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Effective Use of Corrosion Inhibitors in Highway Structures

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Summary

The corrosion of European concrete highway structures leads to traffic disruption, significant expenditure on remedial works and ultimately threatens to impact on European competitiveness. A potentially more efficient component in maintenance strategies is the use of surface applied corrosion inhibitors, which may delay the onset of corrosion or retard the corrosion rate of steel in concrete. This paper presents a proposed framework of guidelines for the effective use of corrosion inhibitors based on a study conducted as part of the EU Fifth Framework SAMARIS project. The proposed guidelines call for an initial desk study to assess the potential use of inhibitor and an assessment of risk control to the specifiers satisfaction. If necessary (for risk assessment and control) a preview trial is recommended, based on defined performance criteria from which a proposed rehabilitation strategy is finalised and again considered against the risk assessment. If resources permit, performance monitoring post repair is recommended as part of a pro-active maintenance strategy, since such an approach may represent one of the most effective uses of corrosion inhibitors in service life management.

Keywords: Amino alcohol, concrete, corrosion, durability, inhibitor, reinforced concrete.

1. Context and test programme

Surface-applied corrosion inhibitors are applied to hardened concrete with the purpose of penetrating the cover to the reinforcing steel and forming a protective film to mitigate the corrosion processes. Inhibitor technology is a continually developing rehabilitation technique. Their market position in the context of highway structures is to offer a solution that, if used in appropriate circumstances, can extend the service life of a structure in an economical way, through delay of depassivation and/or reduction of rate of corrosion, once it is propagated.

This paper reports on trends identified in trials on concrete specimens in the laboratory. In addition an indicative performance envelope is presented that resulted from the reported tests and other trials that formed part of a work package of the EU SAMARIS (Sustainable and Advanced Materials for Road Infrastructure) Project. The work package set out to examine the effectiveness envelope of amino alcohol inhibitors in chloride contaminated concrete based on a hypothesis that significant influences are chloride concentration, sustainability of inhibitor reservoir near the reinforcement and the state of the corroded reinforcement at time of inhibitor application. These constraints represent boundaries of the window of opportunity for use of inhibitors as part of a repair strategy but key to effectiveness is the combination of circumstances. This helps to explain conflicting findings in the literature [1] because the full circumstances of each case were not always known or reported and some conditions may have been outside the effectiveness window of the technology. The trends identified in the SAMARIS trials led to a qualitative determination of an indicative performance envelope that informed the drafting of guidelines for specifiers, published as a main

Table 1 *Outline of test programme*

Phase	Summary Description
I	Study of inhibitor use in concrete with high and very high chloride concentrations at the reinforcement and high corrosion rates.
II	Study of inhibitor use in concrete with moderate chloride concentrations at the reinforcement and moderate corrosion rates.
III	Study of inhibitor use in concrete with low to moderate chloride concentrations at the reinforcement with inhibitor applied before depassivation or while corrosion rates remained low

conditions and then progressively worked towards studies of moderate conditions, where inhibitors might be considered for use in reactive rehabilitation strategies to ‘buy time’, and then to less aggressive conditions, where inhibitors might be considered for use in proactive maintenance strategies before damage was significant but where intervention is required to achieve the required service life. This led to a three phase study summarised in Table 1.

2. Materials and methods

2.1 Materials

The experimental programme was based on concrete specimens with plan dimensions 280 x 280 mm and a depth of 75 mm, incorporating a 20mm recess for chloride ponding. The specimens were reinforced with two 10 mm diameter high yield ribbed bars with a cover of 18 mm. The protruding ends of the reinforcing bars were coated in a protective paste to eliminate crevice corrosion. Later the protective paste was filed down to the metal surface to provide a clean connection during corrosion monitoring. Prior to casting the steel bars were cleaned by grit blasting. Following chloride ponding and prior to inhibitor application the top surfaces of the specimens were lightly grit blasted (simulating preparatory work in full scale applications) and the sides of the specimen were coated to minimise or eliminate boundary influences on chloride and inhibitor migration.

