $0.1 \text{ mV}^{-1}$  in the range of + 10 mV relative to the corrosion potential with a Zahner IM6) were recorded over time.

Experiments in mortar were performed with cylindrical lollipop type samples containing a sand blasted rebar (Fig. 2). Mortar with a w/c ratio of 0.75, cement content of  $350 \text{ kg m}^{-3}$  and cement/sand ratio of 1:3 was used. After casting and demoulding the samples were cured for 70 days in 100% relative humidity. One series of samples was prepared with admixed inhibitor blend in concentrations (0, 0.015, 0.075 and 0.375% by weight of cement); after curing and drying in the laboratory the samples were subjected to cyclic treatment with 2.5 days drying in air and 1 day immersion in 6% NaCl solution. A second series without inhibitor was subjected to cyclic treatment as above. After the onset of corrosion the samples were dried for 24 h at  $30^\circ\text{C}$  and 40% RH and then soaked once with pure solution of the inhibitor blend for 24 h. The corrosion potential, the ohmic resistance and the polarisation resistance of all the embedded steels was determined after each cycle by rapid galvanostatic pulse measurement [9].

### 3. Results

The formation of a passive film in chloride-free solution in the first seven days results in increases of the corrosion potential and the polarisation resistance. After the change to chloride-containing solutions, a sharp drop of the corrosion potential and the polarisation resistance was observed, indicating the onset of pitting corrosion. As previously reported, concentrations below 10% of the inhibitor blend cannot avoid pitting corrosion in saturated  $\text{Ca}(\text{OH})_2$  with 1M NaCl [2]. In solutions with 1% inhibitor an increase of the polarisation resistance by a factor of about 3 compared to the non-

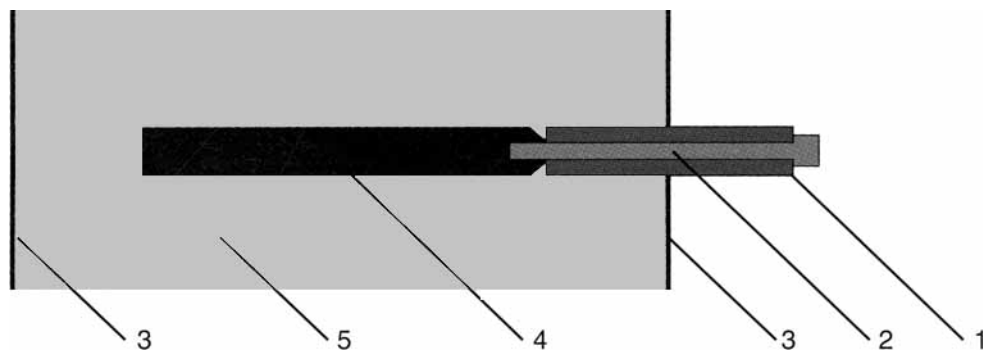


Fig. 2 Sample geometry for the investigation of the inhibiting of the inhibitor in mortar. The diameter of the mortar cylinder is 42 mm; 1. PVC pipe; 2. stainless steel screw; 3. epoxy resin; 4. rebar; 5. mortar.

inhibited solution was observed [10]. Opening of the cell after 50 days of exposure of the rebars to a saturated  $\text{Ca}(\text{OH})_2$  + 1M NaCl solution with 10% of inhibitor blend resulted in a drop of the open circuit potential and the polarisation resistance within a few days (Fig. 3), indicating the initiation of pitting.

Chemical analysis of the inhibitor blend revealed that it consists of more than 90 % of a volatile hydroxyalkylamine (mainly dimethylethanolamine), while the other non-volatile part was composed of carboxylic acids (mainly benzoic acid) that were separated by distillation at 30°C at 40 mbar. The two fractions were added separately to the saturated  $\text{Ca}(\text{OH})_2$  solution in the relative concentration corresponding to a 10% inhibitor content in the solution (0.5% and 9.5% respectively). As reported already [10], the potential drop after the change of the solution shows that neither the volatile nor the non-volatile fraction of the inhibitor alone can prevent the initiation of pitting corrosion, but addition of both fractions result in an increase of the polarisation resistance by a factor of 2–3 compared to the non-inhibited solution.

