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Effectiveness of amino alcohol-based surface-applied corrosion inhibitors in chloride-contaminated concrete

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Abstract

In the present study, the effectiveness of two generations of amino alcohol (AMA) based surface-applied corrosion inhibitors (SACI) is investigated. The inhibitors were applied on the surface of the hardened concrete. The results showed that the new generation of the SACIs was effective in keeping the corrosion rate low compared to the control samples despite high chloride content at the level of the embedded steel and the effectiveness increased with chloride concentration. However none of the inhibitors were effective when they were applied after the initiation of corrosion.

Keywords: Corrosion; Durability; Chloride; Admixture; Inhibitor

1. Introduction

Reinforcement corrosion is one of the major causes of degradation in concrete structures. In the USA, more than $50 billion was spent annually on the repair of inter-state highway systems in late 1980s. In the UK, £20 billion was spent on building repair and maintenance, out of which £500 million was utilized per annum for concrete repairs by the end of 1980s [1]. Deicing salts cause corrosion damage in reinforced concrete with losses of $325 million to $1 billion per year in the US alone [2].

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 garages, 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. The use of surface-applied 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. 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 are less relevant.

Vapour phase inhibitors or migrating corrosion inhibitors have been used to impregnate packaging material, greases and waxes for many years to protect steel machinery and components, particularly for shipment and storage. An American company realised in the 1980s that they might be effective in diffusing through concrete pores and protecting reinforcing steel. Several companies now offer proprietary formulations, which are amine- and ester-based, with amino alcohols as the main volatile component [3].

Amine- and ester-based inhibitors have dual actions in concrete as the amine compound acts as an inhibitor whereas the carboxylate ester compound has pore-blocking effect, which blocks the ingress of the chlorides [4–7]. Surface-applied type amino carboxylates-based inhibitors have the pore-blocking property as suggested by their manufacturers as

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Table 1
Mixture proportions

Materials (kg/m^3)	
CEM I 32.5N	350
Coarse aggregate	991
Fine aggregate	791
Water	227
Water/cement	0.65

a secondary protection mechanism against reinforcement corrosion. Although the pore-blocking effect is not mentioned as one of the protection mechanism for amino alcohol-based inhibitors, the same effect can be expected due to the presence of a second component, which is an acid [8]. SACIs are not expected to have an effect on hardened concrete properties. However, when applied to relatively young concrete, the precipitation of calcium containing products has been reported for SACIs to cause a pore-blocking effect [8–10]. Some inconvenience arising from this effect was also reported as it could hinder the penetration of the main compound, amino alcohol [8,9].

Another problem reported for the SACIs is about the evaporation of the main component amino alcohol [9]. SACI on concrete structures may present even more difficulties in achieving the necessary concentration at the rebar level due to the variation of chloride contamination and carbonation along the concrete surface, due to the variation of thickness and permeability of the concrete cover. Therefore, it is crucial to specify the critical concentration to be achieved at the rebar level and not – as in the application notes of surface-applied inhibitors – an average weight of inhibitor solution to be applied per m^2 concrete [10,11].

The present paper studies the effect of two amino alcohol-based SACIs on the initiation and propagation stages of corrosion in chloride environment.

2. Experimental programme

Concrete slabs of size 280×280×75 mm, which were reinforced by two horizontally placed and fixed reinforcing bars were used for corrosion testing. All specimens featured a recess cast into the top surface to allow chloride solution ponding over an area 200-mm square. The concrete cover was 18 mm. The selected reinforcement was a 10 mm-diameter plain bar. The cement used was an Irish Portland cement (CEM I 42.5N). The mixture proportion of concrete is given below in Table 1. Slump, relative density and entrapped air were measured (Table 2). Compressive and tensile strength at 28 days were measured by 100 mm-cubic samples (Table 3). The inhibitors used were two new-generation amino alcohol-based surface-applied organic corrosion inhibitors.

Table 2
Tests on fresh concrete

Slump (mm)	79
Relative density	2.38
Entrapped air (%)	1.9

Table 3
Compressive and tensile strength at 28 days (MPa)

Compressive strength	40.3
Tensile strength	4.4

For Group 1 specimens, chloride cycles involve four-day ponding (70 g/l NaCl solution) followed by three-day air-drying in the laboratory. Both of the inhibitors were applied in the same way, on the ponding-surface by a brush as recommended by its manufacturer and at the recommended dosage (500 g/m^2). The inhibitors were applied: a) before chloride application, b) after first chloride cycle, and their effect on corrosion were compared to control samples. The specimens are named accordingly as ORG1a, ORG1b, ORG2a and ORG2b; the number shows the type of the inhibitor and the letter the application time. The first generation inhibitor is denoted ORG1, while the new-generation ORG2. These are proprietary amino alcohol-based surface-applied migrating corrosion inhibitors.

