

FINAL REPORT

Project Title: S47: Impact of Corrosion Inhibitor Admixtures on
Durability of Concrete (Year 1 2018–19)

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SUMMARY

The state of Queensland has a long coastline which stretches for almost 7000 km, meaning that there is a large volume of infrastructure situated in aggressive marine environments either in or near saline water and soil. Therefore, much of the infrastructure construction in Queensland is at risk of corrosion.

Corrosion inhibitors are marketed by chemical companies as a method of proactively protecting reinforcing steel in concrete. Their performance in 100-year design life structures, and in comparison to other durability-enhancing measures, is not yet known. During consultation on MRTS70, suppliers have asked TMR to consider corrosion inhibitors as an alternative to triple-blend cements for aggressive environments.

A literature review was conducted within this project to assess the use, performance and specifications of CIAs (corrosion inhibitor admixtures), as well as their effectiveness. A survey to local suppliers regarding CIAs was also included to understand the current application of CIAs in Australia.

Key findings from the literature review and suppliers' survey include:

- In a laboratory environment, CIAs can improve the corrosion inhibition of reinforcing steel in concrete by producing longer corrosion initiation times, higher critical chloride thresholds, and a reduction in the chloride penetration.
- Test results have shown that CIAs are effective in uncracked concrete, and not effective in concrete with cracks present or in patch repairs. There is a lack of long-term data to verify the long-term effectiveness.
- The impacts of CIAs on concrete properties vary among available products (concrete strength, setting time, permeability, etc.). There are also additional additives that can be used to mitigate the adverse impacts.
- There exist some environmental concerns due to the toxic nature of inorganic CIAs for handling and disposal of concrete with CIAs.
- CIAs may provide some reduced life-cycle costs in chloride-rich environments however, the service data is not available to quantify the economic benefits of CIAs.
- International standards and other Australian road agencies' specifications are available for testing and mix design of concrete with CIAs.
- CIAs may be of use to increase the corrosion resistance of concrete in chloride-rich environments for various transport infrastructure works such as bridges, wharfs, retaining walls, etc. However, the use of CIAs is not a substitute for a good concrete mix design and use of concrete cover.

A number of recommendations have been made including maintaining the current approach of allowing the use of CIAs if they are registered with TMR, while restricting their use for improving the service life of concrete instead of other proven methods.

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1 INTRODUCTION

1.1 Background

A major durability concern for reinforced concrete structures is steel corrosion. Corrosion causes material deterioration of the reinforcing steel bars, leading to a build-up of rust which can cause concrete cracking which further exacerbates steel deterioration ([Austroads 2016](#)). Corrosion occurs in the presence of moisture and oxygen and can be accelerated by the presence of chlorides. Corrosion occurs in the presence of moisture and oxygen, but in concrete is kept to an insignificant level by a passive oxide film on the reinforcing bars. This film is stable in the highly alkaline concrete environment and prevents further corrosion (Austroads 2016, Berke & Hicks 2004). However, the processes of carbonation or chloride ingress can break down the protective passive layer, and initiate reinforcement corrosion. These processes are most prevalent in marine, acidic and other aggressive environments ([Austroads 2016](#)). Therefore, to create structures with a long service life, it is important that protection from corrosion be considered for these aggressive environmental conditions.

The state of Queensland has a long coastline which stretches for almost 7000 km, meaning that there is a large volume of infrastructure situated in an aggressive marine environment either in or near saline water and soil. Therefore, much of the infrastructure construction in Queensland is at risk of corrosion. In order to achieve the specified 100-year bridge design life, the reinforced concrete used for infrastructure constructed in these aggressive environments must be augmented to slow or delay the onset of the reinforcement corrosion. One method to protect reinforcement from corrosion and/or slow its onset is the use of mineral and chemical admixtures.

There are a number of mineral and chemical admixtures which are reported to delay or slow reinforcement corrosion in concrete ([Civjan et al. 2005](#)). These include:

- supplementary cementitious materials (SCMs)
 - silica fume (SF)
 - fly ash (FA)
 - ground granulated blast furnace slag (BFS)
- chemical corrosion inhibiting admixtures (CIAs)
 - calcium nitrite
 - organic chemical
 - others.

Queensland Transport and Main Roads (TMR) currently specifies the use of blended cements in MRTS70 with SCMs used in all concrete structures ([TMR 2018](#)). For aggressive environments (C1, C2), a minimum of 25% fly ash with additional SCMs, or a minimum of 60% slag, is required. Blended concretes are known to produce good results for the protection of reinforcement in aggressive environments ([Kwon et al. 2017](#)), but it is not always economical to procure the required SF or BFS.

CIAs have been proposed as another method to provide required corrosion resistance for reinforced concrete structures. CIAs are chemicals which are applied to the concrete as an admixture during batching and provide an inhibiting action to delay the onset of reinforcement corrosion. CIAs have been available commercially since the mid-20th century, but there is limited real-world performance data available regarding their ability to improve the durability of concrete and maintain effectiveness over a 100-year structure design life. Currently, some CIAs have been approved to be used in TMR projects as an additive to enhance performance, but not as an alternative to SCMs.

1.2 Aims and Objectives

The primary aim of this review is to determine whether the use of CIAs can be considered as a viable method for improving durability and delaying reinforcement corrosion in concrete structures constructed and managed by TMR in Queensland. Specific objectives that will allow the primary aim to be achieved include:

- investigation of the current use, performance and specification of CIAs
- review of the outcomes of field and laboratory studies on CIAs
- review of specifications relating to the use and formulation of CIAs
- review of CIA impacts on concrete properties
- review of effectiveness requirements for CIAs
- consultation with industry to investigate the current use and performance of CIAs in Australia.

1.3 Methodology

The methodology used to achieve the stated aims and objectives can be summarised in the following steps:

- review of national and international literature to collate research and studies regarding the use of CIAs for corrosion resistance in concrete structures
- engagement with TMR Engineering and Technology (E&T) and admixture suppliers to evaluate the use, performance, specification and effectiveness of CIAs for corrosion resistance in practice
- report on the findings for consideration by TMR to assist in determining the suitability of CIAs as a viable method to inhibit corrosion.

1.4 Scope

The scope of this project includes a review of literature and consultation with key industry stakeholders to gather evidence regarding the applicability of CIAs as a suitable method of protecting reinforcing steel and enhancing the durability of reinforced concrete. This provides either evidence to use CIAs to improve reinforced concrete durability in aggressive environments, or a sound basis for not including them as an option.