The time to corrosion initiation (drop in corrosion potential and in polarisation resistance) was determined for all mortar samples of the series with admixed inhibitor subjected to cyclic chloride ponding. The first activation occurred in the series without inhibitor, after about 60 days. The first activation in the series with high concentration of the inhibitor was observed 30 days later, thus the initiation of pitting corrosion when chlorides penetrate from outside is delayed. Additionally, the time period to activate all six samples of a series is much longer for the inhibited samples than for

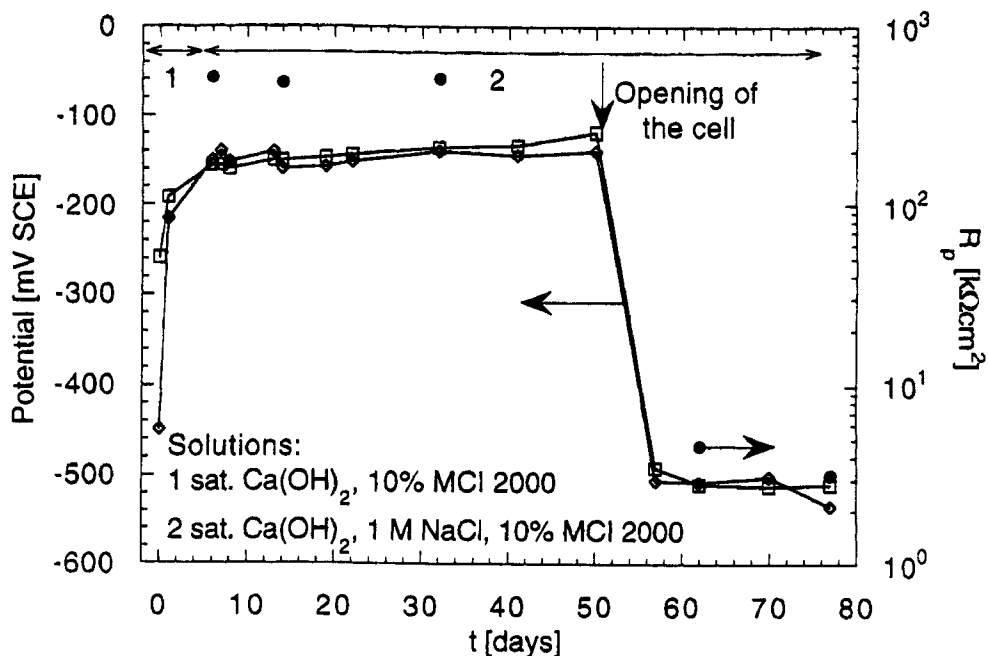


Fig. 3 Repeated experiments of corrosion potential and polarisation resistance of rebars in satd  $\text{Ca}(\text{OH})_2$  containing 10% inhibitor. After 50 days the cell was opened by removing the plug in the cover (MCI 2000 is the commercial amine-based inhibitors).

