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Corrosion inhibitors in concrete
Part III. Effect on time to chloride-induced corrosion initiation and subsequent corrosion rates of steel in mortar

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Abstract

The effectiveness of four commercially available corrosion inhibitors for use in cement-based materials was assessed in mortar exposed to chloride solution. Although, in a parallel study of steel in synthetic pore solutions, the inhibitors were observed to be ineffective in increasing the chloride threshold value of reinforcing steel exposed to chlorides, in the present study all inhibitors were found to delay the onset of corrosion, but to differing degrees. Moreover, in agreement with the parallel study, the inhibitors were found to have little detectable effect on the corrosion rate of the embedded steel once active corrosion had been initiated. This study confirmed that calcium nitrite inhibitors delay the onset of corrosion but raises questions regarding the mechanism of inhibition. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Researchers and engineers are continuously in search of cost-effective means to prevent the corrosion of reinforcing steel for the duration of a concrete structure's design life. The use of epoxy-coated steel has been the preferred method for the last 15 to 20 years but its long-term effectiveness is now being questioned. The deterioration of several structures built using epoxy-coated reinforcement has forced officials to review its use. Other barriers such as waterproofing membranes and sealers can effectively reduce penetration of water and chlorides into the concrete, but they generally require maintenance and reapplication several times during a structure's life. Corrosion-inhibiting chemical additives are potential solutions to this problem. The effectiveness of some commercially available inhibitors is the subject of this research.

This paper describes one part of a four-part series, the objectives of which were to evaluate the effectiveness of those corrosion inhibitors available commercially at the onset of the project, to determine the factors influencing their effectiveness and, where possible, to determine the mechanism of inhibition and whether or not the admixtures are consumed in the process of providing corrosion inhibition. Possible mechanisms of corrosion inhibition, as they apply to steel in concrete, have been described in Part 1 [1]. In practice, the inhibitor can (i) delay the onset of corrosion by reducing the rate of ingress of chlorides[1] or by increasing the chemical binding of chlorides or by raising the chloride threshold value for corrosion initiation and/or (ii) by reducing the rate of corrosion once it is initiated. Many corrosion inhibitors can be categorised as anodic, cathodic or mixed inhibitors based on the processes they influence [1]. Other inhibitors, named pore blockers, retard the ingress of chlorides and/or oxygen by filling pores in the concrete matrix.

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[1] Whether or not these should be included in the term "inhibitor" is currently under discussion.

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Six corrosion inhibitors were identified as being available commercially and their manufacturers were invited to supply samples of their inhibitors for testing. One manufacturer declined and, after examination of the constituents of a second product, it was decided not to include it in the investigation. Thus four products, two calcium nitrite-based, designated CN(1) and CN(2), and two organic compounds, designated ORG(1) and ORG(2), were investigated. The investigation was carried out in three parts. The first part [4] involved studies of the electrochemical behaviour of steel in synthetic concrete pore solutions to determine the chloride threshold values and subsequent rates of corrosion and whether or not the inhibitor was "consumed" in the process of providing inhibition and, thus, would lose its effectiveness over time. The second part, reported here, measured the time to corrosion initiation and subsequent corrosion rates of steel in mortar. Finally, the effect of these inhibitors on the physical and mechanical properties of the concrete was evaluated [5].

2. Experimental procedure

Cylindrical mortal samples, having the dimensions shown in Fig. 1, were cast at water–cement ratios (W/C) of 0.5 and 0.7. The higher W/C was used to produce a highly porous mortar to assure that corrosion would begin within the time frame of the project and, more importantly, to determine whether any protection would be afforded in those parts of a structure in which there is an inadvertently high water/cement ratio. Mortar was used instead of concrete because the cover around the steel was insufficient to allow the use of coarse aggregate. In order to eliminate the effects of carbonation at the top of the specimen and to control the area of steel susceptible to corrosion, the 12 mm diameter steel bars were partially coated with an epoxy paint, leaving 150 mm of bare steel at one end. As illustrated in Fig. 1, the uncoated portion of the steel bar was centred in the cylinder. The mixture proportions of the mortar are shown in Table 1.

