

THE ROLE OF CORROSION INHIBITORS IN MAINTAINING CONCRETE DURABILITY; 15 YEARS EXPERIENCE IN NEW ZEALAND AND AROUND THE WORLD

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SUMMARY

The last thirty years have seen a growing demand for increased durability of concrete repairs. This period has seen improvements in the understanding of the causes of concrete deterioration, improvements in concrete repair products and in repair specifications (Tanner et al, 2012). The period has also seen development of advanced rehabilitation and protection methods such as corrosion inhibitors. Corrosion inhibitors for the construction industry were first developed in the 1950's and a considerable volume of research has been undertaken by academic institutions and industry to quantify their effectiveness and limitations. This paper reviews some of these studies and the performance of repairs on the Scarborough Clock Tower near Christchurch. It concludes that corrosion inhibitors can be a good approach to adopt for providing cost effective improvements in concrete durability for concrete suffering from chloride and carbonation induced reinforcement corrosion.

INTRODUCTION

Prior to the 1990's most concrete repair work was undertaken without a proper understanding of the causes of concrete deterioration and without knowledge of the most suitable materials to use. Unsurprisingly the durability of concrete repairs was frequently shorter than asset owners expected. Since the 1990's there have been significant advances in the performance of concrete repair materials and the development of more advanced concrete repair methods and specifications such as EN1504 *Products and systems for the protection and repair of concrete structures* (Tanner et al, 2012). These developments are helping asset owners to obtain increased value for money from repair and refurbishment expenditure. This has never been more necessary than it is today as global climate change is predicted to accelerate the rate of decay of concrete structures (Stewart, Wang and Nguyen, 2010).

The advances in the understanding of the causes and mechanisms of reinforced concrete decay have also led to developments in concrete protection and rehabilitation techniques such as corrosion inhibitors, galvanic protection, cathodic protection, electrochemical chloride extraction and electrochemical realkalisation. These techniques have also led to significant improvements in the efficacy and durability of concrete refurbishment projects and have provided significant improvements in return on investment for asset owners.

However, while galvanic protection and impressed current cathodic protection are commonly used in New Zealand to improve repair durability by providing corrosion protection to reinforcing steel, the adoption of corrosion inhibitors in the concrete industry is relatively limited (Büchler, 2005). This is despite the fact that the development of corrosion inhibitors for concrete started in the 1950's and they are commonly and successfully used in other applications such as fuels, hydraulics, heating and cooling.

Corrosion inhibitors are substances that decrease the corrosion rate, or delay the onset of corrosion, when added in a small concentration to a corrosion environment. They function by influencing the corrosion reaction itself. Coatings and treatments that prevent the ingress of deleterious substances and consequently the transport of these substances to the steel are not, therefore, corrosion inhibitors (Elsener, 2011).

Corrosion inhibitors function by suppressing the corrosion reaction on the steel reinforcement. The corrosion reaction is an electrochemical reaction with a cathode and anode as illustrated in figure 1. The corrosion inhibitor functions by inhibiting the reactions at the anode, cathode or both. Those acting at the anode are termed anodic corrosion inhibitors, those acting at the cathode are cathodic inhibitors and those that suppress the reactions at both are termed ambiotic. Anodic inhibitors are typically the least preferred as they need to be present in a sufficiently high concentration to be effective and are sometimes degenerative (consumed in the inhibition process) so sufficient dosage and ongoing dosage may be required (Vaysburd and Emmons). In addition it is reported that some anodic inhibitors may in fact increase the corrosion rate if insufficiently dosed. By virtue of the fact that ambiotic inhibitors work on both the anodic and cathodic reactions simultaneously they are typically perceived as being the most efficient.

Unlike surface coatings, corrosion inhibitors have the advantage of providing benefits when the corrosive agents are at the rebar or corrosion has already been initiated (Büchler, 2005).