Exclusions from this project are:

- investigation of other tools for achieving enhanced durability of concrete
- physical testing of corrosion inhibiting admixtures.

1.4.1 Type Heading Level 3

2 CORROSION MECHANISMS AND CORROSION INHIBITORS IN CONCRETE

2.1 Corrosion Mechanisms of Reinforcing Steel in Concrete

2.1.1 Chemistry of Corrosion

The corrosion of reinforcing steel in concrete is an electrochemical process involving iron, oxygen, and water ([Farshadfar, O'Reilly & Darwin 2017](#)). Corrosion is defined by the American Concrete Institute (ACI) and International Concrete Repair Institute (ICRI) as the 'destruction of metal by chemical, electrochemical, and electrolytic reaction within its environment' ([Hughes 2013](#)). Corrosion occurs when an electrochemical cell is created, where electrons flow from the anode to the cathode and hydroxyl ions flow back from the cathode to the anode. In the anodic reaction, iron atoms lose electrons to form ferrous ions, as shown in Equation 1.



where

Fe = iron atom

Fe²⁺ = ferrous ion

e⁻ = electrons

The electrons are then passed to the cathode, where they interact with available oxygen and water to produce hydroxyl ions, as shown in Equation 2.



where

H₂O = water

O₂ = oxygen gas

OH⁻ = hydroxyl ion

The hydroxyl ions produced at the cathode then travel back to the anode, where they react with the ferrous ions to produce ferrous hydroxide [Fe(OH)₂], as shown in Equation 3.



The ferrous hydroxide ultimately oxidises into rust ([Austroads 2016](#), [Gong et al. 2006](#)). Rust has a larger volume than the reinforcing steel it was created from, creating pressure in the concrete, which in turn leads to cracking and spalling of the concrete cover ([Saaoudi, Assouli & Srhiri 2003](#)).

Due to the high pH of concrete, a passive oxide film or thin rust layer forms around the reinforcing steel bars, which protects the reinforcement by slowing the rate of corrosion to an insignificant level ([Austroads 2016](#), [Bertolini et al. 2016](#)). If the passive film remains intact and the pH of the concrete pore solution remains high, significant corrosion of the steel reinforcement will not occur. There are, however, several processes which can disrupt this passive state and cause corrosion of reinforcement to progress and impact on the durability of the concrete. The most prevalent of these are chloride ingress and carbonation.

2.1.2 Chloride Ingress

The penetration of chloride ions into concrete typically occurs in marine environments, saline soil environments, or from the presence of de-icing salts (which are not commonly used in Australia). Due to the porous nature of concrete, chloride ions can penetrate through the concrete cover, eventually reaching the reinforcing steel ([Bertolini et al. 2016](#), [Cement Concrete & Aggregates Australia 2009](#)). When the chloride ions at the reinforcing steel exceed a threshold value, called the critical chloride threshold, the passive oxide film protecting the reinforcing steel dissolves causing corrosion to initiate. Further penetration of chloride will result in an increase of the chloride concentration at the steel and accelerating the reinforcement corrosion.

2.1.3 Carbonation

Carbonation is a process whereby carbon dioxide gas enters concrete and reacts with calcium hydroxide to produce calcium carbonate ([Austroads 2016](#)). The presence of calcium carbonate lowers the pH of the concrete pore solution, which in turn leads to destruction of the oxide film on the reinforcing steel and accelerated corrosion when moisture and oxygen are available. The carbonation of concrete is usually a slow process, so it takes time for the reaction to progress and reach the reinforcement. The actual time that the carbonation process will take to impact on reinforcement varies and depends on several factors including exposure conditions, concrete humidity, binder composition, concrete quality, water content and the depth of cover to reinforcement ([Austroads 2016](#), [Xing, Darwin & Browning 2010](#)).

2.2 Corrosion Inhibitors

Corrosion inhibitors are defined as chemical substances which have the capability to reduce the rate of steel corrosion, such as from chloride ingress or carbonation, in an aggressive environment. Research into corrosion inhibitors began in the 1960s and their use in Japan and the USA can be traced back to the 1970s ([Kepler, Darwin & Locke 2000](#), [Söylev & Richardson 2008](#)). They have been utilised as a protective measure for new structures, and as a rehabilitation methodology for existing structures at risk of corrosion.

Corrosion inhibitors can be applied in one of two ways, as an admixture in the concrete mix or as a surface applied treatment. This review focuses on admixtures (CIAs) only. The ACI and ICRI define a corrosion inhibiting admixture as ‘an admixture that reduces ingress of chlorides or enhances the passivating layer on the surface of steel reinforcement, or both, thus reducing or preventing corrosion’ ([Hughes 2013](#)).

When used in concrete, CIAs can elevate the critical chloride threshold, delay corrosion initiation, and slow the rate of corrosion ([Gong et al. 2006](#)). Myrdal ([2010](#)) states that CIAs in concrete typically impact steel reinforcement corrosion in two possible ways:

- by strengthening the oxide film on the reinforcement so that it takes a longer period of time for it to be broken down
- by slowing the rate of reinforcement corrosion once the passive film is broken.

CIAs can be classified based upon their protection mechanism as being either: anodic, cathodic, or mixed (both anodic and cathodic actions) ([Ramachandran 1984](#), [Söylev & Richardson 2008](#)).