Group 2 specimens consist of control, ORG1 and ORG2 specimens exposed only to one ponding cycle but a higher concentration (5 M NaCl solution). For this group of specimens, the inhibitor was applied after the chloride ponding and the results are compared with control specimens until the end of the testing period without adding any other chloride. The specimens were wetted before corrosion measurement to obtain lower resistivity for concrete during the measurement.

The corrosion of the specimens was measured with the GalvaPulse apparatus, which allowed measuring the corrosion potential (E_{corr} with Ag/AgCl reference electrode), corrosion current density (I_{corr}), and the resistance of the concrete (R) in the same time. A visual inspection was conducted after the tests by breaking the specimens.

The chloride profiles were obtained for each sample after the completion of corrosion measurements.

Typical rates of corrosion [12] are given in Table 4, which is necessary for the interpretation of the results in the following section.

3. Results and discussion

The results of E_{corr}, I_{corr} and R for group 1 specimens are given in Figs. 1, 2, and 3 respectively. After the chloride application, there was a sharp drop in E_{corr} values for all specimens, varying between approx. −350 and −395 mV.

Table 4
Typical corrosion rates for steel in concrete [15]

Rate of corrosion	Polarisation resistance R_p kΩ cm^2	Corrosion current density I_{corr} μA/cm^2	Corrosion penetration μm/year
Very high	2.5–0.25	10–100	100–1000
High	25–2.5	1–10	10–100
Low/moderate	250–25	0.1–1	1–10
Passive	>250	<0.1	<1

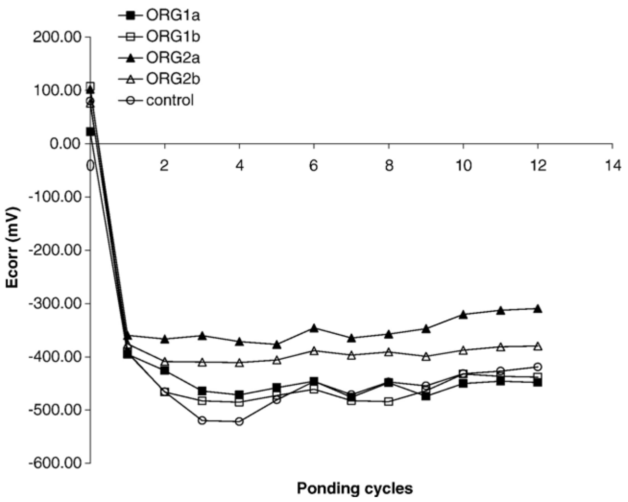

Fig. 1. Corrosion potential–time curves Group 1 specimens.

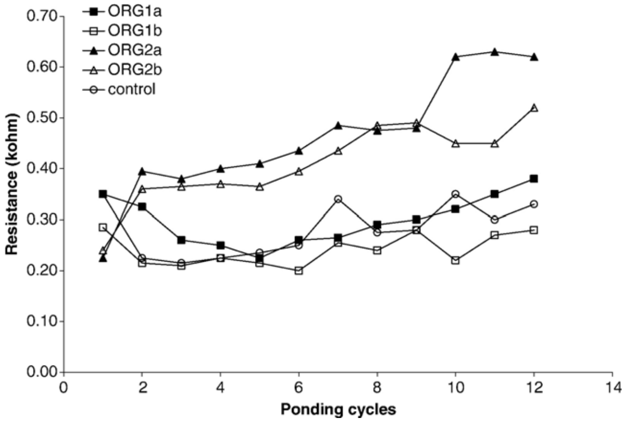

Fig. 3. Concrete resistance–time curves for Group 1 specimens.

Those values correspond to the potential range of corroding steel in chloride-contaminated concrete. The E_{corr} value of the control specimens decreased gradually with increasing chloride ponding cycles from −393 mV up to −522 mV, and fluctuated between approx. −500 mV and −420 mV. The higher E_{corr} was measured for ORG2b specimens, remaining almost stable at first cycles and then increasing despite increasing chloride ponding cycles. The behaviour of the ORG2a specimens was quite similar except for a higher decrease in E_{corr} after first chloride cycle; this difference must be due to the later inhibitor application. ORG1(a,b) specimens displayed lower (more negative) E_{corr}, the drop for ORG1b being slightly lower. However, there is no significant difference between ORG1(a,b) and control specimens.