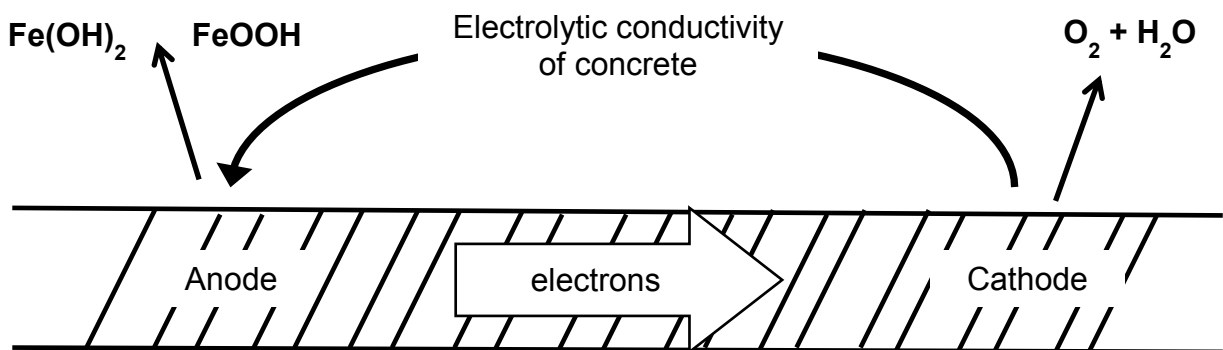
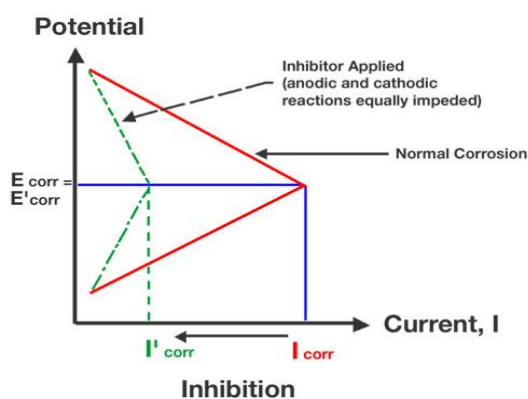


Figure 1 - simplified diagram of the steel reinforcement corrosion process



The function of corrosion inhibitors is frequently explained using the Evans Diagram reproduced in figure 2 (Jones, 2011). Inhibition of the anodic reaction rotates the upward sloping line to a steeper gradient (reducing the current produced at each potential) and inhibition of the cathodic reaction similarly rotates the downward sloping line to steeper gradient. Equilibrium is reached where the lines intersect resulting in a lower corrosion current and therefore reduced corrosion activity.

Figure 2 - Evans Diagram illustrating the function of an ambiotic corrosion inhibitor

In the concrete industry corrosion inhibitors are used in two ways; they may be cast into fresh concrete at the batching plant or they may be applied topically to existing concrete. The latter method is applicable to concrete repair and maintenance applications and is the focus of this paper. Such topically applied corrosion inhibitors are frequently referred to as surface applied corrosion inhibitors (SACI). SACI have been used in New Zealand on high profile structures such as Britomart Post Office and the Mohaka Bridge (SH5).

REVIEW OF CORROSION INHIBITOR PERFORMANCE

The use of corrosion inhibitors for protection of reinforced concrete structures affected by corrosion of steel reinforcement may provide an effective extension of service life. When corrosion inhibitors began to be adopted by the concrete industry almost twenty years ago several factors were considered and these are still relevant today. These factors are:

- How well do penetrating corrosion inhibitors actually move through concrete, especially when concrete is either carbonated or contaminated with salt-containing chloride ions?
- How effectively do corrosion inhibitors reduce the rate of corrosion of reinforcing steel that is actively corroding from either carbonation or chloride-induced corrosion?
- How long will the inhibition of corrosion be effective in reinforced concrete structures that have been treated with penetrating corrosion inhibitors?

The first two questions have been considered and largely answered over the last fifteen years but there is still some uncertainty over the answer to the third question and more research is needed. A review of these three key issues is given below:

Penetration of Corrosion Inhibitor

Surface applied corrosion inhibitors (SACI) penetrate into concrete by a combination of absorption and diffusion (Tritthart, 2002). The depth of penetration of amino-alcohol corrosion inhibitors can be tracked quantitatively using mass spectrometry to measure traces of nitrogen. A test kit has also been developed that allows qualitative assessment using a liquid chromatography method similar to that commonly used to measure biochemical species such as amino acids (Sika). Laboratory research has found the following (Elsener, 2011 and Heiyantuduwa, 2006):

- Penetration of corrosion inhibitor through new concrete was relatively quick (e.g. more than 50 mm after a month) provided the concrete was sufficiently dry
- Surface applied corrosion inhibitor was able to penetrate through carbonated concrete as easily as uncarbonated concrete
- Penetration through heavily chloride contaminated or saturated concrete was poor with little evidence of the material beyond a depth of 30mm