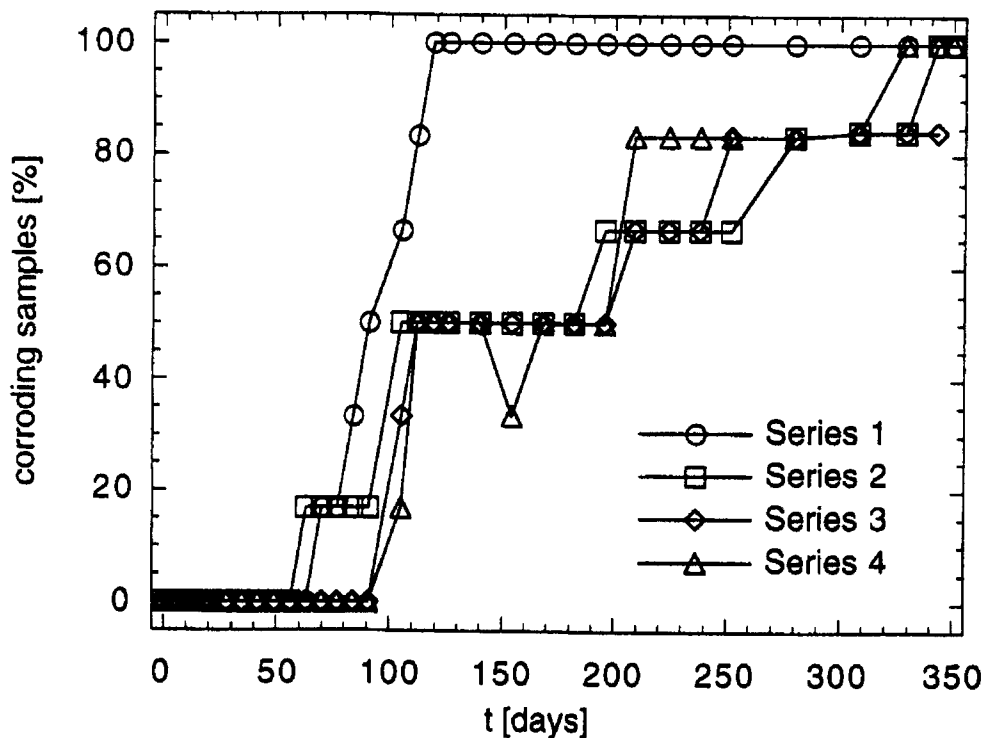


Fig. 4 Percentage of corroding samples plotted against the time of cyclic wet/dry treatment. Inhibitor content: series 1, 0; series 2,  $0.35 \text{ kgm}^{-3}$ ; series 3,  $1.75 \text{ kgm}^{-3}$  (recommended dosage); series 4,  $8.75 \text{ kgm}^{-3}$ .

the inhibitor-free-samples (Fig. 4). No significant differences between the different inhibitor contents can be observed. This result from electrochemical measurements was confirmed by measuring the mass loss of all the samples studied [10].

Samples with active chloride-induced corrosion in saturated,  $\text{Ca}(\text{OH})_2 + 1\text{M NaCl}$  solutions showed an increase of the polarisation resistance by a factor 3–4 after addition of 10% of inhibitor blend (Fig. 5). The effect of adding inhibitor to chloride-containing mortar samples with corroding steel bars (Fig. 6), simulating a restoration treatment with surface applied inhibitor was to show a slight increase of the open circuit potential but no significant change in polarisation resistance.

## 4. Discussion

### 4.1. Corrosion Initiation

When sufficiently high concentrations are present at the steel surface, the organic inhibitor blend demonstrates a marked effect on pit initiation in the solutions containing  $1\text{M NaCl}$ : no pitting corrosion occurs at an inhibitor content of 10% but at

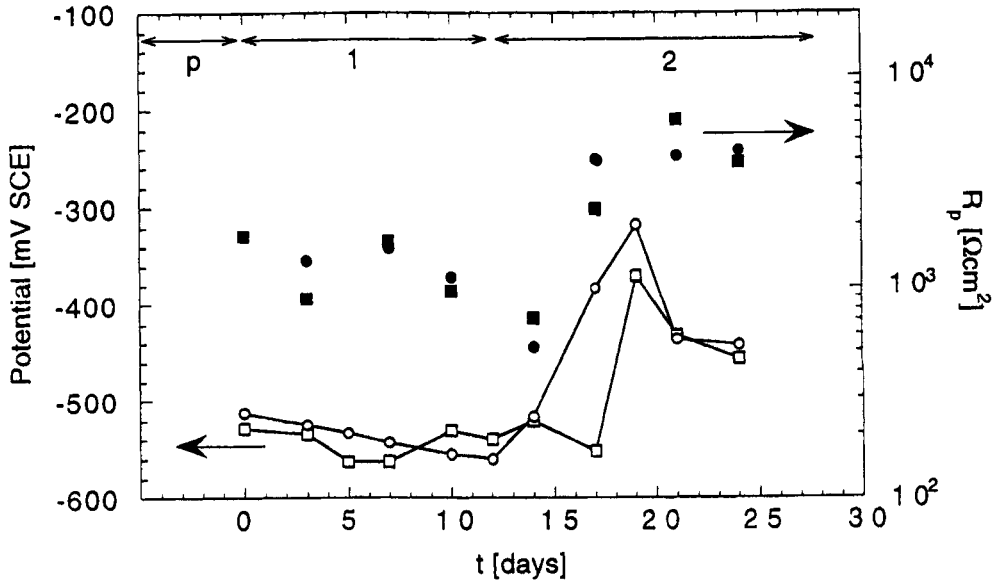


Fig. 5 Corrosion potential and polarisation resistance of rebars pre-corroded in satd.  $\text{Ca(OH)}_2 + 1\text{M NaCl}$  (phase 1). After 12 days 10% of inhibitor was added to the solution (phase 2).

