RESEARCH MONOGRAPH No. 7

The Effectiveness of Organic Corrosion Inhibitors for Reinforced Concrete

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Contents

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INTRODUCTION

Reinforced concrete has become the most popular global construction material due to its versatility, low cost and durability. Usually the alkalinity of concrete maintains the passivity of embedded steel and prevents corrosion from occurring. This passive layer may be disrupted by carbonation or the ingress of chlorides which thereby allow corrosion to occur in the presence of moisture and oxygen.

Durable concrete can be constructed relatively cost-effectively but reinforced concrete structures may be compromised by poor design, bad practice, marginal materials or severe environments. This has led to an increasing amount of corrosion-damaged structures that require repair during service [1]. In many countries repairs have also become more frequent as concrete infrastructure ages and longer service lives become necessary. The growth of the concrete repair market has meant that engineers require more effective and reliable systems of repairing corrosion-damaged structures.

Many different approaches to concrete repair and protection exist, with varying degrees of cost and reliability. Options such as localised patch repairs may be cost-effective in the short-term but have limited durability whereas more elaborate techniques such as cathodic protection may be reliable but too costly for many applications. The use of corrosion inhibitors has been widely promoted as a more pragmatic means of concrete repair and protection [2]. Like all repair techniques however, the use of corrosion inhibitors in concrete has limitations that need to be understood before use.

The purpose of this research monograph is to introduce the use of organic corrosion inhibitors both for repair and protection of reinforced concrete. Guidance is given on the use of these materials such that practising engineers may make the best use of available materials and technology. This monograph derives from two research projects at the University of Cape Town on the effectiveness of organic corrosion inhibitors in reinforced concrete. One project addressed the problem of chloride-contaminated concrete, while the other focussed on carbonated concrete [3,4].

CORROSION OF STEEL IN CONCRETE

a) Theoretical background

Steel reinforcement cast into fresh concrete is immediately passivated by the highly alkaline environment present within concrete. Passivation is caused by a dense ferric oxide layer that stifles further corrosion despite the presence of moisture and oxygen. This passive layer may however be disrupted by a reduction in alkalinity due to carbonation or by the presence of sufficient chloride ions at the steel surface.

The alkalinity of concrete may be lowered by acidifying gases such as carbon dioxide and sulphur dioxide. Once the pH of concrete has been lowered below 10.5 the passive film begins to break down and general corrosion may occur along the steel surface. Chloride ions in contrast initiate corrosion in a different manner since they cause local failure of the passive layer and allow pitting corrosion to occur. This breakdown of passivation occurs when chloride levels exceed a certain threshold level at the steel surface (typically taken as 0.4% chloride by mass of binder). Corrosion of steel in concrete is an electrochemical process involving two half cell reactions; an anodic reaction where iron dissolves into solution and a cathodic reaction where water and oxygen are reduced to hydroxyl ions. Further oxidation of the corrosion products produces hydrated oxides (rust) that expand and disrupt the surrounding concrete. The corrosion process is shown schematically in Figure 1.

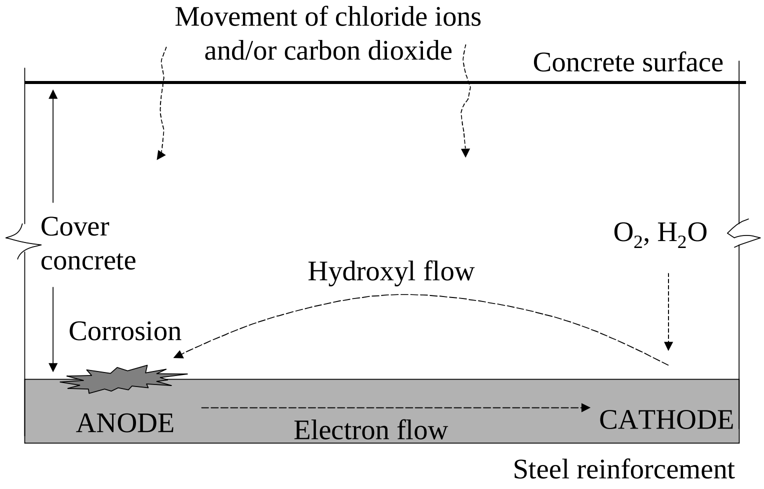


Figure 1: Process of corrosion of steel in concrete

The establishment of depassivating conditions at the steel surface is not necessarily indicative of future corrosion damage, since other factors such as moisture content and oxygen availability will ultimately determine the rate of corrosion. Consequently, corrosion rate measurements are advantageous in providing information on the corrosion state of reinforced concrete.

b) Corrosion monitoring

Specialised corrosion monitoring techniques are used to assess the probability of corrosion occurring, as well as the extent and severity of the problem. The more commonly used and accepted methods are briefly described below.

Half-cell potential measurements

Corrosion of reinforcement is associated with anodic and cathodic areas along the reinforcement with consequent changes in electropotential of the steel. Rebar potentials are measured using a reference electrode connected to a handheld voltmeter, with an external attachment to the reinforcing steel (shown in Figure 2). This technique is better suited to chloride-induced corrosion than carbonation-induced corrosion where clearly defined anodic regions are not present [5,6].

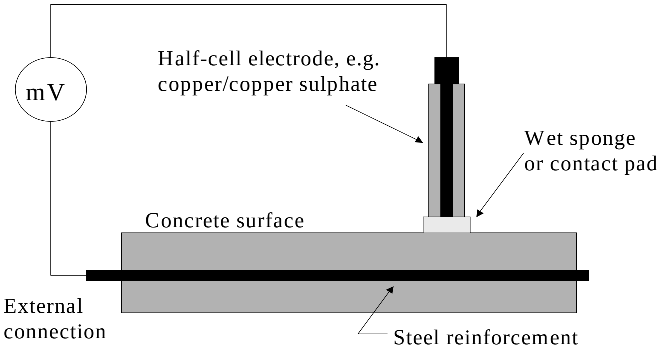


Figure 2: Measurement of half-cell electro-potentials

The half-cell potential is a function of the extent to which steel is depassivated, and thus indicates the extent of carbonation or the presence of sufficient chlorides to break down the passive layer, as well as the presence of oxygen to sustain the passive layer. Therefore half-cell measurements cannot evaluate the kinetics of the corrosion reaction and should only be used for an indication of the corrosion risk of the steel. Half-cell potential readings should be supplemented with corrosion rate measurements. Table 1 shows the ASTM guidelines for interpreting rebar potentials measured with a copper/copper sulphate half-cell [5].