I_{corr} values keep the same trend as E_{corr}. I_{corr} values, which were lower than 1 μA/cm^2 suddenly increased after chloride application. After this first sharp increase, I_{corr} of control continued a sharp increase from 1.14 to 2.69 μA/cm^2 and fluctuated between 2.69 μA/cm^2 and 1.59 μA/cm^2. ORG2(a,b) specimens, which had the highest E_{corr} (less negative) had the lowest I_{corr} values. I_{corr} of ORG2a decreased from 1.17 to 0.90 μA/cm^2 after the first sharp increase and remained stable around this value. ORG2b had very similar behaviour and the values are very close to those of ORG2a. The I_{corr} values for ORG1(a,b) are not very different from the control as in the case of E_{corr}.

The consistency between E_{corr} and I_{corr} values also exists for R values. After the first sharp drop, the changes are well correlated to $\mathrm{I}_{\mathrm{corr}}$ values. The increase after the first chloride cycle for ORG2(a,b) specimens may explain the initial high I_{corr} value for ORG2b specimen: the inhibitor causes an increase in concrete resistance and I_{corr} starts to decrease. As the concrete resistivity is a direct function of the moisture content and chloride contamination of the concrete, higher open porosity can lead to lower resistivity. The reduction in concrete resistance may be interpreted by a pore-blocking effect due to the inhibitor application. The pore-blocking effect can reduce the moisture content, which can cause an increase in the resistivity. Then, it can also decrease the chloride penetration, which will cause relatively lower concrete resistivity. For control and ORG1(a,b) specimens, as expected, the resistivity goes down as the chloride ponding increases. Increasing chloride content causes a decrease in the resistivity of the pore solution. The pore-blocking effect of ORG1 was reported in previous research studies [8–11]. The same effect was studied for ORG2 by the authors of the present paper and it is

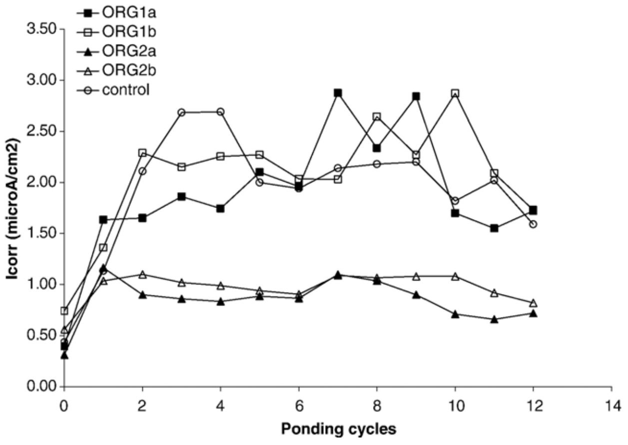

Fig. 2. Corrosion current density–time curves for Group 1 specimens.

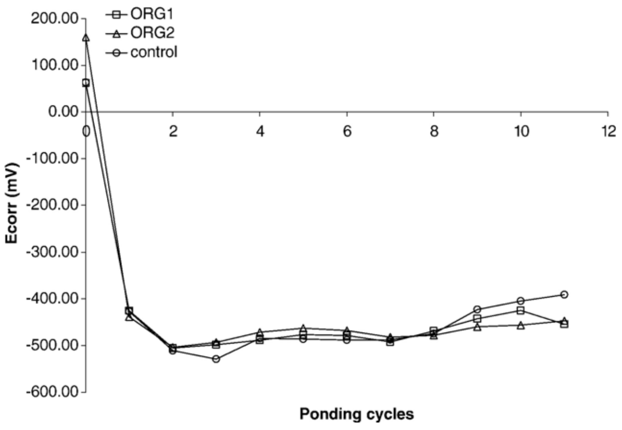

Fig. 4. Corrosion potential–time curves for Group 2 specimens.