A number of mixes were trialled and two (coded ‘A’ and ‘B’) were finally adopted for the chloride study. The first mix was a laboratory-based mix with a high cementitious matrix to encourage accelerated migration of chloride and inhibitor. This was achieved by eliminating the 20 mm coarse aggregate and substituting it primarily by 10 mm aggregate. The second mix was more typical of practice and was intended to simulate concrete of moderate quality that might typically give rise to durability problems in advance of the end of a long service life. The mix compositions are presented in Table 2. Following casting all specimens were left overnight covered by hessian cloth. Stripping of moulds took place on the day following casting, after which the specimens were cured in air.

Table 2 *Mix designs*

	Mix Type ‘A’	Mix Type ‘B’
Cement (kg/m ³)	350	280
D 20 aggregate (kg/m ³)	-	759
D 10 aggregate (kg/m ³)	991	370
Sand (kg/m ³)	791	809
Water (kg/m ³)	220	182
w/c ratio	0.63	0.65

deliverable in the SAMARIS Project [2].

Taking account of continual developments, even during the SAMARIS Project timeframe, it was decided to study the effect of two amino alcohol formulations. One was a commercially available product, typical of current generation material (designated ‘Org1’). The other was a laboratory-experimental product including elements of the potential next generation inhibitor (designated ‘Org2’). The test programme initially scoped out the effect in aggressive

The amino alcohol surface-applied inhibitor was applied to all specimens at

the manufacturers recommended dosage rate of 500 g/m². This was applied in several coats using a brush, with each coat being allowed to dry before the next coat was applied. The timing of inhibitor application was also varied to take account of cases where steel was depassivated, where further ingress of chloride was prevented by additional protective measures, as part of the inhibitor rehabilitation strategy, and cases where chloride ingress continued after rehabilitation.

The desired combination of chloride level and corrosion activity (characterised by corrosion rate) was achieved by variations in the chloride content of the solutions to which the specimens were exposed and the contact time with these solutions (number of ponding cycles). Two solution strengths were used, 1.2 mol/l and 5 mol/l. The adopted regime of ponding encouraged maximisation of the rate of chloride absorption to accelerate both the build-up of chlorides at the level of the reinforcement and the initiation of corrosion. This was achieved by cycles of contact with solution followed by a drying period. Each cycle involved four days during which the recesses were kept full of solution followed by three days without solution, during which the top surface of the recess was freely exposed to the atmosphere in the laboratory. A check on corrosion initiation was conducted at the end of each ponding cycle by potential mapping using a digital half-cell kit. Thereafter readings of the corrosion rate and corrosion potential were taken before and after inhibitor application by linear polarisation resistance measurements, using a GalvaPulse apparatus.

3. Results

3.1 Stage I: Aggressive conditions

Table 3 Chloride levels at reinforcement

No of Ponding Cycles	Mix Type 'A'	Mix Type 'B'
4	1.96	1.53
6	2.21	2.27
8	2.40	

Figure 1 Performance, Mix A, high chloride / high corrosion rate environment

Figure 2 Performance, Mix B, high chloride / high corrosion rate environment

Phase I of the study was an initial testing programme that helped to range-find the limit of effectiveness of inhibitors. The conditions were aggressive to encourage acceleration of corrosion in the laboratory. A 5 M NaCl solution was used to pond the specimens and inhibitor was not applied until it was clear from half-cell measurements that corrosion was active. The chloride levels at the reinforcement were high, in a range of the order of 2% (see Table 3) and corrosion rates exceeded 15 $\mu\text{m}/\text{yr}$. The range-finding study was therefore characterised as one of inhibitor use in concrete with high (to very high) chloride levels combined with high corrosion rates. One commercially available inhibitor product was used.