Table 1: Copper/copper sulphate potentials and associated risk of corrosion

Rebar potential (mV)	Qualitative risk of corrosion
> -200	Low
-200 to -350	Uncertain
< -350	High

Resistivity measurements

Corrosion of steel in concrete is an electrochemical process that can be electrolytically stifled by a dry or impermeable material. Concrete resistivity therefore influences the corrosion rate of embedded steel once favourable conditions for corrosion exist. Resistivity depends on the moisture condition of the concrete, permeability and diffusivity of the microstructure and on the concentration of ionic species in the pore water. Resistivity measurements should not be seen as definitive measures of corrosion activity but rather be used to complement other techniques.

The Wenner probe is commonly used to measure resistivity and consists of four equally spaced probes, which make contact with the concrete surface. This method, shown in Figure 3, uses a small alternating current that is passed between the two outermost contacts, and the resulting potential difference between the inner two contacts is measured. The resistivity of the concrete is then determined. Table 2 provides an interpretation of resistivity measurements from the Wenner four-probe system, when referring to depassivated steel[7].

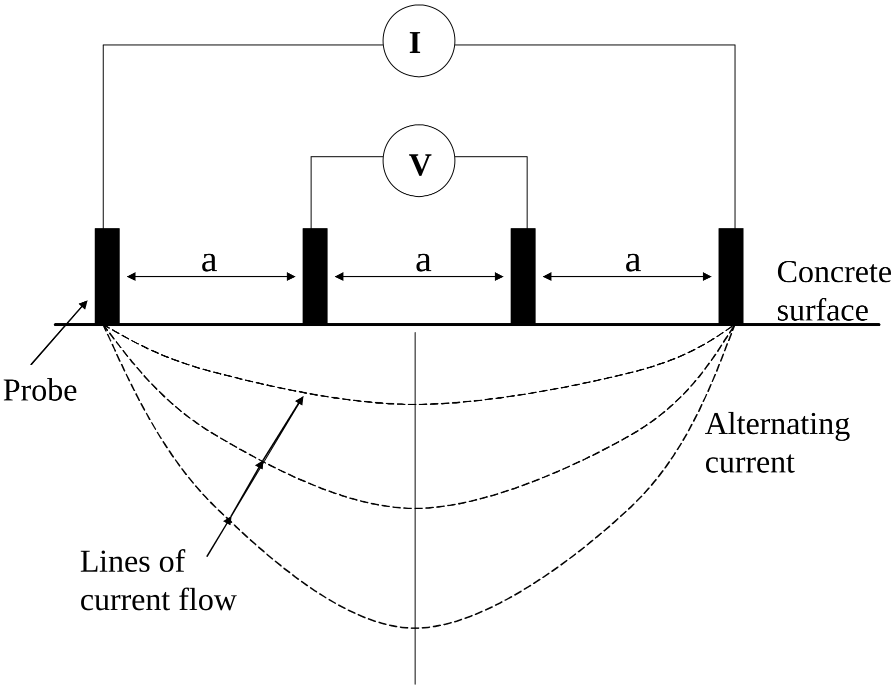


Figure 3: Wenner probe for measuring concrete resistivity

Table 2: Likely corrosion rate based on concrete resistivity[7]

Resistivity of concrete (kΩ.cm)	Corrosion rate
< 5	Very high
5 – 10	High
10 – 20	Low to moderate
> 20	Low

Corrosion rate measurements

Corrosion rate measurements are the only reliable method of assessing corrosion activity in reinforced concrete. Corrosion rates of embedded reinforcement can be measured relatively simply using linear polarisation resistance (LPR) techniques. Corrosion rates measurements on field structures are most commonly done using galvanostatic LPR techniques (application of a small current) with a guard-ring sensor to confine the area of steel under test. The LPR instrument used in this work was a commercial device called the Gecor 6. Measurements are taken by placing the sensor on the concrete surface directly over the rebar and making an electrical connection to the reinforcing steel. Figure 4 shows a typical Gecor 6 instrument.

Figure 4: Typical Gecor measurement instrument

Experience indicates that corrosion rates fluctuate significantly in response to environmental and material influences, and single readings are generally inadequate. Several readings over different days are therefore recommended to obtain a reliable indication of corrosion rate. Table 3 shows a qualitative guide for assessing corrosion rates of site structures [6].

Table 3: Qualitative guide for the assessment of corrosion rates [6]

Corrosion rate ($\mu A/cm^2$)	Qualitative assessment of corrosion rate
> 10	High
1.0 – 10	Moderate
0.1 – 1.0	Low
< 0.1	Passive

c) Corrosion damage

Two consequences of reinforcement corrosion are commonly observed; cracking and spalling of the cover concrete as a result of expansion of the corrosion product, and a reduction of cross-sectional area of the steel bar by pitting (usually only a problem in prestressed concrete structures). The severity of corrosion damage depends on the geometry of the element, cover depth, moisture condition, age, environment and service stresses. The nature and extent of corrosion damage is therefore quite specific to each structure and not easy to predict.

The effect of corrosion damage on a reinforced concrete structure generally follows three distinct phases:

- an initiation period before corrosion activation, during which little deterioration occurs
- a propagation period after corrosion activation, that generates expansive corrosion products causing cracking of the cover concrete
- an accelerated period of damage where corrosion increases due to easy access of oxygen and water through cracks and spalls

Unfortunately most reinforced concrete structures experiencing cracking and spalling damage are beyond the point where simple cost-effective measures can implemented to restore durability. It is critical therefore that the repairs are undertaken as early as possible [8].

CORROSION INHIBITORS

a) Background

A corrosion inhibitor may be defined as "a chemical substance that decreases the corrosion rate when present in the corrosion system at suitable concentration, without significantly changing the concentration of any other corrosion agent" [9]. The principle of corrosion inhibitors is to develop a thin chemical layer, usually one or two molecules thick, on the steel surface, that inhibits the corrosion by either forming a protective film on the substrate to be protected, or by immobilising the corrosive species and preventing them from reaching the steel. Inhibitors can affect the cathodic reaction, the anodic reaction or both.

Corrosion-inhibiting chemicals are either mixed in to the fresh concrete, or are applied to hardened concrete and then penetrate through the concrete to react on the reinforcing steel surface to slow down the rate of corrosion [10]. This difference is fundamental and will be discussed in a later section. Corrosion inhibitors are not miracle cures that totally stop corrosion; rather they 'buy time' by increasing the time to the onset of corrosion and then by reducing the rate of eventual corrosion as shown in Figure 5.