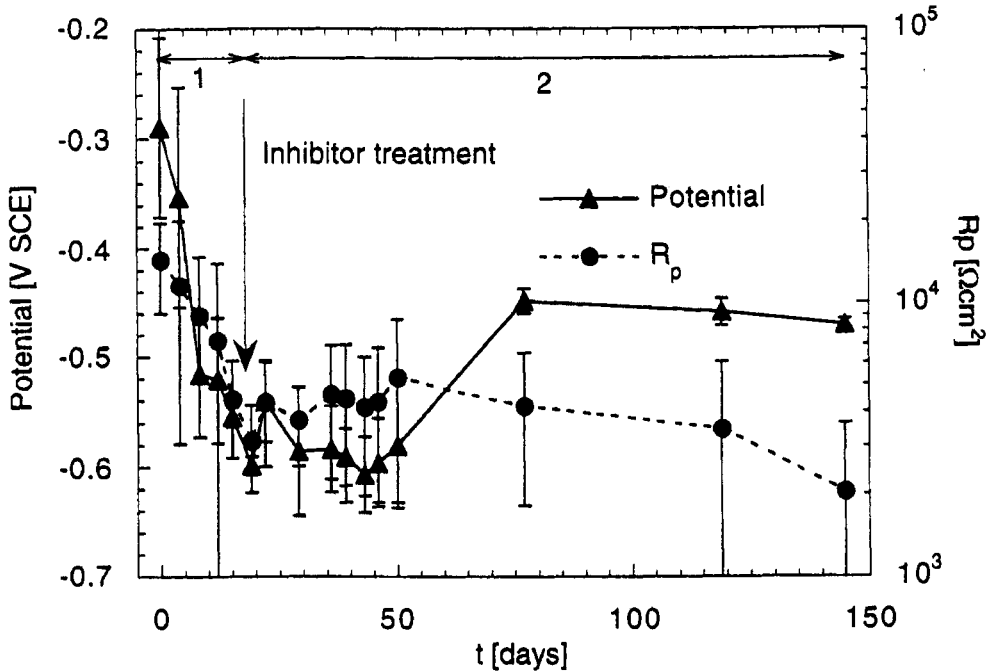


Fig. 6 Polarisation resistance and corrosion potential of steel in mortar samples. Time period 1: cyclic treatment with 1M NaCl solution; Time period 2: 80% humidity. After 12 days the samples were dried and soaked for 24 h in pure inhibitor.

concentrations of 1% pitting corrosion is initiated similar to the non-inhibited solution. For the inhibition of pit initiation, both constituents of the inhibitor blend have to be present on the steel surface, as has been shown by the separate investigation of the two fractions of the inhibitor [10]. Despite the comparatively high concentration of 9.5%, the volatile fraction (mainly dimethylethanolamine) cannot prevent the onset of pitting corrosion. This result is in agreement with the relatively poor inhibiting properties reported for the pure dimethylethanolamine [7,11] and surface analytical studies, where no specific adsorption of dimethylethanolamine on passive steel in alkaline solution was found [12,13]. The presence of the non-volatile fraction is thus crucial for the observed inhibiting effect of the inhibitor blend, but this fraction alone also cannot prevent steel from the initiation of pitting corrosion. Evaporation of the volatile fraction (after opening of the cell) results in a decrease of the dimethylethanolamine concentration in solution and chloride-induced corrosion that starts (Fig. 3). Hence, for the inhibition of the corrosion initiation in chloride-containing solutions a sufficiently high concentration and the presence of both inhibitor fractions are required.

Experiments in mortar with inhibitor demonstrated clearly (Fig. 4) that the corrosion initiation is delayed. However, unlike the experiments in solutions, initiation of pitting corrosion cannot be prevented. The evaluation of the chloride content yielded comparable values for all sample series after 380 days of cyclic treatment in chloride solution. Thus, the inhibitor blend does not influence the chloride transport and the observed delaying effect on the initiation of pitting corrosion is caused by its inhibiting properties.

#### 4.2. Corrosion Propagation

Besides the inhibition of the corrosion initiation, corrosion inhibitors can also influence the corrosion rate after the onset of pitting. In the present work the corrosion rate was obtained by determination of the polarisation resistance. The use of these values for absolute comparison can be critical, as the area of the active corrosion site is not known. The polarisation resistance is normalised with the whole sample surface, which is of course mainly passive. Therefore, differences in the polarisation resistance could be exclusively due to a different pit size instead of a different propagation rate of the pit. Nevertheless, the obtained polarisation resistances are useful for a qualitative comparison of the effect of the corrosion inhibitor.

