Significance of the concentration of chloride in the repair of concrete highway structures using surface applied corrosion inhibitors

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ABSTRACT: Advances in surface-applied corrosion inhibitors suggest that they have the potential to prevent or significantly retard corrosion of steel in reinforced concrete structures. It is thought that the effectiveness of the inhibitor depends on both the chloride concentration at the steel reinforcement and the inhibitor concentration. This paper presents the preliminary findings of a laboratory study into this assumption. Concrete specimens were ponded with chloride solutions to initiate corrosion. Inhibitor was applied to one face and the influence on corrosion activity was monitored by linear polarisation resistance measurement. The preliminary results of this continuing study showed that the surface-applied inhibitors could reduce the corrosion rate and this reduction depends on the chloride concentration. The practical implication is that there exists a chloride concentration range within which inhibitor use is most effective.

1 INTRODUCTION

Reinforcement corrosion is one of the major causes of degradation in concrete structures. Considerable resources have to be diverted towards the repair and rehabilitation of these structures. In the USA, more than \$50 billion has been spent annually in the past on the repair of inter-state highway systems. In the UK, £20 billion was spent on building repair and maintenance, out of which up to £500 million was utilized per annum for concrete repairs (Al-Amoudi et al. 2003). Deicing salts cause corrosion damage in reinforced concrete with losses of \$325 million to \$1 billion per year in the U.S. alone (Allyn & Frantz, 2001). Effective repair strategies are being studied in the SAMARIS (Sustainable and Advanced MAterials for Road InfraStructure) project, funded under the EU 5th Framework Programme. The objectives of the project of relevance to this paper include (Žnidarič et al. 2003):

- To find optimal repair strategies for a large number of critical concrete structures on main road networks in CE countries as well as in some EEA countries.
- To achieve greater efficiency and durability of repairs, resulting in reduced number and duration of necessary road closures.
- To considerably reduce the associated costs and increase users' safety.

Steel embedded in concrete is normally protected from corrosion by the formation of a passivating iron

oxide layer on the steel surface, which can remain stable due to the alkalinity provided by the concrete. The corrosion process involves the breaking down of this protective layer, which leads to an expansion in the cross section of the reinforcement due to the formation of high-volume corrosion products. This process can lead to cracking or spalling of the concrete and a dangerous loss of structural stability. The most common cause of the corrosion is the attack by chlorides in marine structures or in multi-story car parks, and bridge decks due to de-icing salts.

The traditional approach of removing cracked and contaminated concrete, cleaning the exposed steel and reinstating with a repair mortar or concrete can be disruptive, time-consuming and expensive if it is to be carried out thoroughly enough to be effective for more than a few years. The use of surfaceapplied corrosion inhibitors as components of proprietary concrete repair systems has therefore increased over the last few years since this appears to offer an economical and simple alternative to other available methods, particularly in cases where only modest extensions of service life are required (Page et al. 2002). In addition, fewer restrictions apply to the choice of corrosion inhibitive substances for surface-applied inhibitors than for those used as admixtures, because the effects on cement hydration kinetics are less relevant (Elsener 2000).

Concrete corrosion inhibitors are chemical compounds that, when added in relatively small amounts to concrete, can reduce the corrosion rate by a direct interaction with the steel reinforcement. The use of organic inhibitors such as alkanolamines has been increasing in recent years as a cost effective and efficient repair strategy.

The present paper studies the effectiveness of an alkanolamine-based surface-applied corrosion inhibitor for reducing the corrosion rate of pre-corroded steel bars at different chloride levels.

2 EXPERIMENTAL PROGRAMME

2.1 Concrete specimens

For this programme, a series of concrete slabs were manufactured of size 280 x 280 x 75 mm, which were reinforced by two horizontally placed and fixed reinforcing bars. All specimens featured a recess cast into the top surface to allow ponding. The exposed length of each steel bar was 280 mm. The concrete cover was 18 mm. The selected reinforcement was 10 mm diameter ribbed bar, and these were cleaned prior to casting using a dry grit blasting method. Two different mix designs were used. The mix composition and details of the concretes used in the experimental programme are given below in Table 1. Mix Type 'A' maximized the cementitious component to aid rapid inhibitor ingress

Prior to casting the weight of each individual reinforcing bar was also recorded. This data will be used at a later stage to assess any weight loss that has occurred due to corrosion.

Table 1. Mix designs.