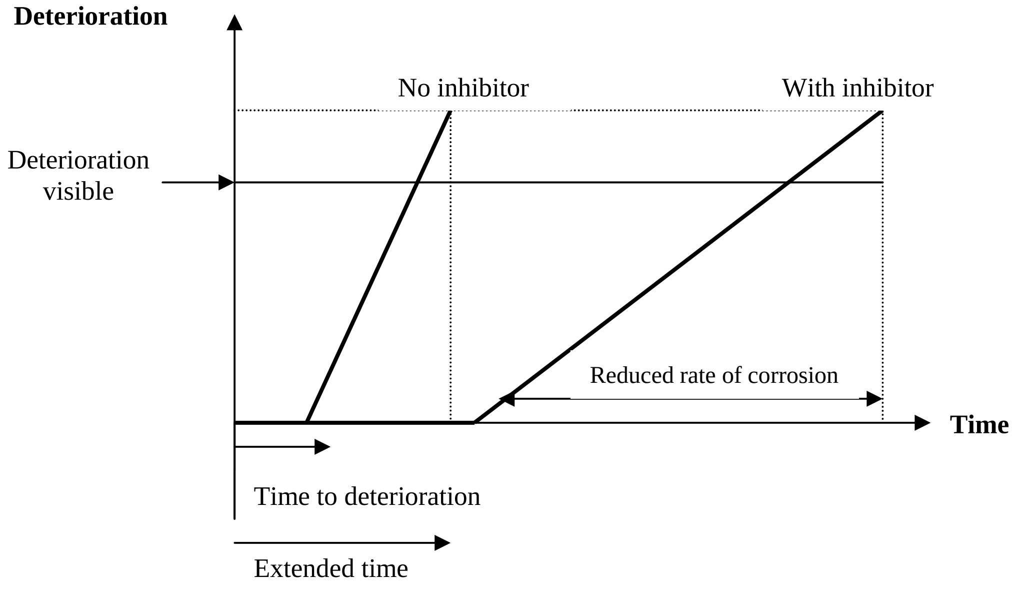


Figure 5: Extension of the service life of a concrete structure with corrosion inhibitor treatment [11]

Anodic inhibitors

Anodic inhibitors reduce the rate of reaction at the anode by accepting electrons. They usually react with the corrosion products to form a protective coating on the metal surface. The most commonly used anodic corrosion inhibitor is calcium nitrite.

Cathodic inhibitors

Cathodic inhibitors act to prevent the reaction at the cathode. Cathodic inhibitors adsorb on the steel surface and act as a barrier to the reduction of oxygen. The main types of cathodic inhibitors are based on sodium hydroxide and sodium carbonate.

Multi-functional or mixed inhibitors

Mixed inhibitors influence both the anodic and cathodic regions. Amino alcohol based inhibitors are typically mixed inhibitors, since they give both cathodic and anodic protection. They form a monomolecular layer on the reinforcing steel, which strongly adsorbs to the metal surface and interferes with the anodic and cathodic reactions in the area of adsorption[11]. Typical of such products is a commercial product called FerroGard, a multi-functional corrosion inhibitor based on a blended amino compound that allows the inhibitor to diffuse through the concrete as a liquid as well as a vapour.

b) Admixed corrosion inhibitors

There are two main types of inhibitors specifically for protecting reinforced concrete; admixed corrosion inhibitors (ACI) and migrating or penetrating corrosion inhibitors (PCI). The most widely applied admixed corrosion inhibitor is calcium nitrite.

Calcium nitrite

Calcium nitrite has been successfully used since 1978, particularly in parking, marine and highway structures. Calcium nitrite is known to reduce corrosion without affecting the properties of concrete apart from slightly raising the pore water conductivity.

This corrosion inhibitor has been widely used in the United States to protect reinforcement from corrosion especially on bridge decks exposed to deicing salts. Several laboratory and field studies have shown the effectiveness of the admixed inhibitor in resisting chloride-induced corrosion [12]. The level of protection depends on the dosage of inhibitor used and the chloride level during service. Bridge decks in Illinois, New Hampshire, and Maine containing calcium nitrite were recently cored and the results show that calcium nitrite is still present at original quantities and corrosion measurements indicate passivity [13].

Organic admixed corrosion inhibitors

A number of proprietary organic inhibitors for use in fresh concrete have been introduced, including various amines, alkanolamines, their salts with organic and inorganic acids and emulsified esters, alcohols and amines. Tests conducted to determine the inhibition mechanism of amines and amino-alcohol based inhibitors found a surface layer made up of amino alcohols and associated radicals on the surface of the steel reinforcement. These inhibitors were able to displace chloride ions from the steel surface and form an inhibitive film around the reinforcement thus protecting it from corrosion [14].

c) Penetrating corrosion inhibitors

Vapour phase inhibitors have been used to impregnate packaging, greases and waxes for many years to protect steel machinery and components. In the 1980s it was realised that they might be effective in penetrating through concrete and protecting the reinforcing steel. Tests carried out on the ability of these surface applied amine and alkanolamine-based inhibitors to control the rate of corrosion of steel in concrete which has been subjected to prior contamination with chloride salts or carbonation have been reported in the USA and Europe [15].

These surface applied corrosion inhibitors contain organic amines, amino-alcohols, fatty acids or a combination of these chemicals. Penetrating corrosion inhibitors are able to diffuse considerable distances through concrete both in the pore solution phase and, because of their relatively high vapour pressures, through the gaseous phase of the material when exposed to unsaturated environments [14]. They penetrate to the steel surface developing a multi-molecular layer on the steel. In principle their ability to diffuse as a vapour gives them an advantage over liquid inhibitors.

Site surveys and experimental test results have indicated that the inhibitor can penetrate through concrete at a rate of up to 5-10 mm per day and to a depth of up to approximately 50-60 mm in 3 months, depending on porosity and permeability of concrete[16]. Depth profiles show that a concentrated band of the inhibitor passes through the cover concrete over a period of days, allowing of the inhibitor to penetrate to embedded steel surfaces irrespective of the orientation of the application, with the rate of transportation declining as the depth of penetration increased.

Mixed organic and inorganic penetrating corrosion inhibitors

The inhibitor used in the investigation reported here was typical of this type of material: a multi-functional inhibitor based on an organic and inorganic, film forming, blended amino compound that allows the inhibitor to diffuse through the concrete as a vapour as well as a liquid. *Such products, like all other inhibitors, form a protective film on the steel surface, which inhibits both the ferrous decomposition (anodic reaction) and restricts oxygen access to the steel surface (cathodic reaction).* These more recent products (compared to the first generation basic amino-alcohol inhibitors) display improved penetration rates and depths and a greater affinity for the steel, therefore producing a thicker protective layer that also forms faster than previously [10].

Based on results obtained from laboratory testing and monitoring of actual repairs undertaken in the USA as part of the Strategic Highways Research Program (SHRP), this type of inhibitor appeared to [17]:

- Improve resistance to the initiation of pitting corrosion in chloride contaminated concrete and reduce the risk of general corrosion in carbonated concrete.
- Retard the onset of corrosion in new structures, and reduce the risk of incipient anode corrosion taking place in areas adjacent to repairs.
- Achieve a rate and penetration depth of up to 20 mm per day and 80 mm in 28 days respectively.
- Adsorb on the surface of the reinforcing steel in a layer of 20-100 Å and displace chloride ions from the steel surface.
- Be active in alkaline and neutral (carbonated concrete) environments.