Anodic inhibitors

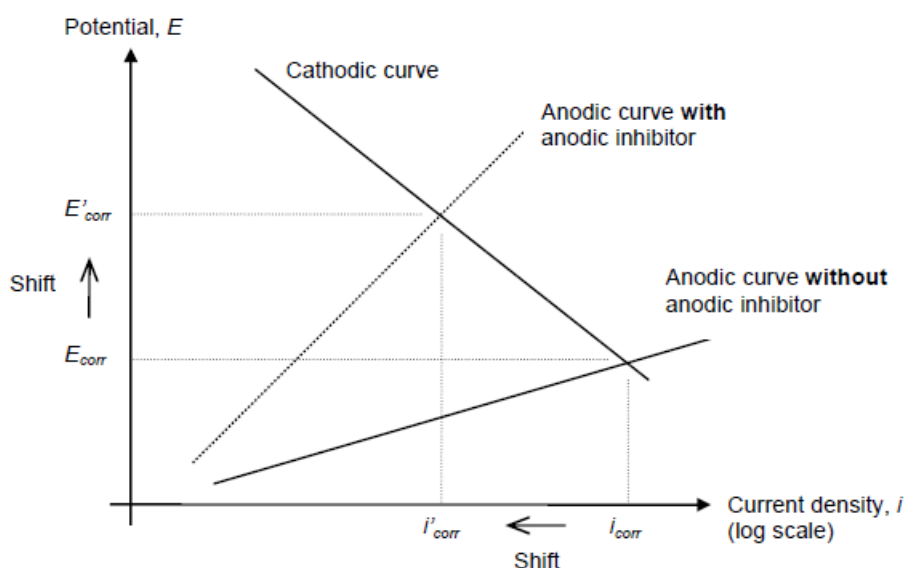
Anodic inhibitors assist in the production of the oxide film on the reinforcement by oxidising ferrous ions to ferric ions, which suppresses the corrosion reaction. During the generation of the passive oxide layer, the anodic inhibitor is consumed ([Saaoudi, Assouli & Srhiri 2003](#)). For anodic inhibitors to be effective, they must be present in an adequate concentration relative to the amount of chloride present in the concrete. Anodic inhibitors essentially compete with the chloride ions to oxidise steel, by transforming the ferrous ions required for corrosion into ferric ions (Fe^{3+}) which

creates the passive layer. If an insufficient concentration of inhibitor is available, the chloride-induced corrosion will still occur (Myrdal 2010). This leads to concerns that if the amount of inhibitor used is too small, accelerated corrosion and pitting can occur, as well as concerns that the inhibitor may leach out of concrete over long periods of time (Saaoudi, Assouli & Shiri 2003, Kepler, Darwin & Locke Jr 2000).

Figure 2.1 presents a schematic current-potential diagram showing the effect of an anodic inhibitor on corrosion. The anodic inhibiting action will result in a rise in the electrochemical potential of the anodic reaction. Consequently, the anodic and cathodic curves in the current-potential diagram will intersect at higher corrosion potential and lower corrosion current.

Calcium nitrite is the most commonly used anodic corrosion inhibitor, as well as being one of the oldest and most widely used CIAs in concrete. Other anodic inhibitors include calcium nitrate, sodium nitrite, sodium benzoate, and sodium chromate (Söylev & Richardson 2008).

Figure 2.1: A schematic current-potential diagram showing the effect of an anodic inhibitor on corrosion



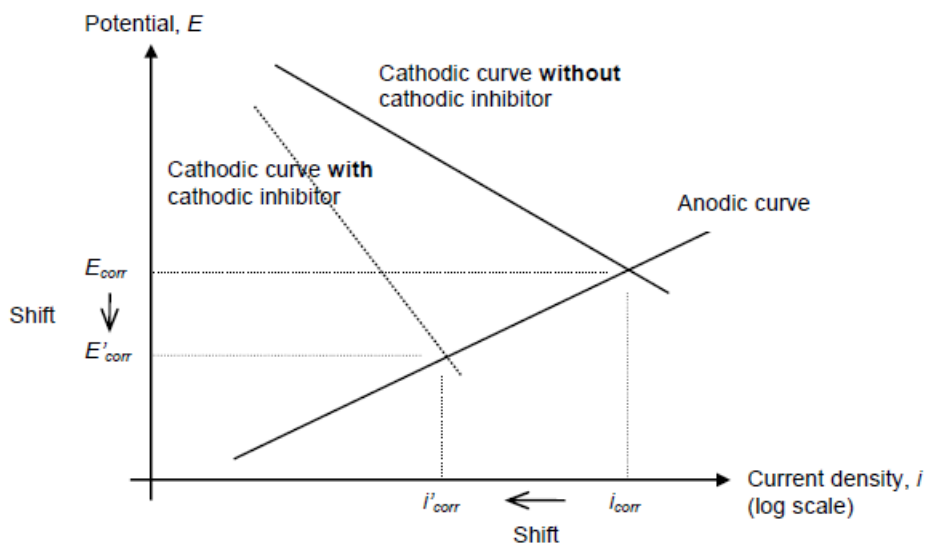
Source: Myrdal (2010).

Cathodic inhibitors

Cathodic inhibitors act to slow down the cathodic reaction on the surface of the steel reinforcement by reacting with corrosion products (e.g. Fe^{2+} , Fe^{3+} , OH^-) to produce salts, which have poor solubility in water, and will precipitate on cathodic sites. The precipitated salts form a layer on the steel surface which works to prevent oxygen from reaching the cathodic zones of the reinforcement. The reduction in oxygen supply to the corrosion process will lower both the corrosion potential and the corrosion rate (Myrdal 2010, Söylev & Richardson 2008). Figure 2.2 shows that the presence of a cathodic inhibitor causes a shift in the corrosion potential and the corrosion rate. The corrosion rate is reduced, while the corrosion potential shifts towards lower (more negative) values.

Cathodic inhibitors include carbonates, phosphates, polyphosphates and silicates. No commercially available cathodic inhibitors were found in the review of literature.

Figure 2.2: A schematic current-potential diagram showing the effect of a cathodic inhibitor on corrosion



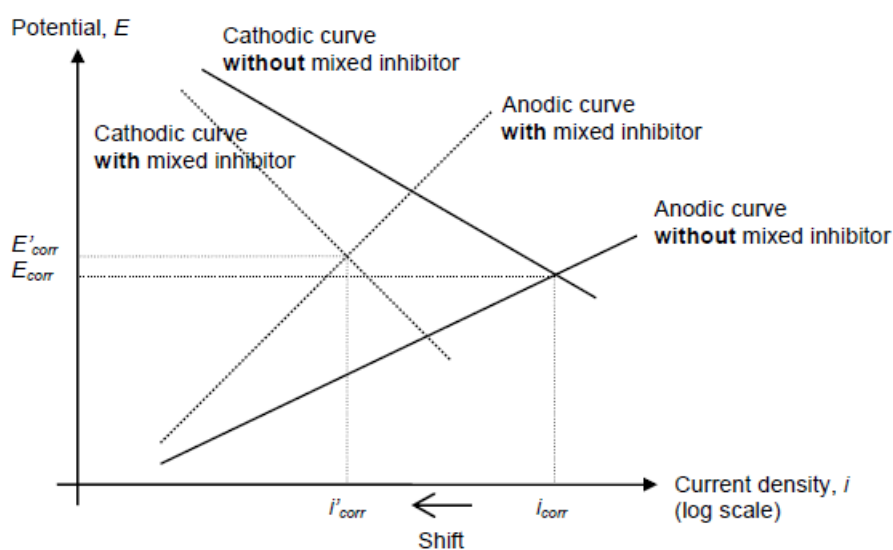
Source: Myrdal (2010).