Depth of penetration of surface applied corrosion inhibitors in the field have not been widely reported in the literature (Soylev, 2008). However findings from South Africa by the second author are typical for performance in situ and are as follows (Mackechnie, 2004):

- Penetration of corrosion inhibitors into reinforced concrete structures affected by carbonation-induced corrosion was found to be satisfactory and was ascribed to the combination of relatively dry concrete, moderate concrete strength and relatively low cover depths to reinforcing steel
- Penetration of surface applied corrosion inhibitor was slow but adequate (e.g. achieved depth of 40-50mm) in structures exposed to carbonation and some airborne salts, typical of structures in coastal locations but not directly exposed to seawater

- Surface application to high strength repair mortars and concrete used to provide localised patch repairs was slow but effective with penetration after several months in some cases up to a depth of 75mm
- Chloride contaminated concrete in most marine structures was found to be too saturated to allow any significant vapour phase diffusion and penetration of corrosion inhibitor was restricted to the outer 15-25 mm even for relatively low concrete strengths

Corrosion inhibition performance

Several laboratory and field trials have been undertaken using surface applied corrosion inhibitors to protect structures affected by carbonation and/or chloride-induced corrosion. These have been found to be effective in reducing the corrosion rate of steel, especially when treating carbonation-induced corrosion and when combining treatment with a waterproof coating. Typical findings from medium term corrosion monitoring of structures are shown schematically in Figure 3.

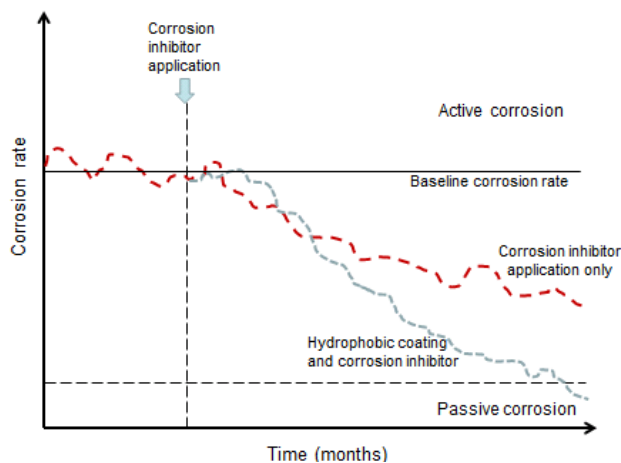


Figure 3 – reduction in corrosion rates after application of ambiotic corrosion inhibitor

The Kingway Bridge over the River Mersey in Warrington, England is a typical case study where SACI treatment was found to provide significant benefits (Samaris D21). The multi-span arch bridge was built in 1932. Long-term exposure to deicing salts had caused significant chloride penetration with levels near the corrosion threshold concentration but damp conditions had limited carbonation depths to a few millimetres. Treatment with SACI was found to produce effective penetration to a depth of 40mm after six months and post-treatment corrosion rates were less than half the corrosion rates measured before application 18 months earlier.

The high effectiveness of the treatment is as expected from SACI treatment guidelines found in the literature for treatment of structures with a low level of corrosion (Samaris D25a). Table 1 below summarises the Samaris guidelines.

Table 1: Surface applied corrosion inhibitor effectiveness guidelines for non-saturated concrete

Threat level	Chloride content by weight of cement	Corrosion rate of steel reinforcement	Qualitative probability of effectiveness
Low	< 0.5 %	< 5 $\mu\text{m}/\text{yr}$ 0.5 $\mu\text{A}/\text{cm}^2$	Most effective repair scenario
Moderate	< 1.0 %	5 – 10 $\mu\text{m}/\text{yr}$ 0.5 – 1.0 $\mu\text{A}/\text{cm}^2$	Suitable provided good penetration is achieved
High	1.0 - 2.0 %	10 – 100 $\mu\text{m}/\text{yr}$ 1.0 – 10 $\mu\text{A}/\text{cm}^2$	Depends on corrosion rates of steel reinforcement
Very high	> 2.0 %	> 100 $\mu\text{m}/\text{yr}$ > 10 $\mu\text{A}/\text{cm}^2$	Reinforcement heavily corroded consider other options

The following observations have been reported by researchers reporting the corrosion findings after SACI treatment of reinforced concrete structures:-