ASSESSMENT OF REPAIR OPTIONS

Before corrosion inhibitors are considered for use in repairs it is important that an overall risk assessment is undertaken for any particular structure. There are an increasing number of repair systems available that need to be compared on the basis of technical feasibility, probability of success and cost. Expensive repair systems such as cathodic protection may incur greater short-term cost but have inherently greater reliability than cheaper options such as localised patch repairs. Nevertheless many concrete structures exhibit only moderate levels of corrosion damage and these can be effectively repaired at moderate cost.

The success of concrete repairs is determined by a number of factors that need to be evaluated simultaneously:

- diagnosis of the root cause of the problem such that an appropriate repair specification can be formulated
- recognition of the physical constraints of the job such that competent application of repair system on site is possible
- understanding of the practical limitations and special requirements of the chosen method of repair
- assessment of environmental and service conditions to ensure that the repair system is able to perform adequately
- understanding of structural factors to ensure compatibility of repair materials with concrete substrate
- adequate budget to ensure that rehabilitation is not spread so thinly over the structure as to be ineffective

A number of issues need to be evaluated before the engineer settles on a method of concrete repair. These are summarised in Figure 6.

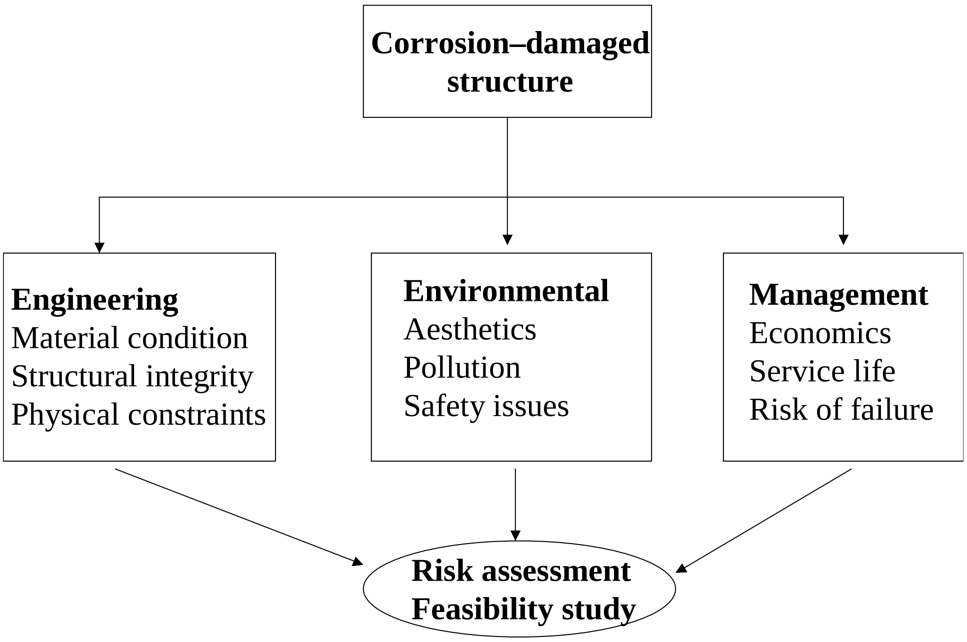


Figure 6: Risk assessment issues for concrete repair

Information needs to be collected from a variety of sources and analysis is often complex. Further details about condition survey and repairs of corrosion-damaged reinforced concrete structures is given in Monograph No. 5 of this series [8].

The remainder of this monograph deals with the outcome of two laboratory projects that evaluated the effectiveness of a multi-functional penetrating corrosion inhibit (Ferrogard). Data from field studies are also evaluated.

CARBONATION-INDUCED CORROSION

Carbonation-induced corrosion causes general corrosion with multiple small pitting along the reinforcement. Carbonated concrete tends to have fairly high resistivity that discourages macro-cell formation and generally only sustains moderate corrosion rates. This means that damage from carbonation-induced corrosion is often fairly superficial and easy to repair.

Conditions conducive to rapid carbonation (50-70% R.H.) are generally too dry to maintain significant corrosion levels in concrete. Reinforcement embedded in carbonated concrete will therefore only corrode when exposed to moist conditions during periodic wetting of the concrete. Carbonation-induced corrosion of reinforcement at cover depths greater than 25 mm is rare due to insufficient penetration of wetting fronts (this is not true of water-retaining structures where a wet and dry face are in close proximity) .

a) Laboratory studies

A series of laboratory trials were undertaken between 2000 and 2002 to assess the effectiveness of an organic corrosion inhibitor for treating carbonation-induced corrosion [4]. The penetrating corrosion inhibitor Ferrogard 903 (PCI) was tested, either before corrosion initiation (BC) or after corrosion activation (AC) and results compared with control concrete.

Testing procedure

Specimens used in this investigation were blocks of size 120x120x380 mm with a CEM I concrete grade of 30 MPa and 16 mm high yield reinforcing bars at cover depths of 10 or 20 mm. Carbonation of the cover concrete was accelerated using a control chamber operating at 30°C, 80±5 % relative humidity and containing 10% carbon dioxide. This achieved a carbonation rate of up to 5 mm per month. Specimens were treated with PCI either before or after the carbonation process. The application rate was three coats at 0.1 litres per square metre applied on consecutive days, followed by water saturation. Thereafter, the concrete blocks were exposed to cycles of 5 days of wetting and 2 days of drying in a laboratory environment to promote corrosion.

It would be expected that a vapour phase material such as PCI would easily penetrate through a fairly dry concrete as used in this laboratory trial. A range of the concrete mixes from 20 to 50 MPa was used in initial penetration trial work. (See Appendix A). The depth of penetration of the PCI was confirmed 28 days after application by analysing cores extracted from the blocks. All concrete was found to have sufficient penetration of the inhibitor with the exception of the grade 20 blocks, which had penetrated only to a depth of 30 mm (see Table 4). This anomaly may be ascribed to the fact that the volatile PCI material was easily lost from such an open microstructure.