Mixed inhibitors

Mixed inhibitors act on both the anode and cathode, forming a thin film on the surface of the steel reinforcement. Mixed inhibitors work to slow down the corrosion rate without a major change in the corrosion potential. Common mixed inhibitors are organic compounds, such as amines and alkanolamines, with polar groups containing nitrogen, sulphur, and hydroxy ([Myrdal 2010](#), [Söylev & Richardson 2008](#)).

Figure 2.3 shows a schematic current-potential diagram showing the effect of a mixed inhibitor on corrosion. The presence of a mixed inhibitor causes a reduction in the corrosion rate, but a slight increase in the corrosion potential.

Figure 2.3: A schematic current-potential diagram showing the effect of a mixed inhibitor on corrosion



Source: Myrdal (2010).

Another classification of CIAs is based upon their chemical composition, depending upon if they are composed of organic or inorganic compounds, which are discussed in the following sections.

2.3 Organic Inhibitors

Organic inhibitors are typically composed of amines or amino-acids, alkanolamines, or esters ([Paredes et al. 2010](#)). Commercial organic inhibitors have been available in the concrete industry since the 1980s ([Peek, Ali & Green 1999](#), [Bolzoni et al. 2014](#)). Organic inhibitors typically act as mixed inhibitors, forming a protective film over the steel at both the anodic and cathodic sites ([Söylev & Richardson 2008](#), [Saaoudi, Assouli & Srhiri 2003](#)). There have also been claims that they can reduce the rate of chloride penetration in concrete by acting as pore blockers ([Peek, Ali & Green 1999](#), [Kepler, Darwin & Locke 2000](#)). Organic inhibitors are also regarded as being non-toxic and environmentally safe ([Saaoudi, Assouli & Srhiri 2003](#), [Al-Amoudi et al. 2003](#)).

Refer to Appendix A for the details of several organic CIAs currently available on the market.

2.4 Inorganic Inhibitors

Inorganic CIAs are usually based upon nitrites, but also include zinc oxide, alkalis, phosphates, chromates, benzoates, and metasilicates among other compounds ([Austroads 2016](#), [Rivetti et al. 2018](#)). The use of sodium nitrite as a CIA was studied in the Soviet Union in the late 1950s, with nitrites being used in concrete beginning in the 60s and 70s in Japan and the USA ([Söylev & Richardson 2008](#), [Bolzoni et al. 2014](#)). While initial testing utilised sodium nitrite, it was later replaced with calcium nitrite due to issues with reduced compressive strength and increased probability of alkali-silica reactions (ASR). Since its introduction, calcium nitrite has been widely favoured as an inorganic CIA, since it does not cause reductions in compressive strength or an increase in the chance of ASR.

Calcium nitrite is an inorganic, anodic inhibitor, which acts by forming a protective, passive ferric oxide film around the reinforcing steel ([Gong et al. 2006](#), [Song & Shayan 1999](#), [Söylev & Richardson 2008](#), [Xing, Darwin & Browning 2010](#)). The ferric oxide film is formed when the nitrite combines with the hydroxyl ions and ferrous ions, as illustrated in Equations 4 and 5.



where

NO_2^- = nitrogen dioxide

$\text{NO}\uparrow$ = nitric oxide gas

Fe_2O_3 = ferric oxide



where

$\gamma\text{-FeOOH}$ = γ -Ferric oxide

The ferrous ions (Fe^{2+}) used in the formation of the ferric oxide are the same ions which are part of the corrosion reaction. As the nitrite reacts with the ferrous ions faster than the transport of the ferrous ions from the anode to the cathode in the corrosion cell, the passive ferric oxide film forms over the reinforcement instead of corrosion occurring.

A concern regarding the use of calcium nitrite as a CIA is that if the concentration of chloride ions is sufficiently high in comparison to the nitrite, then corrosion will still occur as there will be available ferrous ions to complete the corrosion cell. It is therefore important to maintain an appropriate ratio of calcium nitrite to chloride for an effective application. Reports by

Austroroads (2016) and Song and Shayan ([1999](#)) have recommended keeping the $[\text{Cl}^-]/[\text{NO}_2^-]$ ratio under 1.0 to prevent corrosion activity. Additional ratios have been documented in the literature, with Ann et al. ([2006](#)) experimentally finding corrosion initiation to occur at ratios between approximately 1.5–3.0 and Smith and Vermani ([2000](#)) stating that the ratio should be below 1.1 for improved corrosion resistance. Typical dosages of calcium nitrite for an application can be estimated from early work by W.R. Grace and Company (Berke & Rosenberg 1989), or from numerical models such as used in the Life 365™ software ([Life-365™ Consortium III 2018](#)).

Studies have shown that calcium nitrite acts as an accelerator and increases the concrete's early age compressive strength ([Ann et al. 2006](#), [Xing, Darwin & Browning 2010](#)); however, the strength gain may not hold up over time (Ann et al. [2006](#)). Another concern with the use of calcium nitrite is its toxicity, as it forms NO_2^- ions when dissolved in water which are toxic in blood, causing problems with its implementation in some European nations ([Elsener 2001](#), [Rivetti et al. 2018](#)).

The most common type of commercially available inorganic CIA is calcium nitrite, with the first commercial product being available since 1978. The majority of calcium nitrite products consist of 30% calcium nitrite and 70% water. Calcium nitrite is purported to accelerate setting time, reduce air entrainment, and reduce water content. Variations are available commercially with admixtures to control setting time or produce similar cement properties to mixes without CIAs.

Refer to Appendix A for the details of several inorganic CIAs currently available on the market.