Batches of control samples, containing no inhibitor, and batches of samples mixed at three dosages of each inhibitor, were cast. A description of each batch is provided in Table 2. The quantity of mixing water was adjusted following the manufacturers' recommendations to account for the water already present in the calcium nitrite inhibitors; no water adjustment was recommended by the manufacturers of both organic inhibitors. The four samples from each batch were poured in cast iron moulds, compacted on a vibrating table, and covered with plastic bags to help prevent evaporation. The moulds were removed after 24 h. The specimens were then allowed to cure inside a tightly sealed plastic bag for a period of 2 weeks before being partially immersed in a 3.5% sodium chloride solution.

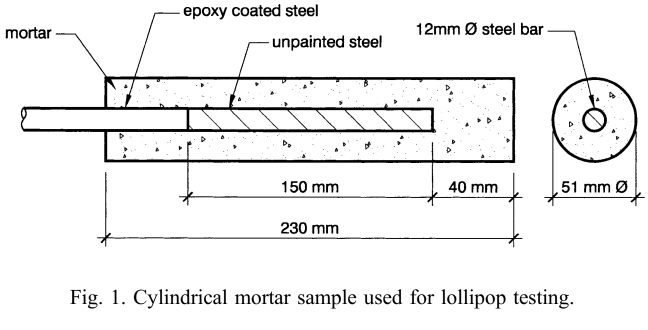

Fig. 1. Cylindrical mortar sample used for lollipop testing.

Table 1
Mixture proportions for the mortar samples

W/C	Component	Quantity in batch, kg
0.50	Ordinary Portland cement, Type 10	2.94
	Water	1.47
	Sand	10.02
0.70	Ordinary Portland cement, Type 10	2.68
	Water	1.88
	Sand	9.16

Half-cell potential tests were conducted, following the ASTM C876 guidelines, to determine the likelihood of active corrosion. The potential difference between the working electrodes (embedded steel bars in lollipop samples) and a saturated calomel reference electrode (SCE) placed in the solution was measured using a high-impedance voltmeter.

Table 2
Batch admixture additions

Batch	Inhibitor type	Inhibitor concentration l/m^3	W/C
1	control	–	0.5
2	control	–	0.7
3	CN(1)	10	0.5
4	CN(1)	10	0.7
5	CN(1)	20	0.5
6	CN(1)	20	0.7
7	CN(1)	30	0.5
8	CN(1)	30	0.7
9	ORG(1)	5	0.5
10	ORG(1)	5	0.7
11	ORG(1)	7	0.5
12	ORG(1)	7	0.7
13	ORG(1)	9	0.5
14	ORG(1)	9	0.7
15	ORG(2)	20	0.5
16	ORG(2)	20	0.7
17	ORG(2)	25.75	0.5
18	ORG(2)	25.75	0.7
19	ORG(2)	30	0.5
20	ORG(2)	30	0.7
21	CN(2)	2	0.5
22	CN(2)	2	0.7
23	CN(2)	3	0.5
24	CN(2)	3	0.7
25	CN(2)	4	0.5
26	CN(2)	4	0.7

AC impedance tests were also carried out to determine the corrosion rates. The theory and merits of this corrosion measuring technique have been discussed in numerous papers [6–10]. In addition to providing information on the kinetics of the electrochemical system (i.e. corrosion rate), this nondestructive test can also show which mechanism is involved in the process (i.e. passivation, activation, or diffusion control). For this investigation, the AC impedance tests consisted of applying a 10-mV sinusoidal potential signal to the working electrode, and measuring the current response. The AC signal was stepped logarithmically over the frequency range 100 kHz down to 10 mHz (or less). Since this test required about 40 min, and testing to lower frequencies exponentially increases the time required for each measurement, it was impractical to use a final testing frequency inferior to 10 mHz for all the samples. This technique allows the determination of the polarisation resistance (R_p) value which is used to compute corrosion rates.