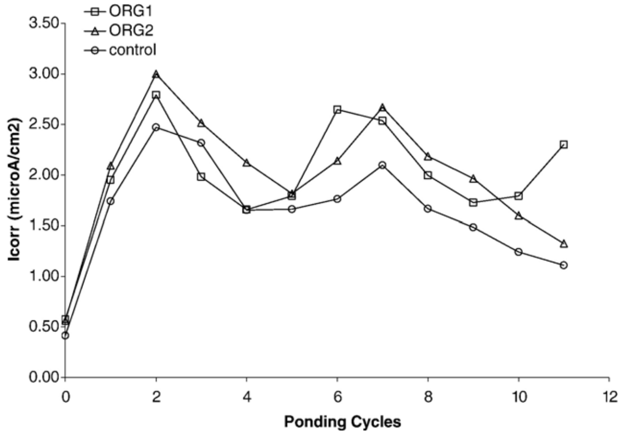

Fig. 5. Corrosion current density–time curves for Group 2 specimens.

found that ORG2 reduces surface absorption and increases freeze–thaw resistance of the concrete [13].

The literature generally indicates a delaying effect on the initiation of corrosion by the use of amino alcohol-based SACIs in mortar or concrete [9,14,15]. However, this effect occurred only for low chloride contents (<1 wt.% of cement). For higher chloride at the level of the embedded steel, the SACI was not effective [14,15]. Also after the initiation of corrosion, the amino alcohol-based inhibitor is reported to be ineffective in mortar and concrete [9,14–17]. For a chloride content 0.5 wt.% of concrete near the rebar surface, the ineffectiveness of the amino alcohol-based admixed, and surface-applied inhibitors was attributed to very high chloride to inhibitor ratio [18].

In most of the research studies mentioned above, the chloride content was not measured but only the exposure condition is given. Therefore it is difficult to conclude on the effectiveness of the inhibitor. Some results given above [14,15], measured the chloride content and when carefully analysed, the results reflects a reducing effect on chloride penetration into concrete by the use of amino alcohol-inhibitors and when the Cl^- level is close to control concrete, there is not any effect by the inhibitor.

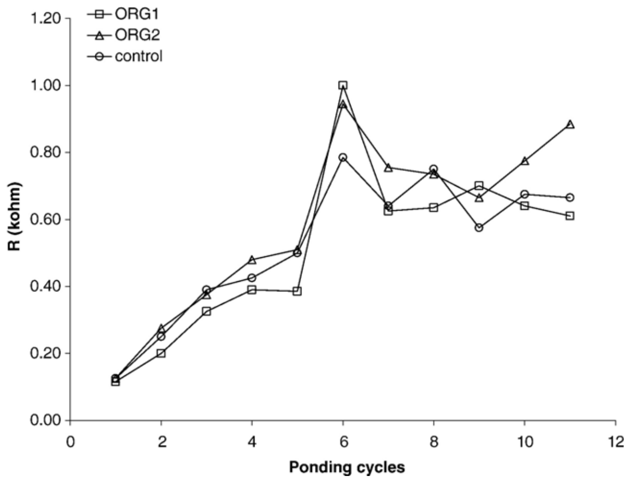

Fig. 6. Concrete resistance–time curves for Group 2 specimens.

However, the amino alcohol-based inhibitors were reported to be effective in simulated concrete pore solution [9,14,18–22] and this effectiveness increased with an increase in the inhibitor content [9,19]. The amino alcohol-based inhibitor was able to avoid corrosion when mixed to the solution with a molar ratio of 1 (inhibitor/Cl^-), but its effect disappeared when the solution was opened to air and the volatile component evaporated [9]. Thus, according to the literature, amino alcohol-based inhibitor seems to be more effective in simulated pore solution than in concrete.

In Group 2 specimens the relatively high chloride application (5 M NaCl ponding solution before inhibitor application) caused high corrosion rates for concrete specimens. However it should be emphasized that the chloride application was stopped after only one chloride ponding. E_{corr}, I_{corr} values (Figs. 4 and 5) show that there is no difference between Control, ORG1 and ORG2 specimens. E_{corr} values are very stable after the first sharp drop due to the chloride application, and they indicate high corrosion potential. I_{corr} sharply increased after the chloride application and indicated high corrosion rates. Then I_{corr} started to decrease gradually, remaining always in high corrosion rates. However this drop in I_{corr} is very well correlated with the sharp increase in R (Fig. 6) as the concrete dried (also the chloride might be washed out because only water is applied