2.5 Other Inhibiting Admixtures

New CIAs are being evaluated in laboratory settings, to determine if they can provide an improved performance and counter drawbacks associated with currently available products. These include:

- A new non-toxic corrosion inhibitor called siloxane was tested by Holmes, O'Brien and Basheer ([2014](#)), who determined that it reduced the probability of corrosion and water absorption, but caused a reduction in compressive strength.
- Green corrosion inhibitors, which are a popular experimental topic due to their environmental benefits, are made from natural products such as bitter leaf ([Eyu et al. 2013](#)), Indian bamboo extract ([Abdulrahman & Ismail 2012](#)) and leaf extract ([Okeniyi, Popoola & Loto 2017](#)). They have been shown to provide varying levels of corrosion resistance, depending on the substance.

3 STUDIES ON CORROSION INHIBITOR ADMIXTURE PERFORMANCE

3.1 Testing for Corrosion Inhibiting Admixtures

The capability of a CIA to improve the corrosion resistance of a concrete structure can be evaluated through experimental testing. Measurements gathered from these tests can be used to determine if a CIA provides the required corrosion protection for a given application, and if its use provides a cost-effective solution. This section discusses some commonly used measurements and tests for the evaluation of the effectiveness of CIAs.

3.1.1 Corrosion Measurements

Corrosion potential

To detect if corrosion is occurring, the corrosion potential of reinforcing steel is commonly measured with respect to a standard reference electrode, using a half-cell test as specified in the American Society for Testing and Materials (ASTM) standard ASTM C876 ([Cheng & Robertson 2006](#), [Farshadfar, O'Reilly & Darwin 2017](#), [Xing, Darwin & Browning 2010](#)). Common reference electrodes include a saturated calomel electrode (SCE), or a copper/copper-sulphate electrode (CSE). The corrosion potential represents the likelihood of corrosion occurring in the reinforcing steel, with the more negative the value the higher the chance that corrosion is occurring. Guidelines on interpreting measured corrosion potential measurements are provided by ASTM C876, shown in Table 3.1.

Table 3.1: ASTM C876 corrosion potential interpretation

Measured Potential (V)		Corrosion Activity
SCE	CSE	
> -0.125	> -0.200	>90% probability corrosion is not occurring
-0.125 to -0.275	-0.200 to -0.350	corrosion activity uncertain
<-0.275	<-0.350	>90% probability corrosion is occurring

Source: Farshadfar, O'Reilly and Darwin (2017).

The half-cell potential measurements can be affected by factors like concrete resistance, humidity, oxygen, chloride concentration, and carbonation ([Farshadfar, O'Reilly & Darwin 2017](#)). Measuring corrosion is inexpensive with easy to interpret data; however, it does not provide an absolute indication of the reinforcement condition and requires access to the reinforcing steel (Cheng & Robertson 2006).

Macrocell corrosion rate

The macrocell corrosion rate can be used to quickly determine the performance of a corrosion-protection system ([Darwin et al. 2011](#)). The macrocell current is a measurement of the voltage drop between the anodic and cathodic bar in a series circuit across a resistor, from which the current density and corrosion rate can be calculated using Equations 6 and 7 ([Farshadfar, O'Reilly & Darwin 2017](#), [Cheng & Robertson 2006](#)).

$$i_{\text{corr}} = \frac{V}{RA} \quad 6$$

where

i_{corr} = corrosion current density, $\mu\text{A}/\text{cm}^2$

V = voltage drop, mV

R = resistance of resistor, kilohms

A = area of exposed metal on anode bar, cm^2

and

$$R_{\text{corr}} = k \frac{i_{\text{corr}} a}{nF\rho} \quad 7$$

where

R_{corr} = corrosion rate, $\mu\text{m}/\text{year}$

k = conversion factor, $k = 315\,360 \frac{\text{A} \cdot \mu\text{m} \cdot \text{s}}{\mu\text{A} \cdot \text{cm} \cdot \text{yr}}$

a = atomic weight of corroding metal, g/mol

n = number of electrons lost per oxidised metal atom

F = Faraday's constant, 96 500 Coulombs/mol

ρ = density of the metal, g/cm^3

Once determined, the corrosion rate can be integrated across time to determine the cumulative reinforcement loss due to corrosion ([Darwin et al. 2011](#)). According to Cheng and Robertson ([2006](#)), the macrocell current method is low-cost, simple, and reliable, with different studies finding either good correlations between the overall corrosion and the macrocell current, or that the macrocell current underestimated the corrosion.

Linear polarisation resistance

Linear polarisation resistance is a measure of the total corrosion rate, or both the macrocell (anode and cathode on separate bars) and microcell (anode and cathode on the same bar) corrosion ([Farshadfar, O'Reilly & Darwin 2017](#)). In the linear polarisation resistance test, a counter electrode and a reference electrode are used to establish a polarisation, or current-voltage, curve for the corroding reinforcement using a potentiostat ([Darwin et al. 2011](#), [Farshadfar, O'Reilly & Darwin 2017](#)). The slope of the polarisation curve is roughly linear between approximately -20 mV

to 20 mV and can be used to determine the corrosion current density using Equation 8, which can then be converted into the total corrosion rate using Equation 7.

$$i_{\text{corr}} = 0.026/R_p \quad 8$$

where

R_p = slope of the polarisation curve

3.1.2 Testing Corrosion Resistance of CIAs

To effectively evaluate the performance of different CIAs, it is important to use consistent experimental setups to ensure comparable results. This section reviews testing methodologies which have been used in the evaluation of corrosion protection systems and can be applied to evaluating CIAs. These tests can be used to evaluate a number of factors of corrosion resistance, such as reductions in corrosion initiation time, chloride penetration, corrosion rates, and increases in critical chloride threshold. Evaluations of the effectiveness of CIAs using these tests is often based upon comparisons to measurements from control specimens.

ASTM G109

A standard method to evaluate the corrosion resistance provided by chemical admixtures is detailed in ASTM G109 2007 ([2013](#)), *Standard Test Method for Determining the Effects of Chemical Admixtures on the Corrosion of Embedded Steel Reinforcement in Concrete Exposed to Chloride Environments*. The method involves standard preparation of test beam specimens, which are subjected to cycles of two weeks of salt ponding followed by two weeks of drying. Measurements include the macrocell current and corrosion potential every four weeks, starting at week two. The ASTM G109 test method is used in ASTM C1582 ([2017](#)) for the acceptance of admixture in concrete, with requirements based upon mean macrocell current and test beam corrosion in comparison to a control value.