3. Results and discussion

3.1. Time-to-corrosion

The time-to-corrosion is the time required for chlorides to penetrate the concrete cover in sufficient quantities to initiate corrosion and was determined with the combination of half-cell potential and AC impedance tests. All specimens having a half-cell potential more negative than -275 mV SCE which were tested using AC impedance gave a response indicative of active corrosion. No specimens giving passive responses in the AC impedance tests were found to have very negative half-cell potentials, as would be the case if the specimens lacked oxygen. Since the more rapid half-cell potential tests were performed more frequently than AC impedance tests, the time-to-corrosion of some samples was based partially or solely on half-cell potential results, following the ASTM C876 guidelines.

Fig. 2(a) and (b) show the time-to-corrosion for samples having W/C ratios of 0.5 and 0.7, respectively. The left side of each bar corresponds to the last measurement taken before active corrosion began in any of the four samples in a given batch. The right side corresponds to the first measurement taken after all samples in a given batch were actively corroding. In other words, it can be said that all four samples in a particular batch started to corrode in the time range indicated by the bar. Because of the interval between corrosion measurements, the left end of the bar only indicates that no samples were corroding at that specific time, not necessarily that corrosion began at that time. Similarly, the right side of the bar shows that all four samples were corroding at that time, not necessarily that the last sample started to corrode at that particular time.

All four corrosion inhibitors delayed the onset of corrosion but to varying degrees, depending on the W/C and the inhibitor dosage. The only inhibitor to provide a substantial delay in corrosion initiation time, however, was CN(1). At both W/C ratios, the degree of effectiveness of CN(1) increases with increasing dosage. This result is consistent with earlier work [2,3] stating that corrosion can only be inhibited if the nitrite to chloride ratio is high enough. In fact, one sample at the higher CN(1) dosage (30 l/m^3) and at W/C = 0.5 still was not corroding after 640 days of exposure to chlorides. The severity of the chloride environment in this test meant that a high concentration of nitrites (to maintain a sufficient NO^{2-}/Cl$^-$) was necessary to inhibit corrosion.

The other inhibitors delayed corrosion to a lesser degree. Only the low dosages of ORG(2) and CN(2) successfully delayed corrosion at the lower W/C, while they did not have any appreciable effect on corrosion initiation time at their higher dosages.

As expected, the onset of corrosion occurred earlier in the samples at W/C = 0.7. Aside from CN(1), only CN(2), at the recommended dosage, substantially delayed corrosion. The only inhibitor whose dosage had the same effect on the time-to-corrosion at both W/C ratios was CN(1) with the onset of corrosion being increasingly delayed as the dosage