Table 4: Penetration depth of inhibitor at 28 days

Concrete Grade (MPa)	Depth (mm)	Indicator colour	Qualitative rating [#]	Organic nitrogen . [*] (mg/g of concrete)
20	0-15	Red	Excellent	0.55 – 2.20
	15-30	Pink	Good	0.17 – 0.55
	30-45	Trace	Inadequate	0.06 – 0.28
	45-60	-	-	-
30	0-15	Red	Excellent	0.55 – 2.20
	15-30	Pink	Good	0.17 – 0.55
	30-45	Pink	Good	0.17 – 0.55
	45-60	Pink	Good	0.17 – 0.55
40	0-15	Red	Excellent	0.55 – 2.20
	15-30	Pink	Good	0.17 – 0.55
	30-45	Pale pink	Adequate	0.06 – 0.28
	45-60	Pale pink	Adequate	0.06 – 0.28
50	0-15	Red	Excellent	0.55 – 2.20
	15-30	Pink	Good	0.17 – 0.55
	30-45	Pale pink	Adequate	0.06 – 0.28
	45-60	Pale pink	Adequate	0.06 – 0.28

[#] This rating was provided by the manufacturer based on the indicator colour

[*] These values were estimated from total organic nitrogen (TKN) measurements of concrete [18]

Discussion of results

Concrete blocks were exposed to cycles of wetting and drying for a period of one year or more to simulate outdoor exposure. At weekly intervals concrete resistivity, rebar potentials and corrosion rates for each block were measured. These measurements were found to be quite variable initially but the variability reduced with time as conditions stabilised. The optimum wetting and drying cycle that was selected was five days wetting and two days drying. This cycle permitted the concrete to dry sufficiently to allow oxygen to be available at the cathode, and provided sufficient moisture to promote corrosion.

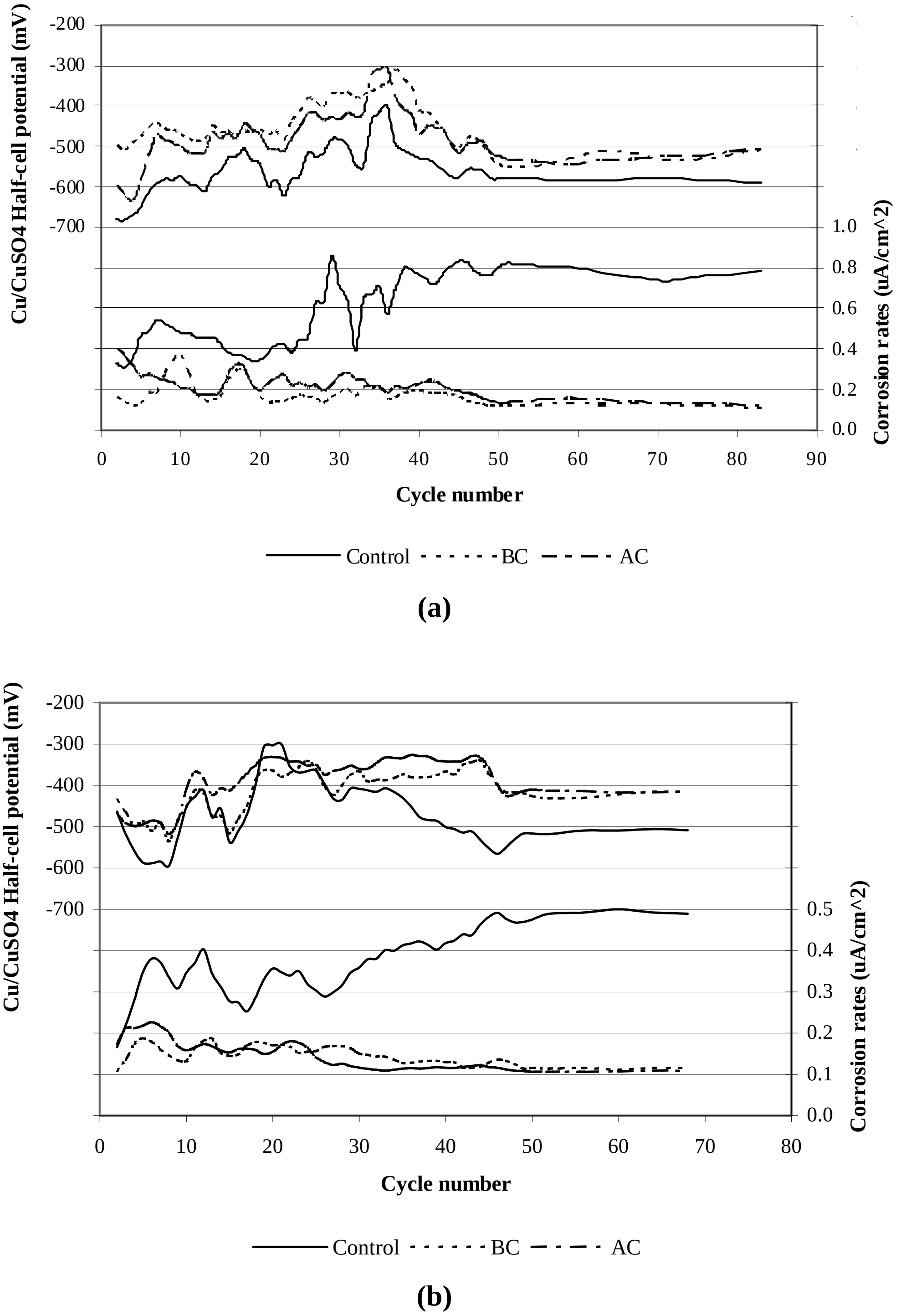
Resistivity of concrete was found to fluctuate in the range from 20-50 kΩ.cm with no significant difference between concrete with or without inhibitors. Typical values recorded during the testing programme are shown in Table 5. These resistivity values are fairly typical for carbonated concrete and indicate that high corrosion rates are unlikely.

Table 5: Resistivity values of carbonated concrete (kΩ.cm)

Cycle number	Control		BC		AC	
	10 mm	20 mm	10 mm	20 mm	10 mm	20 mm
5	22	37	22	39	30	43
45	27	32	26	30	32	30
72	29	24	23	30	31	26
87	29	-	36	-	29	-

Results for rebar potentials and corrosion rates are shown in Figures 7 (a) and (b) for 10 and 20 mm cover specimens respectively. The results are expressed as three point moving averages of two specimens in each case.

Rebar potentials all showed a strong shift towards more negative values after wetting cycles had started. Reinforcement in concrete containing inhibitor tended towards less negative potentials than controls. Rebar potentials are poor indicators of corrosion activity, particularly in carbonated concrete, and values are useful only as a basis of comparison.



(a)

(b)

Figure 7: Rebar potentials and corrosion rates for (a) 10 mm and (b) 20 mm cover samples

Corrosion rates of all samples were unstable initially but clearer trends became apparent after about 30 cycles. BC and AC samples exhibited steadily lower corrosion rates that were approaching passive levels after 60 cycles. In contrast, control samples showed active corrosion in the region of 0.8 $\mu A/cm^2$ for reinforcement at 10 mm cover and approximately 0.5 $\mu A/cm^2$ for steel at 20 mm cover.

The phenomenon of variable corrosion rates was far more marked in low cover samples, due to the influence of wetting and drying in the thinner cover. The variations were also more evident in the control specimens. The penetrating corrosion inhibitor was therefore able to control corrosion rates better during wetting and drying cycles, an indication of its effectiveness.