The results for Mix 'A' and Mix 'B' are presented in Figures 1 and 2 respectively. It may be noted that initially high corrosion rates exhibit significant reductions after inhibitor application but that this is not sustained with time. It may be speculated that the high corrosion rates led to significant damage to the bars that was beyond the capacity of the inhibitor to repassivate on an on-going basis.

3.2 Stage II: Moderate conditions

Figure 3 *Performance, Mix A, moderate chloride / high corrosion rate environment*

Informed by Stage I the second stage of the test programme involved an attempt to initiate corrosion and apply inhibitor before the environment had become as aggressive as in Stage I. Only one ponding cycle with 5 M NaCl solution was used on concrete of Mix 'A' and although chloride levels were moderate the environment proved to be more aggressive than intended. Both inhibitors were used. The results are presented in Figure 3, from which it may be seen that the conditions were beyond the effectiveness of the inhibitors. There was a sharp decrease in potential to approximately -450mV (silver/silver chloride reference electrode) for all specimens after the 5 M NaCl solution was added. The corrosion rate reached approximately 40 $\mu\text{m/yr}$ and settled around 30 $\mu\text{m/yr}$ and

remained high in all specimens. There was no significant difference between the controls and the specimens to which inhibitor had been applied.

It seemed that once corrosion became established at a level of the order of 30 to 40 $\mu\text{m/yr}$ in a high chloride environment the inhibitor effectiveness was not significant. The test series was therefore redirected to Phase III.

3.3 Stage III: Effect on passivated and depassivated steel

Stage III of the study sought to examine performance in concrete with low to moderate chloride concentrations at the reinforcement with the inhibitor being applied before depassivation or while corrosion rates remained low. The ponding cycles then continued on a weekly basis. The NaCl solution was lowered to a 1.2 M solution. Both inhibitors were used. The resulting corrosion rates are presented in Fig. 4 and 5.

Figure 4 *Performance, Mix A, in low to moderate chloride environment, inhibitor Org1 applied (a) before chloride ingress and (b) after 1 ponding cycle*

Once corrosion was initiated the potential fell to approximately -450mV for the control and 'Org1' samples after the first ponding cycle and fluctuated around this value.

Figure 5 Performance, Mix A, in low to moderate chloride environment, inhibitor Org2 applied (a) before chloride ingress and (b) after 1 ponding cycle

The performance of the 'Org2' samples differed. The series where inhibitor was applied before ponding (denoted 'a') yielded a potential of approximately -350 mV and the other set (denoted 'b') had a value of about -400mV. The corrosion rates were low at about 10 $\mu\text{m}/\text{yr}$. Thus while the effect of 'Org1' was not significant, 'Org2' demonstrated the potential for inhibitors to achieve their objective in the right combination of circumstances. It was interesting that the continued addition of chloride was not a factor.

3.4 Correlation with field trials

The corrosion inhibitor Org1, used in this research, has also been extensively monitored during use in the field [3]. As part of a planned repair strategy, a car park was assessed for suitability of inhibitor application. The chloride content of the concrete used in the deck was determined and found to range from 6 to 9 kg Cl/m³. The U.K. based company C-Probe Ltd. have developed a corrosion monitoring system that utilises linear polarisation resistance sweeps to ascertain corrosion rate on a weekly basis. The deck of the car park was therefore treated with the inhibitor and the corrosion monitoring system installed. The data recorded represents the real time corrosion rate and is influenced by the in-service environmental conditions experienced by the structure.

The data for Probe 1 in Figure 6 corresponds to a corrosion monitoring probe installed in an area of the parking deck where the inhibitor has worked well.

Figure 6 Example of in-service performance of inhibitor Org 1

The corrosion rate has been reduced significantly and is seen to lie consistently below a value of 1 $\mu\text{m}/\text{year}$. Conversely it can be seen that Probe 2 was installed in an area where the inhibitor has not performed as well, as the corrosion rate initially dropped considerably before rising again. The initial drop was significant, reducing the corrosion rate from approximately 18 $\mu\text{m}/\text{year}$ to approximately 2 $\mu\text{m}/\text{year}$. 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 $\mu\text{m}/\text{year}$.