In chloride-containing solutions the inhibitor indeed has an influence on the corrosion rate after the initiation of pitting. According to Table 1 a concentration of 1% inhibitor cannot prevent the initiation of pitting corrosion, but the polarisation resistance is about four times higher, indicating a lower corrosion rate.

Contrary to the experiments in solution, no effect of the inhibitor on the corrosion rate was found in mortar experiments. This result was obtained by polarisation resistance measurements and was confirmed by determination of the mass loss of the rebar [10]. Hence, the inhibitor added to the mortar mix does not affect the corrosion rate in mortar after initiation. For application on new structures it can thus be concluded that the inhibiting effect is limited only to some retardation of the corrosion initiation.

**Table 1.** Polarisation resistance of the samples immersed in  $\text{Ca}(\text{OH})_2$  solution with different content of inhibitor after the addition of chlorides

| Mass% inhibitor | $R_p$ ( $\text{k}\Omega\text{cm}^2$ ) |
|-----------------|---------------------------------------|
| 10              | $490 \pm 80$                          |
| 1               | $11 \pm 3$                            |
| 0.1             | $2 \pm 1$                             |
| 10              | $3 \pm 1$                             |

## 5. Pre-corroded Samples

No reduction of the corrosion rate was found when applying the inhibitor blend on chloride-containing mortar samples where pitting corrosion of the rebars was ongoing (Fig. 6), despite a significant reduction found in solution (Fig. 5) and a high diffusion rate reported for the inhibitor [14,17]. A similar result was reported in recent work of Page and Ngala [8] which studied another proprietary, alkanolamine-based blended inhibitor known to contain ethanolamine and an inorganic phosphate. Repeated ponding and drying according to the manufacturer's dosage caused only a modest reduction in the corrosion rates of pre-corroded steel bars embedded at 12 mm depth in concrete with 0.65 w/c and with low to modest levels of chloride contamination and was apparently ineffective in cases of high chloride content (2.4% by mass of cement). A possible explanation of this discrepancy may be that the blended inhibitor studied in this work may have fractionated and only the volatile part of the inhibitor (hydroxyalkylamine) shows a high diffusion rate and reaches the steel surface [10]. The same inhibitor as studied in [8] was included in a field test with surface applied inhibitors on chloride-contaminated structures and no reduction in the corrosion rate (macrocell current) was found [18].

## 6. Inhibitor Concentration

The inhibition or retardation of the initiation of pitting corrosion requires a comparatively high concentration of 10%. Typical amine concentrations for the inhibition of uniform corrosion in acidic solutions are in the region of  $10^{-4}$  mol  $\text{L}^{-1}$ . This contrast is a result of the completely different corrosion mechanisms which are taking place for example, in acidic solutions where the bare metal surface is in contact with the electrolyte and the adsorption of specific inhibitor molecules on the metal can result in a strong decrease of the corrosion rate. In alkaline solutions iron is protected against uniform corrosion by the passive film. Corrosion is initiated locally in the presence of chlorides leading to a heterogeneous system with separated anodes and cathodes, adverse mass transport conditions in the pit, and migration of ions. It is beyond the scope of the present work to discuss the detailed mechanisms, but it is



a generally observed phenomenon that inhibitors of pitting corrosion require high concentrations. For nitrite [15] and monofluorophosphate (MFP) [16] the ratio between inhibitor and chloride concentration is reported to be in the order of 1. Considering the molar weight of the dimethylethanolamine of  $89.14 \text{ gmol}^{-1}$  and the chloride concentration of  $1 \text{ mol L}^{-1}$  used in this work, a ratio of inhibitor/ $\text{Cl}^-$  of about 1 is also obtained.

## 7. Stability and Long-term Efficiency

The efficiency of the inhibitor blend was investigated in accelerated tests to obtain information within a reasonable time scale. The acceleration was obtained by a strongly enhanced penetration of chlorides due to the cyclic treatment. However, the obtained results are only correct when no other relevant time-dependent processes are taking place or when they are accelerated in the same way. Surface application of organic inhibitor on mortar samples with corroding steel did not show any reduction in the corrosion rate (Fig. 6) in agreement with long term laboratory studies [8] and with field tests on chloride-contaminated structures [18].