These laboratory trials showed that the corrosion inhibitor was able to significantly reduce the corrosion rates of reinforcement at covers of 10 and 20 mm embedded in 30 MPa concrete. Whilst testing was only carried out for a period of twelve months or so, the accelerated exposure regime could be equivalent to many years of service outdoors.

b) Field studies

Several reinforced concrete structures experiencing carbonation-induced corrosion were selected for study on the University of Cape Town campus. Whilst some showed signs of significant corrosion-damage, corrosion monitoring found that most had very low carbonation rates. This was ascribed to the fact that monitoring was undertaken during early summer when moisture conditions in the concrete were becoming too low to sustain significant rates of corrosion.

The roof of the Menzies Building at UCT was found to be a suitable site to conduct a field trial of PCI material. Compressive strength of the concrete was 20-25 MPa, cover to reinforcement varied from 8 to 20 mm and the depth of carbonation was 30 to 40 mm. Areas of localised spalling (see Figure 8) were apparent and active corrosion rates were measured. The structure was fully exposed to the elements and represented the type of structure that would be considered for repair.

Figure 8: Spalling and cracking of concrete due to carbonation-induced corrosion on parapet walls at the Menzies site.

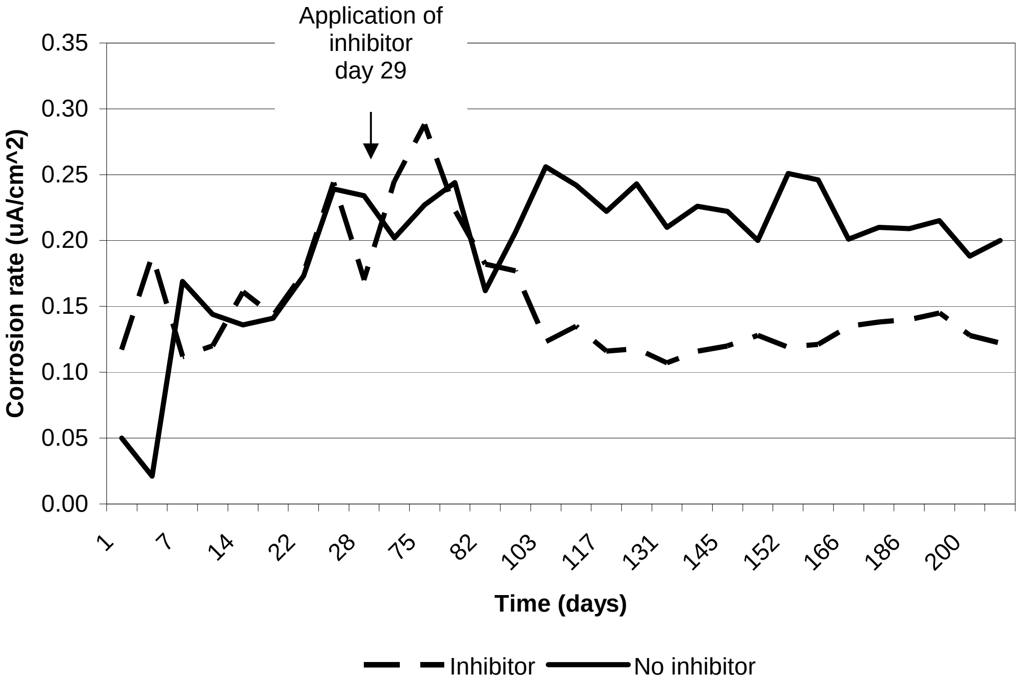


Figure 9: Corrosion rates measured on Menzies roof parapet wall

c) Recommendations

Penetration of PCI through carbonated concrete to reinforcement is generally easy to achieve since:

- carbonated concrete is often fairly dry allowing reasonable levels of vapour diffusion
- most structures exhibiting carbonation-induced corrosion are not made with very dense concrete (unlike some marine structures)
- reinforcement exposed to carbonation-induced corrosion is generally at reasonably low cover depth (i.e. less than 25 mm)

Testing of adequate penetration may be required when the concrete is noticeably damp or when the surface is contaminated or polluted in some way. Testing is also recommended when the concrete is extremely porous and there is concern about retention of the volatile material. It should be noted that these very poor quality concretes should be coated or sealed to improve the environmental conditions under which the PCI has to operate.

Research has shown that PCI treatment is able to largely arrest carbonation-induced corrosion provided the cover concrete is intact. It should be noted however that corrosion control is best achieved before widespread damage has occurred and the corrosion process is entrenched. Steel covered with a thick layer of corrosion product may be difficult to treat while an open concrete microstructure with cracks and spalls limits the effective of corrosion inhibitor systems. Corrosion inhibitors are best used in conjunction with coatings and hydrophobic sealants to achieve long-term corrosion control since these reduce the severity of the external environment.

CHLORIDE-INDUCED CORROSION

Chloride-induced corrosion is generally far more aggressive than carbonation-induced corrosion, being characterised by pitting corrosion with distinct anodic and cathodic sites along the reinforcing steel. The presence of salt concentrations in the cover concrete together with moist conditions means that macro-cell corrosion is able to sustain high corrosion rates leading to significant damage. Only anodic regions show evidence of corrosion whilst cathodic areas may be undisturbed despite being exposed to corrosive conditions.

The pernicious nature of chloride-induced corrosion makes repairs difficult to achieve. Treating only the symptoms of the problem, namely the cracks and spalls, invariably leads to the formation of incipient anodes that cause further deterioration with time. More comprehensive repair systems need to be used to ensure the repairs are durable.

a) Laboratory studies

A series of laboratory trials were undertaken between 1997 and 1999 to assess the effectiveness of organic corrosion inhibitors for treating chloride-induced corrosion [3]. Both ACI and PCI material (i.e. Ferrogard 901 & 903) were tested at varying levels of chloride concentration.

Testing procedure

Concrete blocks were cast of either grade 20 or 40 MPa concrete using CEM I cement. (See Appendix A). The blocks were 300x450x180 mm and each contained two 16 mm high yield reinforcing steel bars at cover depths of 25 and 50 mm with a central stainless steel counter electrode. One set of blocks was left untreated as controls, one set was cast with 2, 4 or 6% ACI (by mass of cement), while the last set was treated after corrosion had been initiated with PCI. The concrete blocks were subjected to weekly cycles of wetting with a 5% NaCl solution followed by drying. This allowed chloride ions to penetrate into the concrete and activate corrosion of the embedded reinforcement.