Southern exposure test

The Southern exposure test simulates the wetting and drying of uncracked bridge decks in a warm climate ([Xing, Darwin & Browning 2010](#)). The test specimen is a small concrete slab with two reinforcing mats, with 15% chloride ponding occurring for 4 days and drying occurring for 3 days. The ponding and drying cycles are repeated for 12 weeks, followed by continuous ponding for an additional 12 weeks, with the process repeated for 96 weeks. The testing simulates an exposure of 15–20 years for marine structures in tropical conditions and 30–40 years for bridges in normal conditions over the course of 48 weeks ([Darwin et al. 2011](#)). Measurements taken during the Southern exposure test include corrosion potential, corrosion current, and linear polarisation resistance.

Cracked beam test

The cracked beam test simulates the performance of a corrosion protection system in a bridge deck with a crack ([Xing, Darwin & Browning 2010](#)). This test utilises a beam specimen with a simulated crack located above the top reinforcing bar parallel to the reinforcement ([Darwin et al. 2011](#)). Crack simulation is performed with the use of a 0.3 mm stainless steel shim, which is removed within 12 hours of the specimen casting. The specimen is then subjected to the same 96 weeks of wetting and drying cycles as utilised in the Southern exposure test.

Rapid macrocell test

The rapid macrocell test is an accelerated method of measuring the corrosion resistance of steel bars ([Farshadfar, O'Reilly & Darwin 2017](#)). Accelerated corrosion occurs as the steel bars, or bars in a mortar, are exposed to a simulated pore solution. One specimen is placed in a container with a

chloride simulated pore solution and designated the anode, while two other specimens are placed in a solution without chlorides and designated the cathode ([Darwin et al. 2011](#)). The anode and cathode are then connected with a 10-ohm resistor and a salt bridge to allow ionic movement. Testing lasts for 15 weeks, with the pore solutions changed every 5 weeks. Measurements from the rapid macrocell test include corrosion rate, corrosion potential, and linear polarisation resistance.

Chloride penetration and critical threshold

Measuring the chloride penetration can provide information on when corrosion will occur and evaluate the pore blocking capabilities of CIAs. Chloride penetration can be measured by taking core samples from a specimen, which are cut at the specified measurement depths ([Ormellese et al. 2006](#)). The samples are then crushed and dissolved into nitric acid, with silver nitrite titrated into the solution until the peak potential occurs, with the amount of titrated silver nitrite used to determine the chloride content ([Ormellese et al. 2006](#), [Farshadfar, O'Reilly & Darwin 2017](#)). This process is described in AASHTO T 260 ([AASHTO T 260 2009](#)), *Standard Method of Test for Sampling and Testing for Chloride Ion in Concrete and Concrete Raw Materials*.

If the chloride content is measured at the reinforcement when corrosion initiates, the critical chloride threshold can be determined. The moment when corrosion initiation occurs can be estimated as being when the macrocell corrosion rate exceeds 0.3 µm/year or the corrosion potential drops below –275 mV with respect to SCE (or –350 mV with respect to CSE) ([Farshadfar, O'Reilly & Darwin 2017](#), [Xing, Darwin & Browning 2010](#)). Chloride sampling is then performed using samples taken adjacent to the reinforcing steel, with the measured chloride content representing the critical chloride threshold.

Another method of analysing chloride ion penetration is presented in ASTM C1202-19 2019, *Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration*. This method estimates the concrete permeability based upon the electrical conductance of the water saturated concrete, which correlates with long-term chloride diffusion ([Paredes et al. 2010](#)). However, the presence of admixtures such as calcium nitrite can interfere with the results from this method ([Brown 1999](#)).

3.2 Laboratory Studies

The evaluation of a CIA requires knowledge of the impact of its addition to concrete. This includes knowledge of both the influence of CIAs on corrosion resistance and the effect on the properties of the resultant concrete. Numerous laboratory studies have been performed on the impact of CIAs on the properties of concrete and their effectiveness as corrosion inhibitors. Due to the lack of commercially available cathodic inhibitors the following information focuses primarily on anodic and mixed inhibitors.

3.2.1 Effects of CIAs on Concrete Properties

To be effective, a CIA should not detrimentally affect the resulting concrete's mechanical properties. Requirements for the mechanical properties of concrete with chemical admixtures is presented in AS 1478. Of major concern is the impact of CIAs on the concrete strength. In C1582/C1582M 2011 ([2017](#)) the compressive and flexural strength of concrete with a CIA is required to be at least 80% the strength of control samples. Having said that, a concrete would still obviously need to meet its performance requirements.

Several laboratory studies focusing on the impact that different CIAs have on the compressive strength of concrete have produced similar results. Brown, Weyers and Sprinkel ([2001](#)) and Balaguru and Nazier ([2002](#)) found that calcium nitrite and amino-alcohol CIAs increased the 28-day compressive strength, but the addition of an ester and amine CIA caused a reduction in compressive strength. Pham and Newton ([2001](#)) also found that calcium nitrite increased the

concrete 28-day compressive strength, whereas amino-alcohol and the ester and amine CIAs had little impact. Research by Paredes et al. (2010) showed that adding calcium nitrite and amino-alcohol CIAs produced little change in the compressive strength with respect to control samples, while a small reduction was observed for ester and amine CIA samples. In addition, Ann et al. (2006) reported that while the early strength of the concretes with calcium nitrite was higher than the control specimen, after 900 days the control specimen had the highest compressive strength.

CIAs impact additional concrete properties beyond compressive strength. Reductions in concrete setting time with increased dosages of calcium nitrite was reported by Ann et al. (2006). Brown, Weyers and Sprinkel (2001) showed how calcium nitrite acts as a hydration accelerator with comparable chloride permeability to control samples, whereas organic esters and amines and amino-alcohol CIAs reduced the chloride permeability and the hydration rate.