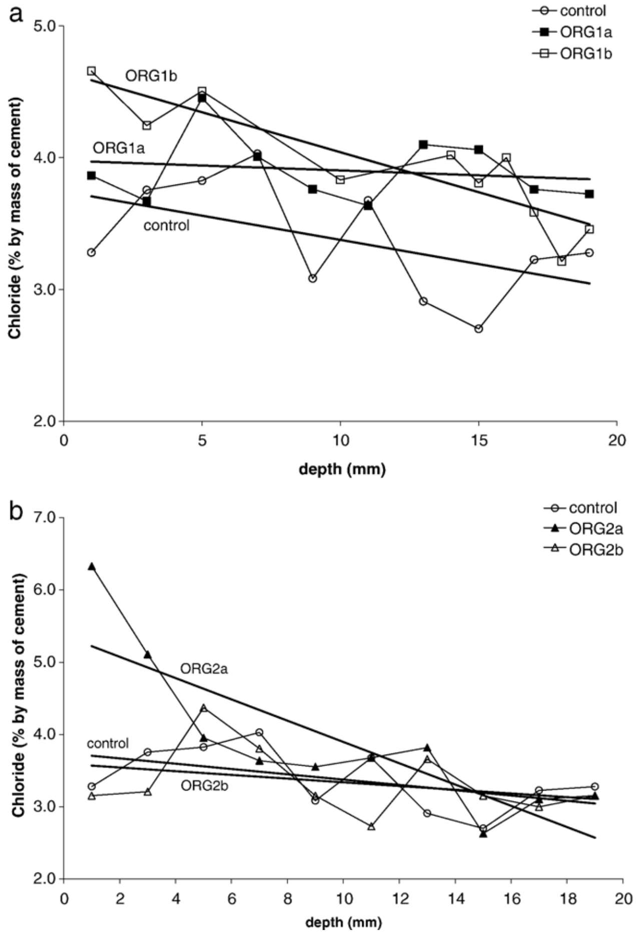

Fig. 7. Chloride profiles for Group 1 specimens (a) ORG1 (b) ORG2.

Fig. 8. Photo of steel bars after breaking specimens at the end of corrosion testing period. From left: 1) ORG1a 2) Control 3) ORG2a.

to the specimens to obtain wet concrete cover for easier GalvaPulse measurement).

These results indicate clearly that there exists a correlation between I_{corr} and R. Therefore, the effectiveness of ORG2(a,b) inhibitors in Group 1 specimens, which had the same correlation may be the result of higher concrete resistivity rather than the inhibition effectiveness. The results of group 2 indicated no efficiency neither by ORG1 nor by ORG2, which was effective in Group 1 testing. There are basically two differences between Group 1 and Group 2:

1) The chloride content was 70 g/l for Group 1 and 5 M (292.5 g/l) for Group 2 at the time of inhibitor application. Once there is high corrosion the corrosion process cannot be reversed or stopped.
2) The chloride application continued for Group 1 but not for Group 2. Therefore it is not clear for Group 2, and especially for ORG2 if it would be further corrosion for control specimens and less corrosion for inhibitor specimens, which could have the ability to keep corrosion at a certain level.

The chloride profiles (Fig. 7) indicate slightly less chloride at the level of the embedded steel for ORG2 specimens compared to ORG1 specimens. However there is no clear difference between the specimens, chloride concentration is significantly high. The higher resistivity must be thus due to the restricted moisture movement in the ORG2 specimens rather than a difference in the chloride contamination.

The results showed that there is a better protection in specimens with ORG2(a,b), which are clearly supported by lower E_{corr} and I_{corr} values throughout the testing period. Also, the visual inspection of the steel bars after breaking the specimens show clearly the difference between ORG2(a,b) and other specimens (Fig. 8).

4. Conclusion

The new-generation amino alcohol-based inhibitor was effective against corrosion when it is applied before the chloride application or just after the first chloride ponding cycle. It kept the I_{corr} at 1 $\mu A/cm^2$, which can be accepted as a threshold value for corrosion initiation, despite high chloride content at the level of the embedded steel. The other amino alcohol-based inhibitor (ORG1) and the control specimen have approximately twice I_{corr} as the ORG2 specimens.

Once concrete is contaminated with chloride and when the inhibitor was applied after a high corrosion rate (2 $\mu A/cm^2$) both of the inhibitors are ineffective.

The effectiveness of the inhibitor may be partly due to a pore-blocking effect as the resistivity of the concrete was higher for ORG2-applied specimens.

The new-generation amino alcohol-based inhibitor appeared to be a good repair strategy when it is applied before the initiation of corrosion or the corrosion rate is relatively low. The inhibitor is effective in highly chloride-contaminated concrete.

References

[1] O.S.B. Al-Amoudi, M. Maslehuddin, A.N. Lashari, A.A. Almusallam, Effectiveness of corrosion inhibitors, Cem. Concr. Compos. 25 (2003) 439–449.