	Mix Type 'A'	Mix Type 'B'
Cement (kg/m ³)	350	280
C20 aggregate (kg/m ³)	-	759
C10 aggregate (kg/m^3)	991	370
Fine aggregate (kg/m^3)	791	809
Water (kg/m ³)	220	182
w/c ratio	0.63	0.65

2.2 Chloride exposure

In all cases chloride ingress was achieved by ponding over the top surface of the specimens. A recess of dimensions 170 mm square and 20 mm deep was cast into the top of all samples. This recess was filled with a saturated sodium chloride solution (~5M). A typical ponding cycle involved application of sodium chloride solution for 4 days continuously, after which the chloride solution was drained off and the specimens were left in the open air. They remained this way for a further 4 days, in order to promote oxygen penetration. In order to assess the effect of chloride concentration levels, the number of applied ponding cycles was varied from 4 to 8 (see Table 2). At the end of each ponding cycle corrosion progress was monitored, by potential mapping using a digital half-cell.

Table 2. Selected ponding cycles.

Chloride exposure level	No. of ponding cycles
Moderate	4
High	6
Very high	8

An example of the degree of corrosion achieved can be seen in Figure 1. However, due to a lack of adequate protection at the edges, some crevice corrosion was also observed.



Figure 1. Example of pitting corrosion associated with high chloride concentration.

2.3 Inhibitor application and verification of ingress

On completion of the ponding cycles the specimens were prepared for inhibitor application. The top surface of each specimen was dry grit blasted and a protective coating was applied to the remaining faces to prevent ingress of oxygen. This ensured unidirectional flow of oxygen into the concrete. The specimens were then placed in a controlled environment of 20°C and ~60% R.H., allowing them to equalise with the environment. The surface-applied amino alcohol based inhibitor was then applied to all specimens at a dosage rate of 500 g/m². This was applied in several coats, with each coat allowed to dry before the next is applied. The corrosion rate and corrosion potential were measured before and after inhibitor application by linear polarisation resistance measurements using the GalvaPulse apparatus. The presence of the inhibitor at the steel-concrete interface was confirmed ion chromatography.

2.4 Corrosion rate measurement by polarization resistance

The polarization resistance R_p represents the ease with which charged iron ions can leave the metal surface and enter solution. The rate of active corrosion is inversely proportional to R_p (Millard et al. 2001). The galvanostatic pulse measurement technique is a fast linear polarization technique for determination of the actual corrosion rate at time of testing. When using the GalvaPulse the half-cell potential, the corrosion rate and the polarization resistance are determined in one measurement.

3 RESULTS

To allow proper assessment of the performance of the corrosion inhibitors, a number of parameters required quantification.

3.1 Determination of chloride content

Dust samples were extracted from the concrete samples at rebar level and the chloride concentration was determined. The method used was that of internal calibration, as developed by Clemeña & Apusen (2002). This alternative potentiometric method involves the cold digestion of concrete sample in acetic acid. This solution is then spiked twice with a relatively small and precisely measured amount of standard NaCl solution. The chloride content is calculated for each sample from the potential readings before and after the spiking by an equation derived from the Nernst equation. Clemeña and Apusen have shown the method to be much faster than standard methods and with negligible loss in accuracy. Average chloride contents for the various concrete samples are given in Table 3.

Table 3. Average chloride contents expressed per mass of cement

Mix Type	Chloride Exposure Level	Chloride content (% mass cement)
A	Moderate	1.96
	High	2.21
	Very high	2.40
В	Moderate	1.53
	High	2.27

A considerable amount of data has been published concerning critical chloride thresholds for corrosion of reinforced concrete. Pettersson (1996) suggests that a chloride concentration of 1-2 % of chloride by mass of cement will yield a high probability of corrosion, while a chloride content of greater than 2 % will lead to certain corrosion.

3.2 Determination of inhibitor concentration

Concrete samples were extracted at rebar level and analysed for inhibitor presence. The test method for quantitative determination of inhibitor is a confidential method and involves an ion chromatographic analysis of a prepared concrete sample, scanning for the presence of selected chemicals. The average results for inhibitor concentrations found at rebar level are listed in Table 4.

Table 4. Average inhil	itor concentration	at rebar	level
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Mix Type	Chloride Exposure Level	Inhibitor concentration (ppm)
A	Moderate High	40.5 47.8
B	Very high Moderate	22.5
D 	High	40.7

A large amount of scatter was found in the results, meaning that any subsequent discussion on optimal inhibitor concentration would be fraught. Rather, it was considered that it was sufficient to detect the presence of inhibitor at rebar level. As the inhibitor acts by forming a mono-molecular layer around the rebar, it was considered that this was a valid assumption.

3.3 Corrosion rate measurement

Table 5 shows the average corrosion rate at different chloride levels for each concrete. Corrosion rates are expressed as loss of cross section over time.