3.2.2 Effectiveness of a Corrosion Inhibitor

Laboratory studies have been performed to experimentally determine the effect of a CIA on the corrosion resistance of reinforcing steel in concrete considering different concrete conditions. For uncracked concrete, it has been shown that the addition of calcium nitrite and organic CIAs can increase the corrosion initiation time, reduce corrosion rate, increase critical chloride threshold, and produce lower corrosion losses, and that organic CIAs can reduce chloride penetration (Ann et al. 2006, Bolzoni et al. 2014, Civjan et al. 2005, Ormellese et al. 2006). In a comparison of CIAs by Bolzoni et al. (2014), the authors found that among calcium nitrite, organic amino-alcohols, alkanolamines and amine-ester, the amino-alcohols provided the longest time-to-corrosion benefit, with the amine-esters providing the least. For concrete repair patches and overlays, a report by Sprinkel (2003) found that the addition of the CIAs (using calcium nitrite, amino alcohol, and ester and amine) did not provide beneficial corrosion resistance. Furthermore, in the presence of cracks, the calcium nitrite, amino alcohol, and ester and amine-based CIAs provide insignificant or no additional corrosion resistance as reported by Paredes et al. (2010) and Civjan et al. (2005), and in some cases the concrete performed worse (Darwin et al. 2011).

3.3 Field Studies

Due to high likelihood of corrosion of reinforced concrete in marine environments, multiple field studies have been conducted on the effect of CIAs in marine environments to determine their effectiveness. In these studies, specimens with CIA were located below sea level or the mean high tide and exposed to the environment for years. Measurements and test results were compared with that of the control specimen. Mixed outcomes have been reported. Paredes et al. (2010) found that after more than 10 years, the majority of calcium nitrite and amino-alcohol specimens did not show corrosion, whereas corrosion had initiated in some of the ester and amine and control specimens. The authors concluded that calcium nitrite was the only inhibitor to provide performance gains. Kondratova, Montes and Bremner (2003) reported that CIAs produced lower corrosion currents in uncracked samples but provided negligible benefits in pre-cracked samples. Nevertheless, Cheng and Robertson (2006) found that the addition of CIAs did not provide significant improvements to chloride penetration resistance or consistent benefits to corrosion potential over control values.

Another area of interest for the application of CIAs is in bridge components due to the high risk and negative impact of corrosion. On bridge barrier walls near Montreal, Cusson and Qian (2007) found low risk of corrosion in uncracked sections and higher corrosion rates in areas with thermal cracking regardless of the addition of a CIA. Sika Services supported a study on Sika's ester and amine Ferrogard 901. The study focused on a splash barrier in the Swiss Alps and was conducted over an 18-year period. The study demonstrated that the addition of the CIA delayed corrosion initiation but did not significantly reduce chloride penetration (Angst et al. 2016). Other studies have utilised CIAs on bridge structures, but the reports indicated that the studies did not last long

enough for significant conclusions to be drawn ([Hopwood, Hunsucker & Courtney 1988](#), [Ozyildirim 1992](#), [Balaguru & Nazier 2002](#)).

The use of CIAs for repair applications has also drawn interest. Islam, Sohaghpurwala and Scannell ([2002](#)) reported on the application of calcium nitrite and amino-alcohol CIAs for deck rehabilitation and patching of four bridge structures in the USA. In three out of the four structures, shrinkage cracks occurred, and the patches developed signs of corrosion. The authors found that the corrosion inhibitors did not provide any protection against corrosion in the environments in which they were evaluated, which agrees with the conclusions presented by Sprinkel ([2003](#)).

4 CORROSION INHIBITOR APPLICATIONS

4.1 CIA Applications Worldwide

Based the results of a survey of US state departments of transportation (DOTs) by Thompson, Yunovich and Lankard (2000), CIAs have been found to be used in reinforced, precast, prestressed, and post-tensioned concrete for a wide variety of structures including concrete roads, bridges, tunnels, marine structures, piles and dams, among others. The majority of the respondents' experiences were with the commercial products Darex Corrosion Inhibitor (DCI) or DCI-S, with some applications of the organic CIAs Rheocrete 222+, Armatec 2000 (bought out by Sika), and an experimental application of MCI 2000 in one state (refer to Table A 1 for the detailed information of these products). The majority of the US DOTs indicated that they were generally satisfied with the impact the addition of CIAs had on the concrete properties, but there was a significant uncertainty regarding their influence on corrosion resistance (Table 4.1).

Table 4.1: DOTs' comments on CIA-related experience

DOT	Effect on Concrete Properties	Effect On Corrosion
CA	Fair	Uncertain
CT	Uncertain	Uncertain
FL	Good	Good
GA	Fair	Uncertain
IA	Uncertain	Uncertain
IL	Good	Uncertain
KY	Good	Good
ME	Good ^a	Good ^b
MN	Good	Uncertain
NC	Uncertain	Uncertain
NJ	Uncertain	Uncertain
NY	Good	Uncertain
OH	Fair	Better Than without ^b
PA	Good	Uncertain
RI	Good	Uncertain
SC	Good	Uncertain
TX	Meets specifications	Uncertain
VA	Good	Uncertain

^aWith respect to DCI-S.

^bOnly with respect to DCI, the only one used for a prolonged period of time.

Source: Thompson, Yunovich and Lankard (2000).

In another survey by Van Dyke et al. (2017) the authors received responses from nine DOTs, with all of them reporting that they do not use inhibiting admixtures to reduce reinforcement corrosion. Five of the respondents had reported using at least one CIA on an experimental basis in the earlier survey by Thompson, Yunovich and Lankard (2000), though no reason for the change in policy was presented.

Literature describing commercial examples of the use of CIAs in structures include: [GCP Applied Technologies \(2018b\)](#), [Dowerman \(2016\)](#), [Cortec Corporation \(2016\)](#), [Angst et al. \(2016\)](#), [Balaguru and Nazier \(2002\)](#), [Ozyildirim \(1992\)](#) and [Hopwood, Hunsucker and Courtney 1988](#)).

4.2 CIAs Applications in Australia

A survey was conducted with several selected CIAs suppliers. The findings from the survey are summarised as follows.

CIAs have been used in Australia for more than 20 years. The most common chemical component of the available CIA products is calcium nitrite. Other chemical components include amines, alkanolamines, hexanediamine and ethanol. The CIAs are based on anodic, cathodic or mixed inhibition, and most of them are used to deal with chloride related corruptions rather than carbonation.

Limited information has been made available by the respondents regarding sample projects. Projects mentioned include: refurbishment of wet dock in Melbourne, Cruise Terminal around Brisbane (GCP), container walls on wharfs at Port of Brisbane (Sika and GCP), 40 m³ base slab for a radio tower in northern Fiji (Parchem).

The dosage used is based on standard testing per specifications for a specific project or determined using a specialist software (e.g. Life-365TM). There is limited environmental and safety concern, since once placed, the CIAs are encapsulated in concrete, and there are no post-hardening issues. Due to confidentiality, information about costing is not available.