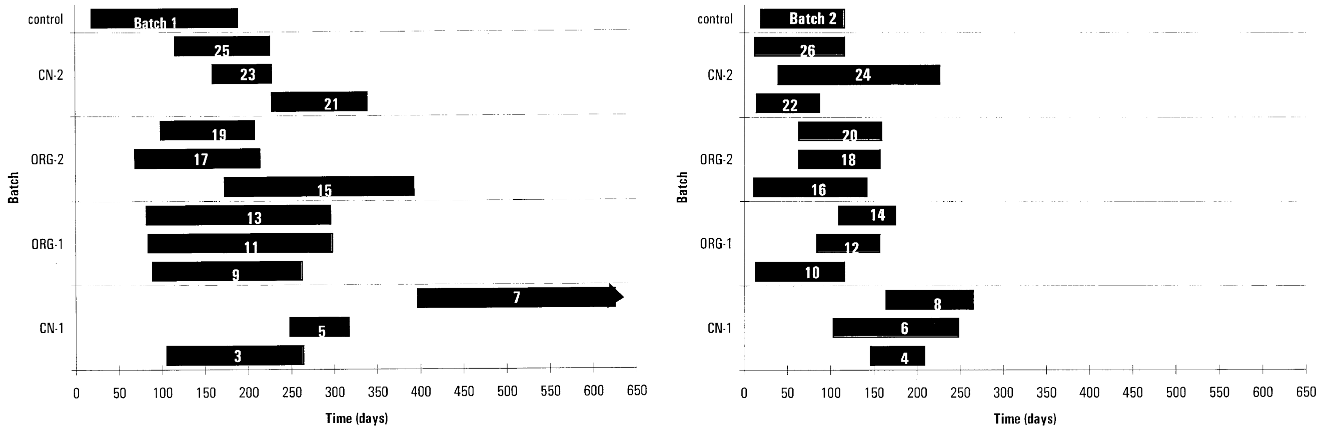

Fig. 2. (a) Time to initiate corrosion for samples with W/C 0.50. (b) Time to initiate corrosion for samples with W/C 0.70.

was increased. The time-to-corrosion of the ORG(1) samples seemed to be independent of the dosage at the lower W/C, but its effectiveness increased with dosage at the higher W/C. This may be explained by the fact that ORG(1) is believed to be a pore blocker and the lower dose is sufficient to block most of the pores in the low W/C mortar, whereas a higher dosage is required to fill the more numerous and/or larger pores of the higher W/C mortar.

3.2. Corrosion rate

Corrosion rates were calculated using R_p values obtained from AC impedance tests. R_p values for each test were determined using equivalent circuit modelling for test frequencies ranging from 100 kHz down to 10 mHz. Results from the final round of AC impedance tests were compared to establish the impact of corrosion inhibitors on the corrosion rate of samples which have been actively corroding for an extended period of time. The final corrosion rate measurements were taken after approximately 550 days of ponding. The rates were calculated assuming that the corrosion took place over the entire exposed steel area of 62.7 cm^2. However, a subsequent visual inspection of split samples revealed that the corrosion was usually confined to an area slightly greater than 1 cm^2 and never exceeded 4 cm^2. Therefore, the actual local corrosion rates are 15 to 100 times higher than those shown in Fig. 3. The calculation of corrosion rates is subject to other uncertainties, including the determination of R_p from curve-fitting of the raw AC impedance test data and the value of the Tafel constant used. Nevertheless, the results allowed a comparative evaluation of the inhibitors' influence on these nominal corrosion rates.

Nominal corrosion rates for the specimens having W/C ratios of 0.5 and 0.7 are illustrated in Fig. 3(a) and (b), respectively. The corrosion rate for specimens having a W/C of 0.5 was usually lower than that of their counterparts with a W/C of 0.7. However, the opposite was true for the control samples and the corrosion rates of the ORG(1) specimens were very similar at both W/C ratios. The reasons for this are not clear but this discrepancy is an indication of the degree of scatter typically observed in corrosion rate measurements. Once corrosion begins, the changes in corrosion rate are very varied. At a W/C ratio of 0.5, there is a general decrease in corrosion rate relative to the control samples, whereas at a W/C ratio of 0.7 the reverse trend was observed. However, this discrepancy may be due to the unexpectedly high corrosion rate of the control samples with W/C of 0.5.

It has been hypothesised that an insufficient dosage of a calcium nitrite (anodic) inhibitor can accelerate corrosion by increasing the cathode to anode ratio [11–13]. This hypothesis is not supported by the current results: the corrosion rates measured in samples containing either calcium nitrite inhibitor were found to be independent of the inhibitor dosage, and to be of similar magnitude or less than those of the control samples. These results indicate that this type of inhibitor does not accelerate corrosion when the chloride to nitrite corrosion threshold is exceeded.