Table 5. Corrosion rates before and after inhibitor application

Mix	Chloride	Corrosion rate (µm/yr)		Reduction
Туре	Level	before	after	(%)
A	Moderate	26.4	12.1	54
	High	26.2	15.9	39
	Very high	32.0	30.8	4
В	Moderate	20.2	17.8	12
	High	18.9	12.5	34

Corrosion rate was monitored continuously after inhibitor application; in all cases the reported corrosion rates are values that have stabilized over time.

4 DISCUSSION

4.1 Chloride and inhibitor concentration

From analysis of the chloride results listed in Table 3 it can be seen that the chloride results are indeed high enough to have initiated corrosion. It has long been acknowledged (Elsener 2000) that corrosion inhibitors are not suitable for all incidents of corrosion, and that parameters such as chloride content are critical. It was considered that the chloride contents achieved are suitably high to promote corrosion, whilst allowing the surface applied inhibitor the opportunity of reducing the corrosion rate.

The mechanism by which the inhibitors penetrate the concrete is a combination of capillary absorption and diffusion. The corrosion inhibitor has been shown to penetrate into the concrete as far as the rebar. The inhibitor action is such that it protects the reinforcement by forming a monomolecular layer on the steel surface, considered to be 100-1000 Å thick. It reduces the dissolution of iron at the anodes and acts as a barrier to oxygen at the cathodes. Through this the onset of corrosion is delayed and the rate of corrosion reduced.

4.2 Effect of inhibitor on corrosion rates

From analysis of the results shown in Table 5 it can be seen that in all cases there was a reduction in corrosion rates observed after application of the corrosion inhibitor. It can be seen that the best results were observed for Mix A at 'Moderate' and 'High' chloride concentrations. These mixes, with chloride concentrations of 1.96 % and 2.21 % by mass of cement, produced reductions in corrosion rate of 54 % and 39 % respectively. The concrete samples with a 'Very high' chloride content of 2.40 % by mass of cement only recorded a reduction in corrosion rate of 4 %. It is considered likely that in this case the corrosion process is simply too active to be inhibited.

For Mix B it can be seen that the best performance was observed in the concrete samples with a 'High' chloride content of 2.27 %, where the corrosion rate was reduced by 34 %. Paradoxically, the concrete sample with a 'Moderate' chloride content of 1.53 % only achieved a corrosion rate reduction of 12 %.

4.3 Evaluation of inhibitor performance

Millard et al. (2001) have offered some guidance on interpreting corrosion rates, as shown in Table 6. Using these criteria, it can be seen that in no locations did the inhibitor transform the corrosion process to 'Low'. However, in the majority of cases the effect of the inhibitor was to move the corrosion rate significantly closer to the 'Low' threshold.

Table 6. Guidance on the interpretation of corrosion rates (Millard et al. 2001)

Description of corrosion	Corrosion rate (µm/year)
Very high	100 - 1000
High	10 - 100
Low/Moderate	1 - 10
Passive	< 1

4.4 *Comparison to field performance*

The same corrosion inhibitor used in this research has also been used in the field. Figures 2-3 show the effect of the use of this inhibitor on a car park structure. The deck in the car park was treated with the inhibitor and a corrosion monitoring system installed. This monitoring system has been developed by the U.K. company C-Probe Ltd. and utilises linear polarisation resistance sweeps to ascertain corrosion rate on a weekly basis. The data recorded represents the real time corrosion rate and is influenced by the in service environmental conditions experienced by the structure.

The data in Figure 2 corresponds to a corrosion monitoring probe installed in an area of the parking deck where the inhibitor has worked well. The corrosion rate has been reduced significantly and is seen to lie consistently below a value of 1 μ m/year.

Figure 3 however represents an area where the inhibitor has not performed as well. It can be seen that the corrosion rate began to drop initially before rising again. The initial drop was significant, as the corrosion rate was reduced from approximately 18 μ m/year to approximately 2 μ m/year. However, the inhibitor proved unable to cope with the continued demands placed on it from the environment, and the corrosion rate has subsequently returned to a value around 12 μ m/year.



Figure 2. Area in the parking deck where the inhibitor has maintained a low corrosion rate



Figure 3. Area in the same parking deck where inhibitor has not coped with environmental change.

5 CONCLUSIONS

From the results of the laboratory and field-testing, a number of conclusions can be presented covering the use of corrosion inhibitors for the repair of concrete structures. The trend identified is that corrosion inhibitors can be effective but that their performance depends on the chloride exposure level. Further research is being conducted to identify the boundaries of the range of chloride levels within which the inhibitor is most effective. This could be used in assessment of optimal repair strategy.

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