- Corrosion rate monitoring has shown significant medium-term reductions in corrosion rates after treatment with surface applied corrosion inhibitors (Heiyantuduwa, Samaris D21, Jones)
- Further reduction in corrosion rates with passivation of corrosion may be achieved when using surface applied corrosion inhibitors together with coating systems that reduce the internal moisture levels in concrete (Building Research Establishment, 2005)
- Monitoring of electrochemical corrosion potentials using traditional half cell measurements is unreliable after treatment with ambiotic corrosion inhibitors (Jones). However corrosion rate measurement using linear polarisation does provide consistent and reliable measurements.
- Treatment with surface applied corrosion inhibitors will significantly disturb the underlying corrosion condition, initially resulting in fluctuating and unstable corrosion potentials. This makes longer-term corrosion monitoring crucial rather than measuring unstable short-term responses that can provide mis-leading results (Richardson)
- Corrosion inhibition is related to the pre-existing corrosion state such that moderate levels of corrosion are more likely to be reduced by surface applied corrosion inhibitor treatment than high and entrenched corrosion of steel (Samaris D25a, Mackechnie et al)

Long-term performance

Most corrosion monitoring reported in the literature was done immediately before application and then for a period of months after treatment with SACI. Almost all reported structures were either suffering from carbonation-induced corrosion or contained relatively low to moderate levels of chloride ions at the reinforcing. There has been few reported corrosion findings for structures after several years of treatment partly because the technology is relatively new. Long-term performance therefore still needs to be properly assessed.

It is generally accepted that corrosion inhibitors can provide up to 15 years of life extension to structures however their efficacy in the field can be influenced by a number of factors as follows and these need to be addressed in the repair strategy:

- Corrosion inhibitors are often vapour phase materials that, being volatile, could eventually diffuse out of the concrete, particularly since it is noticeable how surface concentrations diminish in concentration in the medium-term. This phenomenon could be rapid under high temperature (Samaris)
- Agents causing corrosion of steel, such as chloride ions, may increase in concentration with time and may reactivate or exacerbate the corrosion rate of embedded steel in concrete unless other protective measures such as surface coatings are applied
- Deterioration of concrete with time may cause further cracking and other macro-defects that increase corrosive conditions around the reinforcing steel

Furthermore an understanding of the long-term performance of SACI will help inform engineers whether re-application of SACI is advantageous or if other repair technologies need to be considered too. This is the basis of a testing programme begun in New Zealand the first stage of which the evaluation of Scarborough Clock Tower is the first stage.

INSPECTION OF PREVIOUS PROJECTS



Figure 4 - Scarborough Clock Tower, Christchurch

A limited field investigation on the performance of an ambiotic corrosion inhibitor Ferrogard 903 was conducted on the Scarborough Clock Tower located in Sumner, Christchurch. The clock tower was constructed in 1934 of reinforced concrete. The clock tower consists of an open base supporting an enclosed clock chamber which houses the clock works. The clock tower is located less than 10 m from the beach front and is exposed to wind blown chlorides from the ocean. A picture of the clock tower is provided in figure 4 and a picture of a typical internal wall in the upper clock chamber is illustrated in figure 5.

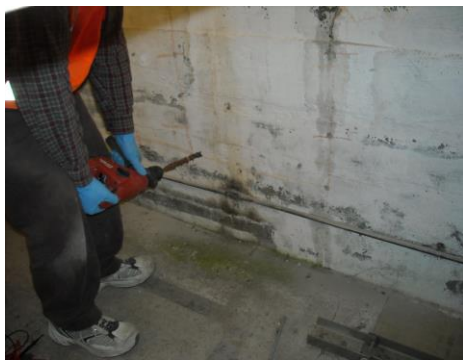


Figure 5 - internal walls of the clock chamber

In 1999 the clock tower underwent significant concrete refurbishment. As the chamber housing the clock mechanism was chloride contaminated and carbonated to reinforcement depth it was treated internally with Ferrogard-903, an ambiotic corrosion inhibitor, to reduce the rate of future deterioration. The clock tower was inspected in July 2013 and the depth of chloride ingress and carbonation was re-assessed in both the exposed base of the lower portion of the structure and the enclosed clock chamber. The presence of the corrosion inhibitor was also determined from the concrete dust samples collected at set depth increments up to 80 mm. The samples were sieved to remove any large particles and analyzed for total chloride ion concentration by means of potentiometric titration and reported as a percentage mass of concrete. The chloride profiles are provided in Figure 6.