On considering the loss of inhibiting effect observed in experiments performed in solutions (Fig. 3) when evaporation of the inhibitor occurs, the question arises whether this process might have an influence on the long-term performance of the commercial inhibitor blend when admixed in mortar or concrete structures. The fast diffusion of the hydroxyalkylamine through the concrete has been demonstrated [14,17]. The diffusion direction follows the concentration gradient of the hydroxyalkylamine. As the hydroxyalkylamine concentration can be expected to be very low on the concrete surface, it can be postulated that the substance should evaporate from concrete structures, which must cause a decrease of concentration over time. Measuring the amine concentration in airtight compartments containing a mortar sample of the series 2 and 3 respectively after 350 days cyclic treatment showed that the amine concentration (determined qualitatively with an amine electrode (Orion; model 9512)) in the air surrounding the samples is increasing with time (Fig. 7). Additionally the evaporation rate is higher for samples with higher inhibitor concentrations which is in agreement with the expected steeper concentration gradient. Hence, the main component of the inhibitor is leaving the concrete structure over time and the question arises whether the observed retardation of the corrosion initiation will still occur under realistic conditions (after several years of service).

## 8. Conclusions

Experiments in solutions are useful for the characterisation of the inhibitor efficiency and the determination of influencing parameters. However, experiments in mortar are more severe and thus necessary to obtain results relevant for practical applications.

- In chloride-containing alkaline solution, the inhibitor can prevent steel from corrosion initiation at sufficiently high concentrations (10%). At lower

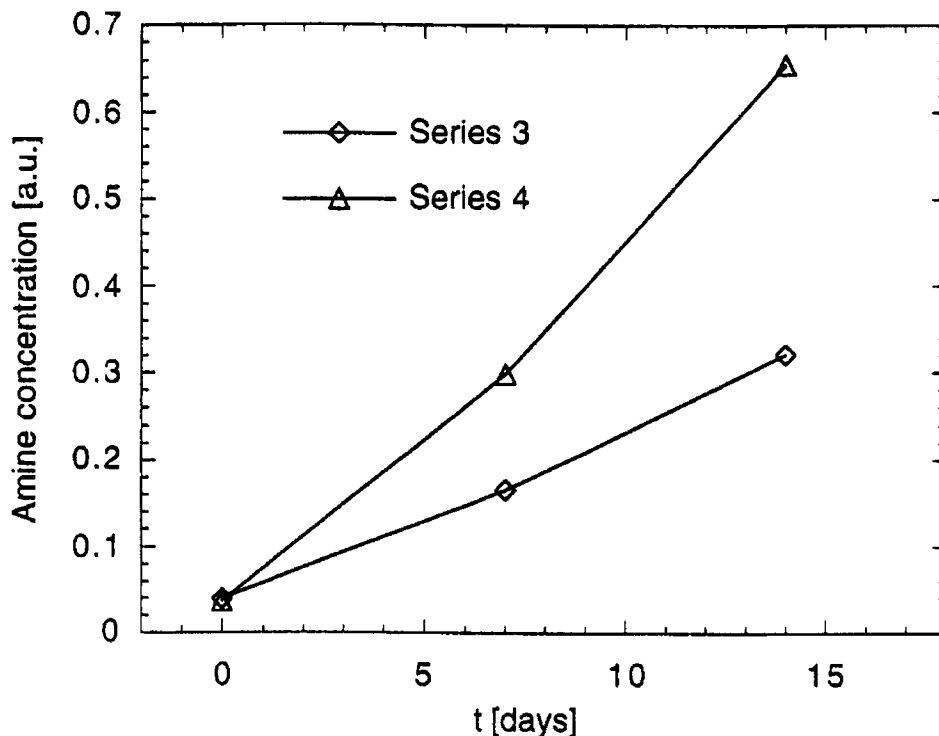


Fig. 7 Relative amine concentration of the air in a closed compartment containing mortar samples with admixed inhibitor.

concentrations pitting corrosion initiated, but the corrosion rate is lowered by the presence of the inhibitor.

- Contrary to the experiments in solution, in mortar neither complete inhibition of the initiation of pitting corrosion nor an influence on the corrosion rate is obtained. Nevertheless, the inhibitor can delay the corrosion initiation.
- The inhibitor reduces the corrosion rate of pre-corroded samples in chloride-containing alkaline solutions, no reduction in corrosion rate was found when the inhibitor was surface-applied on mortar samples. Recent field tests on chloride-contaminated structures gave the same result.
- The volatile constituent of the inhibitor was found to evaporate from solutions and from mortar with a consequent loss in inhibiting properties. The long term efficiency of the admixed inhibitor in field application is questionable.

## 8. Acknowledgements

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