3.3. Electrical resistance of mortar

Increasing the electrical resistance (or resistivity) of concrete is one of several ways for a chemical admixture to reduce the corrosion rate. The value of the mortar's resistance is related to the solution resistance value yielded by AC impedance tests. Assuming that the resistance of the saline solution in the test cell is negligible, the solution resistance (R_s) can be considered to be the electrical resistance of the mortar surrounding the steel of the lollipop sample, and can, therefore, be used as a measure of corrosion resistance.

The solution resistance values obtained from the final round of AC impedance tests, for both W/C ratios, are illustrated in Fig. 4(a) and (b). For a given inhibitor and dosage, the R_s value was usually lower at the 0.7 W/C than at 0.5 W/C, as expected. With the exception of ORG(2), the inhibitors had no effect or caused small increases in electrical resistance. The decrease in resistance caused by ORG(2) could be detrimental to the durability of concrete.

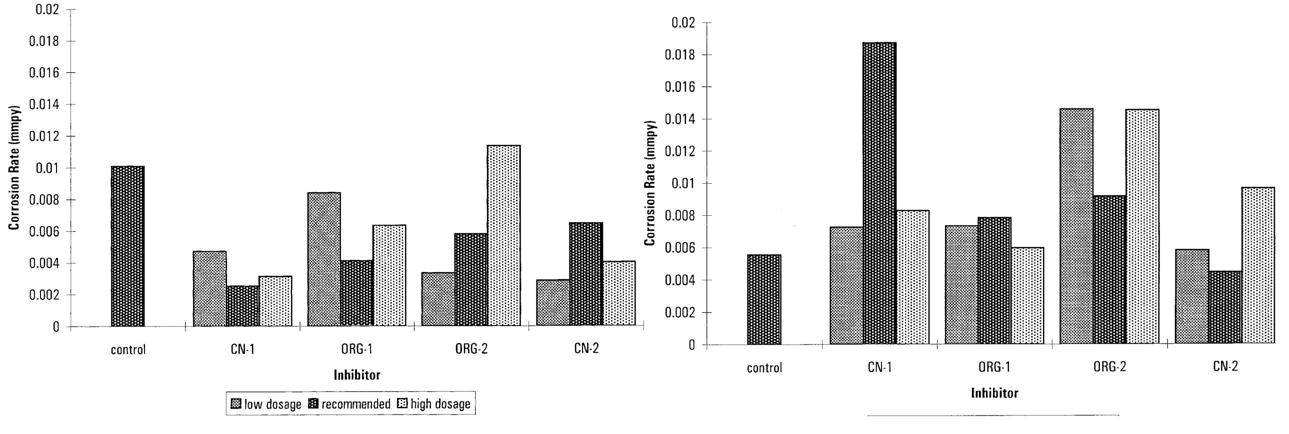

Fig. 3. (a) Nominal corrosion rates for samples with W/C 0.50. (b) Nominal corrosion rates for samples with W/C 0.70.