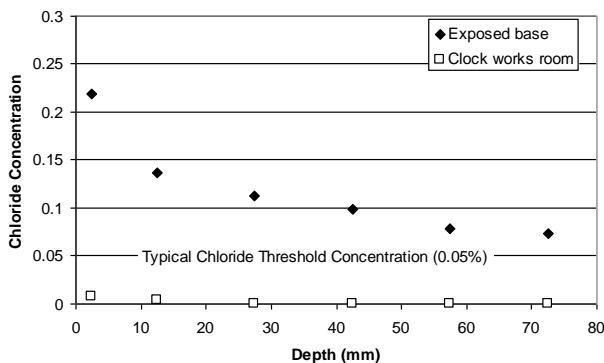


Figure 6 - chloride profiles in Scarborough Clock Tower, July 2013

As shown in Figure 6, chlorides were found in concentrations sufficient to induce corrosion (assumed to be 0.05% by mass of concrete) over the full range of sample depths for the exposed base of the clock tower. The enclosed clock chamber however showed very little penetration of chlorides with concentrations at depths greater than 20 mm below the detection

limit of the measuring equipment (approximately 0.004%). The carbonation depth was measured as 80mm in both the exposed base and the clock chamber. Carbonation is therefore believed to be the cause of the corrosion activity in the clock chamber.

The reinforcing steel in the corrosion inhibitor treated clock chamber was found to be uniformly positioned and electrically connected. The measured ECP (Electrochemical Corrosion Potential) in the clock chamber varied from relatively passive potentials of -126 mV to generally active potentials of -236 mV when measure against a silver / silver chloride reference electrode. The measured corrosion rates (using linear polarization) in the clock chamber however were found to be over a greater range than those in the clock base - from $0.45 \mu\text{A}/\text{cm}^2$ to $2.1 \mu\text{A}/\text{cm}^2$ - despite a lower level of chlorides. The carbonation depth however was sufficient to induce corrosion of the reinforcing steel. It should be noted the corrosion rates were based on assumed surface area of steel of 50 cm^2 . Differences in the diameter of the steel and perturbed surface area would therefore affect the measured corrosion rate. The values should therefore be used only as an indication of corrosion rate rather than as a basis for predicting remaining service life.

Despite the depth of carbonation and the moisture content of the concrete being measured as 3.5 – 4.0% there were very few signs of corrosion or cracking in the clock works room and given the active corrosion rates more might have been expected. The lack of apparent damage may be a result of relatively porous concrete being able to accommodate the corrosion product without cracking or spalling in addition to the corrosion inhibitor limiting the rate of corrosion in previous years. As mentioned previously a more detailed investigation including an assessment of the material properties of the concrete would be required to determine the extent of corrosion. However as detailed baseline corrosion monitoring was not undertaken before, or immediately after, treatment it is impossible to state unequivocally how effective the corrosion inhibitor has

It is apparent from the negative potentials and the relatively high corrosion rate measurements that 14 years after application the corrosion inhibitor has lost much of its efficacy. It is likely that the corrosion inhibitor was more effective at an earlier stage but without preliminary baseline reference measurement prior to its application and monitoring subsequent to its application the true effectiveness of the corrosion inhibitor at this location is unknown.

One of the points that can be drawn from this limited investigation is that the application of a corrosion inhibitor is not permanent solution to corrosion problems and some form of monitoring before and after application should be accompanied by a plan for re-application after a defined period of time. In the case of the present study the effectiveness of the corrosion inhibitor is likely to be less than 14 years.

CONCLUSIONS

Corrosion rate monitoring of concrete refurbishment projects overseas and in New Zealand has provided a wealth of data on corrosion inhibitor efficacy and limitations. There is now a large volume of research demonstrating their effectiveness in penetrating to the steel reinforcement, reducing the rate of reinforcement corrosion and slowing concrete deterioration.

Corrosion inhibitors are not suitable for all concrete maintenance projects and there are limitations on the degree of active corrosion that they can control. The research shows that they are typically effective in limiting corrosion in carbonated concrete and in chloride contaminated concrete where corrosion rates are currently low or moderate. Where corrosion rates or risks are higher other protection techniques such as cathodic protection may provide more suitable strategies for protection. Clear guidelines are now available to assist specifiers on where corrosion inhibitors can be successfully used. In addition monitoring of corrosion rates by linear polarization can provide asset owners with data on how well the inhibitor is performing.

It is generally regarded that corrosion inhibitors provide benefits for up to fifteen years. Nevertheless long term monitoring of projects and guidelines on durability and reapplication are less well documented and are recommended areas of further research.

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