4. Discussion

4.1 Indicative performance envelope

The trends identified in the laboratory trials [4] were combined with information gleaned from monitoring of inhibitor performance in bridge structures [5]. Space limitations in this paper preclude presentation of these trials but the combined findings led to the indicative performance envelope reproduced in Table 4.

Table 4 *Indicative boundaries of inhibitor effectiveness in non-saturated concrete*

Threat State	Indicative [Cl] at Reinforcement (% mass of cement)	Indicative Corrosion Rate (sustained)	Qualitative Probability
Low	$\leq 0.5 \%$	$< 5 \mu\text{m/year}$	Best scenario possible with inhibitor used as part of a proactive preventive maintenance strategy. Corrosion inhibitor potentially viable as a preventive maintenance strategy before any significant active corrosion takes place.
Moderate	$\leq 1.0 \%$	$5 - 10 \mu\text{m/year}$	State of reinforcement is likely to be suitable for consideration of corrosion inhibitor treatment. Corrosion inhibitor may be effective if a satisfactory inhibitor to chloride ion concentration ratio is achieved in the particular circumstances of the project. Protective measures to prevent further chloride build up may be advisable in chloride-rich environments.
High	$1 - 2 \%$	$10 - 100 \mu\text{m/year}$	State of reinforcement will depend on where in this range the corrosion rate lies. Effectiveness of the inhibitor will be correspondingly influenced with higher risk as corrosion rate increases in the range. Chloride levels are such that the inhibitor dosage level may have to be increased beyond typical manufacturer's recommendation and additional protective measures required. May take the technique beyond its recommended effectiveness window, introducing higher risk.
Very High	$> 2 \%$	$> 100 \mu\text{m/year}$	Reinforcement may be heavily corroded. If this is the case, corrosion inhibitor is unlikely to be a successful component of the repair strategy.

4.2 Implications for bridge maintenance and rehabilitation

In practice, once it has been established that the concrete characteristics are suitable for absorption and diffusion of surface-applied inhibitor, such that it reaches the reinforcement in sufficient quantity:

- if the steel is not heavily corroded and the chloride levels are not excessive the inhibitor-based strategy provides a mechanism that can be tailored to meet the client's expectations. This is the optimal use and is further strengthened if used as part of a proactive maintenance strategy;
- if the steel is heavily corroded and the chloride levels are excessive the inhibitor-based strategy cannot meet typical client expectations;
- conditions intermediate between these situations may be addressed by inhibitor-based strategies but only where the client's expectation is one of a holding strategy where the inhibitor 'buys time' for a defined and potentially short period.

Regarding where the boundaries lie, it is difficult to be absolutely prescriptive because the effectiveness is controlled by the combination – a combination of moderate chloride level and heavily corroded reinforcement is a worse scenario in this context than high chloride level and non-corroded reinforcement. Therefore given the current state of knowledge it is necessary to advance advice based on a qualitative probability of expectation being met. The framework used for framing this advice as a main deliverable in the SAMARIS project is that presented in Table 4.

5. Conclusions

In cases of very active corrosion initial high corrosion rates exhibited significant reductions when inhibitor was applied but this condition was not sustainable over time. This has implications for the initial assessment of inhibitor effectiveness in field trials. It appears from the laboratory trends that once corrosion is established at a high rate in a high chloride environment the inhibitor effectiveness was not significant. However if the inhibitor can be applied before damage is significant and while corrosion rates are not excessive it has a much higher prospect of contributing to the successful achievement of the intervention strategy. Although high chloride levels are normally indicative of high corrosion risk it appears that the absolute level of chloride is not as significant as the importance of getting the inhibitor to the reinforcement before corrosion damage is advanced and rates are beyond the effectiveness limit.

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