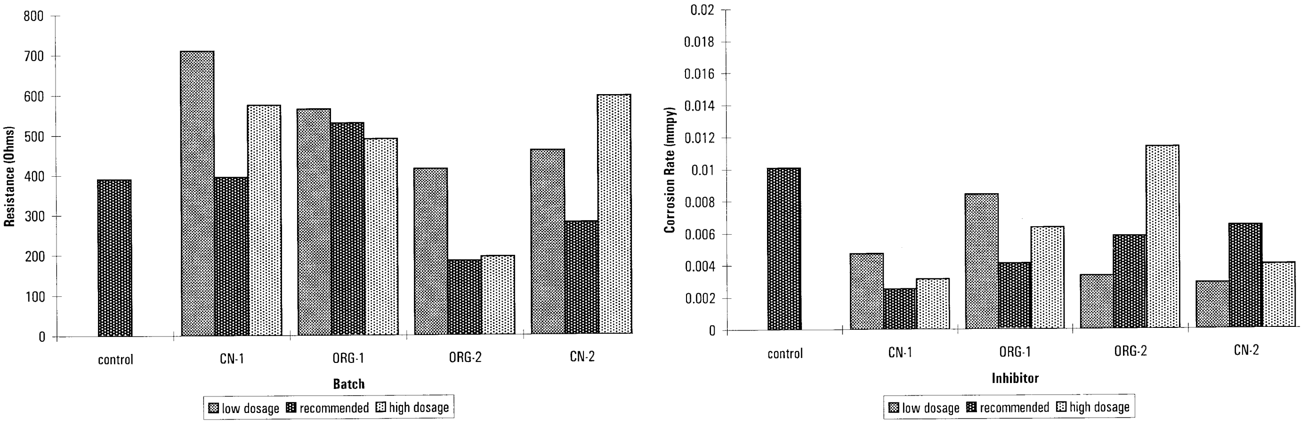

Fig. 4. (a) Solution resistance of samples with W/C 0.50. (b) Solution resistance of samples with W/C 0.70.

3.4. Visual inspection

All the samples which half-cell and AC impedance tests indicated were corroding were confirmed to be actively corroding by visual examination of the steel immediately after removal from the mortar. Although corrosion was observed at various sections along the exposed length of steel bar, most of the corrosion took place just above the water line. This is as anticipated since the concentration of chlorides is highest at that point, through wicking action, and the cathodic oxygen requirement is easily met. The most severe corrosion was observed in the ORG(2) samples with a 0.7 W/C, and the least amount of corrosion was found in the CN(1) samples with 0.5 W/C, thereby agreeing with electrochemical tests.

4. Summary and conclusions

It is evident that the corrosion inhibitors tested in this investigation delay the onset of corrosion to varying degrees, with CN(1) being the most effective and its effectiveness increasing with increasing dosage, but they all failed to prevent the initiation of corrosion. Once corrosion began, there was little variation in nominal corrosion rates among the samples containing the inhibitors. The inhibitors caused slight increases in electrical resistance with the exception of ORG(2), which lowered it. The inhibitors performed better at the lower W/C; this is consistent with the belief that inhibitors work best in higher quality concrete.

The visual inspection of the split lollipop samples confirmed the electrochemical test results. The CN(1) samples were the least corroded while the most severe corrosion was found in the ORG(2) samples at the highest W/C.

There was a considerable difference in the time-to-corrosion of the samples containing the two calcium nitrite inhibitors. The admixtures vary in appearance [4] and their recommended dosages are also different (10 to 30 l/m^3 for CN(1) and 3 l/m^3 for CN(2)). The calcium nitrite content of CN(1) is reported as being 30% by weight while that of CN(2) is listed at 30% to 60%. However, both inhibitors were experimentally found to contain similar nitrite concentrations although the residue after drying exhibited different colours and morphologies [4]. Even if CN(2) had twice as much nitrite as CN(1), its recommended dosage would still provide less nitrite than the lowest recommended dosage of CN(1) (10 l/m^3), not enough to inhibit corrosion at the chloride levels of the lollipop tests. It is probable that the recommended dosage of CN(2) needs to be raised to provide a superior level of corrosion protection. Any resulting impact on concrete properties would need to be assessed.

There is a growing number of commercially available concrete admixtures that are said to have corrosion inhibiting properties. The results from this test show that the incorporation of some of these chemicals (CN(2), ORG(1), and ORG(2)) in concrete will only provide a slight delay in corrosion initiation, which may not justify the additional material cost. The use of the CN(1) calcium nitrite inhibitor enhances the level of corrosion resistance for embedded steel although it does not prevent corrosion and, as shown in Part II of this study [4], does not have any observable electrochemical benefits on steel in synthetic pore solution. The use of calcium nitrite inhibitors, especially in combination with other corrosion prevention methods, should effectively prolong the lives of reinforced concrete structures subjected to salt environments.

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