Discussion of results

Results from the ACI trials on grade 40 concrete with 25 mm cover, are shown in Figure 10 in terms of rebar potentials and corrosion rates. Corrosion activation occurred quite rapidly due to high absorption of the dry concrete during initial wetting. Thereafter corrosion indicators were quite variable due to instability in the system. The data shows that at 25 mm cover, the inhibitor caused a significant delay in the onset of corrosion in some admixed specimens. Conditions were more settled towards the end of the testing with 4% and 6% ACI samples able to slightly reduce the overall corrosion rate compared to the control samples. Nevertheless all reinforcement exhibited active corrosion rates at the end of the test program. Detailed analysis of data from these trials established that the corrosion threshold of reinforcement in normal and ACI concrete was approximately 0.4% and 0.7% total chloride by mass of cement.

At 50 mm cover the inhibitor delayed the onset of corrosion in specimens with 2% and 4% inhibitor, with the 2% ACI sample showing passive corrosion levels for 50 cycles of wetting and drying. The tests showed that the inhibitor is more effective in better grades of concrete and where chloride concentrations are below 1.0% by mass of cement.

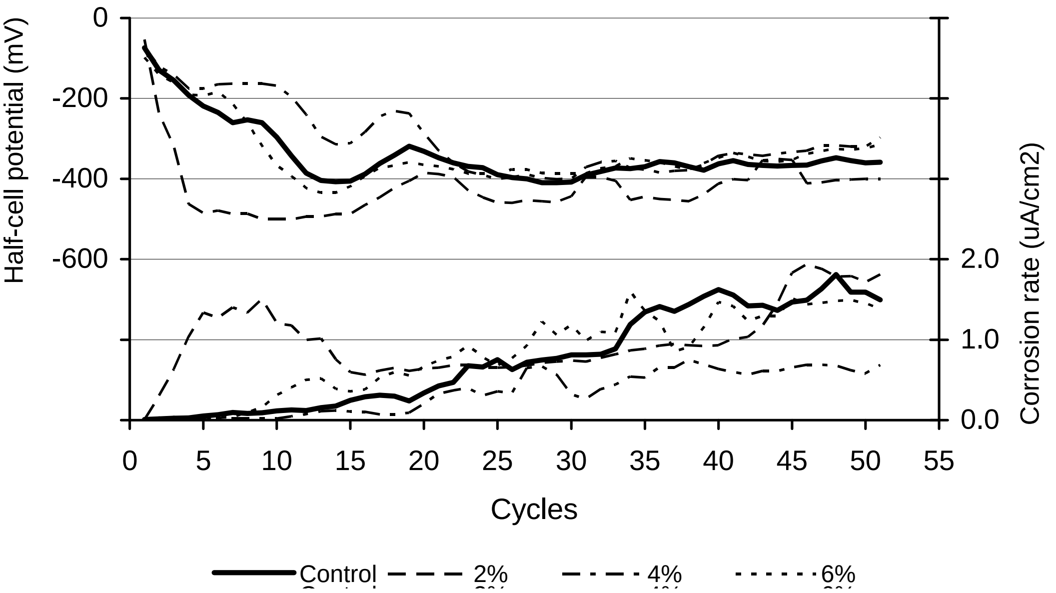


Figure 10: Corrosion of reinforcement in grade 40 concrete with ACI treatment, 25 mm cover depth

Concrete specimens were also treated with PCI after corrosion activation (total dosage 0.5L/m^2). Treatment was applied after 30 cycles and the penetration of the inhibitor measured after two months to check for adequate penetration (results shown in Table 6). Penetration of PCI was significantly slower through 40 MPa concrete compared with 20 MPa concrete. After two months the inhibitor was not detected at 50 mm cover but when retested after nine months, sufficient concentration was detected. Reinforcement at 25 mm cover was therefore exposed to inhibitor within a month of treatment whereas reinforcement at 50 mm would only have received inhibitor after four months (equivalent to eight wetting and drying cycles).

Table 6: Penetration of PCI into grade 20 and 40 MPa concrete after two months

Grade (MPa)	Depth (mm)	Indicator colour	Qualitative rating [#]	Organic nitrogen . [*] (mg/g of concrete)
20	0-15	Pale pink	Adequate	0.06 - 0.28
	15-30	Pink	Good	0.17 - 0.55
	30-45	Pink	Good	0.17 - 0.55
	45-60	Pink	Good	0.17 - 0.55
40	0-15	Pale pink	Adequate	0.06 – 0.28
	15-30	Pale pink	Adequate	0.06 – 0.28
	30-45	Trace	Inadequate	< 0.06
	45-60	None	-	-

[#] This rating was provided by the manufacturer based on the indicator colour

[*] These values were estimated from total organic nitrogen (TKN) measurements of concrete [18]

Corrosion rates measured in the 40 MPa blocks (average of two specimens with one outlier being discarded) are shown in Figure 11. During initial wet/dry cycling the corrosion rates were erratic but started to stabilize after 10-15 cycles. As chloride levels in the concrete increased the corrosion rates of all blocks increased, and after 20 cycles all reinforcement exhibited active corrosion. Towards the end of the testing programme, reinforcement exposed to inhibitor treatment had consistently lower corrosion rates than controls (typically 60% of control rates). When PCI was applied after 30 cycles, the chloride concentration was 1.8% and 0.4% by mass of cement at depths of 25 and 50 mm respectively.

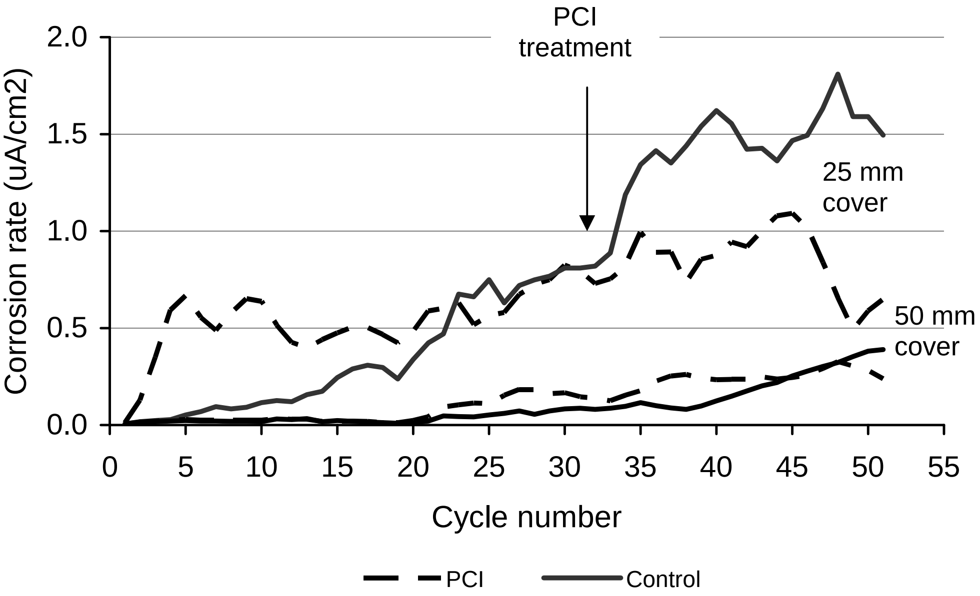


Figure 11: Corrosion of reinforcement in grade 40 concrete, 25 and 50 mm cover

b) Field studies

Monitoring of several reinforced concrete structures treated with PCI was undertaken in South Africa between 1998 and 2000 [18]. Two large structures were repaired with PCI and monitoring after repairs was undertaken for a period of twelve months (Steenbras bridge and Alusaf potbeds). Three precast concrete panels at Koeberg Nuclear Power Station were also monitored after treatment but in this case no repairs were made to cracks and spalls caused by previous corrosion damage.