[2] M. Allyn, G.C. Frantz, Corrosion tests with concrete containing salts of alkenyl-subtituted succinic acid, ACI Mater. J. 98 (3) (2001) 224–232.

[3] J. Broomfield, Corrosion inhibitors for steel in concrete, Concr. Int. (1999) 44–47 (June).

[4] J.K. Buffenbarger, M.A. Miltenberger, B.D. Miller, H.L. Casal, Long-term performance of an organic corrosion inhibitor: a decade of mechanism study and its impact on concrete service life International Congress on Advanced Materials, their Processes and Applications, Munich, 2000.

[5] C.K. Nmai, Multi-functional organic corrosion inhibitor, Cem. Concr. Compos. 26 (2004) 199–207.

[6] J.M. Gaidis, Chemistry of corrosion inhibitors, Cem. Concr. Compos. 26 (2004) 181–189.

[7] J.M. Lafave, D.W. Pfeifer, D.L. Sund, D. Lovett, S.A. Civjan, Using mineral and chemical durability-enhancing admixtures in structural concrete, Concr. Int. (2002) 71–78 (August).

[8] J. Tritthart, Transport of a surface-applied corrosion inhibitor in cement paste and concrete, Cem. Concr. Res. 33 (2003) 829–834.

[9] B. Elsener, M. Büchler, F. Stalder, H. Böhni, Migrating corrosion inhibitor blend for reinforced concrete: part 1 — prevention of corrosion, Corrosion 55 (12) (1999) 1155–1163.

[10] C.L. Page, V.T. Ngala, M.M. Page, Corrosion inhibitors in concrete repair systems, Mag. Concr. Res. 52 (1) (2000) 25–37.

[11] B. Elsener, Corrosion inhibitors for steel in concrete, Proceedings of the International Congress on Advanced Materials, Munich, 2000.

[12] S.G. Millard, D. Law, J.H. Bungey, J. Cairns, Environmental influences on linear polarisation corrosion rate measurement in reinforced concrete, NDT&E Int. 34 (2001) 409–417.

[13] T.A. Söylev, C. McNally, M. Richardson, “The effect of a new generation surface-applied organic inhibitor on concrete properties”, Cem. Concr. Compos. 29 (2007) 357–364.

[14] R. Heiyantuduwa, H.D. Beushausen, M.G. Alexander, The effectiveness of corrosion inhibitors in concretes subjected to chloride attack and carbonation, BFT 8 (2003).

[15] J.R. Mackechnie, M.G. Alexander, T. Rylands, Laboratory trials with organic corrosion inhibitors, Proceedings of the 14th International Corrosion Congress, Cape Town, 1999.

[16] W. Morris, M. Vázquez, A migrating corrosion inhibitor evaluated in concrete containing various contents of admixed chlorides, Cem. Concr. Res. 32 (2002) 259–267.

[17] L. Dhouibi, E. Triki, A. Raharinaivo, The application of electrochemical impedance spectroscopy to determine the long-term effectiveness of corrosion inhibitors for steel in concrete, Cem. Concr. Compos. 24 (2002) 35–43.

[18] A. Legat, M. Leban, J. Selih, Evaluation of the effectiveness of corrosion inhibitors for concrete, International Congress on Advanced Materials, their Processes and Applications, Munich, 2000.

[19] G. Batis, E. Rakanta, E. Daflou, Corrosion protection of steel reinforcement with DMEA in the presence of chloride ions, Proceedings of Eurocorr 2004, Long Term Prediction & Modelling of Corrosion, 2004.

[20] H.E. Jamil, M.F. Montemor, R. Boulif, A. Shriri, M.G.S. Ferreire, An electrochemical and analytical approach to the inhibition mechanism of an amino-alcohol-based corrosion inhibitor for reinforced concrete, Electrochim. Acta 48 (2003) 3509–3518.

[21] H.E. Jamil, A. Shriri, R. Boulif, C. Bastos, M.F. Montemor, M.G.S. Herreira, Electrochemical behaviour of amino-alcohol based inhibitor used to control corrosion of reinforcing steel, Electrochim. Acta 49 (2004) 2753–2760.

[22] J.R. Morlidge, D.J. Bigland, G. Sergi, S. Badger, A localised electrochemical investigation into the adsorption of amino-alcohol corrosion inhibitors to the surface of mild steel under simulated concrete pore solution conditions, International Congress on Advanced Materials, their Processes and Applications, Munich, 2000.