All structures exhibited fairly advanced corrosion damage with chloride levels at the reinforcement in excess of 1.0% by mass of cement. Corrosion monitoring consisted of measurements of rebar potentials after application of the PCI. Rebar potentials immediately after treatment shifted to highly negative values (<-350 mV $Cu/CuSO_4$) but moved to less negative values after six to nine months. Whilst these findings were not definitive, they indicate a positive effect of using PCI even under highly corrosive conditions.

Penetration of PCI into marine concrete was found to be variable, being mostly influenced by the moisture condition of the concrete. Older concrete with high salt concentrations and near saturation allows little vapour diffusion and penetration of

PCI to any depth is suspect. In contrast, PCI penetrated rapidly through newly cast repair mortars despite the high strengths of these materials.

c) Recommendations

The use of admixed corrosion inhibitors such as Ferrogard 901 is relatively expensive and is only practical in small volumes such as repair materials. Little advantage was shown in using higher concentrations of corrosion inhibitor in concrete and best performance was achieved with a dosage of 4%.

Penetration of PCI into marine concrete needs to be guaranteed before repairs are initiated since:

- concrete is salt contaminated and near saturated from splash or spray of sea water
- concrete is often dense with relatively low permeability
- corroding reinforcement may be at cover depths of more than 50 mm

Despite these concerns adequate PCI penetration has been found through some fairly saturated marine concretes but at relatively slow rates. It is recommended therefore that if there is uncertainty about penetration of PCI a field trial application should be done for confirmatory purposes. A reasonable period should be allowed before testing for adequate penetration of PCI (a minimum of one month for marine concrete is recommended).

Control of chloride-induced corrosion using PCI is dependent on the chloride content at the reinforcement, corrosion condition of the steel and amount of concrete damage. Whilst each corroded reinforced concrete structure is unique and requires careful investigation, some general guideline apply:

- reinforcement exposed to chloride levels below 1.0% by mass of binder responds well to treatment with PCI
- reinforcement exposed to chloride levels above 1.0% by mass of binder, if treated with PCI, should also be protected by a high quality coating system
- chloride levels above 2.0% by mass of binder at the reinforcement are too high for any benefit to be achieved from corrosion inhibitors

Chloride-induced corrosion is extremely aggressive and complete corrosion control is difficult to achieve with most repair systems. Treatment of corrosion-damaged reinforced concrete with PCI can provide service life extension in that the overall corrosion rate of corroding reinforcement is reduced in the longer-term. Complementary forms of protection using coating systems should significantly enhance the durability of PCI treatments.

CONCLUSIONS

The performance of two organic corrosion inhibitors in reinforced concrete exposed to either carbonation or chloride-induced corrosion was investigated under laboratory and field conditions. Findings from this work indicate that organic corrosion inhibitors can extend the life of reinforced concrete structures. Both admixed and penetrating forms of the corrosion inhibitor do however have defined limits of performance and should not be used indiscriminately. The technology also has a limited track record in construction and so service life predictions must not be too ambitious.

Consistently good performance of the PCI was found for cases of carbonation-induced corrosion. The material penetrated relatively easily through carbonated concrete due to the fairly dry condition of the concrete. Porous low grade concretes may however allow loss of the volatiles from the system and this needs to be considered. The application of PCI either before or after carbonation was found to significantly reduce the corrosion rate of embedded reinforcement. The effect of the inhibitor was to reduce corrosion to levels approaching that achieved under passive conditions.

The use of corrosion inhibitors to treat chloride-induced corrosion needs to be carefully considered, as their performance is dependent on the severity of corrosion and the environmental conditions at the steel surface. Reinforcement embedded in concrete contaminated with high levels of chloride ions (>2% by mass of cement) is subject to severe corrosion and treatment with organic corrosion inhibitors is almost totally ineffective. At lower chloride levels some reduction in the corrosion rate of steel reinforcement is possible and indeed the corrosion threshold of chlorides may be almost doubled. When using PCI it is critical that the concrete will allow adequate penetration of the inhibitor to the depth of the reinforcement. This is particularly important for marine concretes that are normally contaminated with salts and have saturated or nearly saturated pore structures.

Engineers have an increasing array of materials and systems to choose from when considering durability and repair of reinforced concrete structures. Over the last few years, corrosion inhibitors have increasingly been used as a pragmatic repair solution for corrosion-damaged concrete structures. These materials have the potential to improve the service life of reinforced concrete structures provided they are used appropriately. Further monitoring of treated structures in time will provide a more definitive estimate of the likely service life extension provide by corrosion inhibitor systems.

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APPENDIX A

Carbonation-induced corrosion – Details of concrete mixes for 20, 30, 40 and 50 MPa specimens (kg/m^3), 28 day strengths and measured slumps

Grade	**20 MPa**	**30 MPa**	**40 MPa**	**50 MPa**
w/c ratio	0.83	0.73	0.60	0.52
Water content	180	180	180	180
CEM I 42.5N	217	247	300	346
Stone	1100	1100	1100	1100
Sand	897	871	826	787
28 day* strength (MPa)	22.0	30.1	39.8	50.1
Measured slump (mm)	80	80	80	75

* Average strength obtained by crushing three 100 mm cubes per concrete grade.

Chloride-induced corrosion – Details of concrete mixes for 20 and 40 MPa specimens (kg/m^3), and 28 day strengths

	20 MPa SPECIMENS				40 MPa SPECIMENS			
	Control	2 % Inhibitor	4 % Inhibitor	6 % Inhibitor	Control	2 % Inhibitor	4 % Inhibitor	6 % Inhibitor
Cement	262	250	237	225	357	286	286	286
Water	210	200	190	190	200	160	160	160
Sand	862	862	862	862	749	749	749	749
Stone	1050	1050	1050	1050	1050	1050	1050	1050
Inhibitor	0	4.99	9.48	13.47	0	5.72	11.44	17.16
Average Strength*	26.2	24.1	24.4	27.6	41.0	39.3	38.6	41.5

* Average 28 day strength (MPa) obtained by crushing three 100 mm cubes per concrete grade.