4.3 Corrosion Inhibiting Admixture Specifications

In Australia, the standard which provides guidance (but compliance is not required) on the application of CIAs for reinforced concrete is AS 1478.1, which covers general testing and acceptance requirements for concretes with chemical admixtures. These tests include water content, strength, drying shrinkage, air content standards with respect to a control sample pH value, relative density, non-volatile content, and chloride ion content.

In Queensland, TMR technical specification MRTS70 requires that, for concrete structures, all chemical 'admixtures shall conform with the requirements of AS 1478 and shall be used in accordance with AS 1379' ([TMR 2018](#)). Chemical admixtures used in TMR projects are required to be registered, with a list of the registered admixtures provided periodically by TMR ([TMR 2019](#)).

Other states maintain their own specifications, such as the NSW Roads and Maritime Services (RMS) which specifies that for bridges, CIAs must conform to AS 1478.1 and consist of at least 30% calcium nitrite with at least 9 kg of calcium nitrite per cubic metre, and are mandatory for use in precast concrete members in exposure class C ([Roads and Maritime Services 2018](#)). Testing of the quantity of calcium nitrite in concrete is performed using Nitrite 3000 test strips, per T371 ([Roads and Maritime Services 2012](#)).

Internationally, a number of standards cover the use and testing of CIAs. The British Standard BS 8443 specifies compressive strength, setting time, and air content requirements for concrete with CIAs in comparison to control mixes. The ASTM C1582/C1582M 2011 standard is used for evaluating a CIA in concrete, which defines minimum allowable reductions in compressive and flexural strength, shrinkage, setting time, corroded area when compared to control samples based on ASTM G109 test beams. The tests required by ASTM C1582/C1582M 2011 (2017) include mean polarisation resistance based on ASTM G180 and mean allowable macrocell current based on ASTM G109. In addition, a number of US DOTs also have individual specifications for CIA which only cover the use of DCI (Thompson, Yunovich & Lankard 2000).

The Japanese Industrial Standard JIS A 6205 sets out the requirements for concrete with CIAs for the physical properties including compressive strength and setting time in comparison with control samples. Requirements are also specified for corrosion protection in relation to a control sample, with parameters including chloride content and alkali content, with methods for electric potential and accelerated corrosion testing presented within.

The New Zealand Transport Agency's *Bridge Manual* (NZTA [2013](#)) states that in reinforced concrete or prestressed concrete bridges, the use of CIAs requires a special study as detailed in AS/NZS 1170.0. The Fiji Roads Authority states that bridges with an exposure classification

defined as a Coastal Frontage (B2) or a Tidal/Splash/Spray zone (C) require the inclusion of BASF MasterLife 2006 or another approved organic corrosion inhibitor ([2015](#)).

Requirements for critical concrete properties with CIAs from different standards are summarised in Table 4.2.

Table 4.2: International requirements for CIA concrete

Standard	ASTM C1582	BS 8443	JIS A 6205 ⁽²⁾
Compressive strength (%) ⁽¹⁾	≥ 80%	≥ 90%	≥ 90%
Setting time ⁽¹⁾	Initial: ± 3:30 Final: ± 3:30	Initial: -0:30 to + 1:30	Initial: ± 1:00 Final: ± 1:00
Shrinkage (%) ⁽¹⁾	≤ 135% of control or 0.01% increase over control	–	–
Corroded area (%) ⁽¹⁾	≤ 33%	–	≤ 5%
Macrocell current (C)	≤ 50	–	–
Polarisation resistance (1/R) ⁽¹⁾	≤ 1/8	–	–

1 Values are comparisons between CIA test samples and control samples.

2 Visual inspection also required to assess no corrosion on CIA sample.

4.4 Environmental Considerations

An environmental concern with the use of some inorganic CIAs is their toxicity. An example of toxic CIAs are the inorganic nitrites, commonly found in CIAs, which are toxic and carcinogenic ([Rivetti et al. 2018](#)). The use of toxic CIAs can create an environmental hazard and may cause the concrete to be considered a hazardous waste leading to high disposal costs at the end of the structure's life ([Elsener 2001](#), [Shehata, Korshed & Attia 2018](#)). Environmental concerns have led to more focus on non-toxic organic CIAs. There has also been research into green CIAs, which are composed of the extracts of natural products, such as Indian bamboo, kola leaves, tobacco, and bitter leaf (Section 2.5). However, no examples have been found of CIAs causing a structure to be deemed hazardous waste, and safety data sheets for CIAs typically recommend not ingesting said products, using protective covering to avoid skin and eye contact, and not allowing the CIAs to enter waterways.

4.5 Economic Considerations

In addition to extending the service life of reinforced concrete structures through improved durability, a major purported benefit of using CIAs is for life-cycle cost savings due to reduced long-term corrosion maintenance and repair costs. Life-365™ is a numerical modelling software, developed by a concrete industry consortium, which is capable of predicting the service life of reinforced concrete designs in various environments with calcium nitrite inhibitors and Rheocrete 222+ ([Life-365™ Consortium III 2018](#)). Additionally, various studies have been performed on the cost effectiveness of CIAs over the structure's life-span.

Kepler, Darwin and Locke ([2000](#)) performed an analysis of the economic costs over the life span for a 230 mm bridge deck with 50 mm cover over the top reinforcing mat, with and without CIAs. They factored in repair and replacement costs based upon input from engineers at transportation agencies and literature. They analysed a variety of different corrosion protection methods, including:

- no protection with a 25-year repair time
- silica fume concrete with an additional cost of \$19.60/m³ and which has an estimated repair time of 30 years

- inorganic calcium nitrite (DCI) CIA at a cost of \$1.63/L, which increases the concrete cost by between \$16–55/m³ depending upon specified dosage, and has an estimated repair time of 40 years
- organic Rheocrete 222+ CIA at a cost of \$3.57/L, which increases the concrete cost by \$18/m³, and has an estimated repair time of 36 years.

Based upon a design life of 75 years, and accounting for repairs cycled at the presented times over the 75-year life span, the present costs were determined for each system. Of the specified options, the authors found that the calcium nitrite concrete provided the best present value, followed by the organic CIA, no protection, and the use of silica fume concrete.

Another study regarding the 75-year economic cost of various corrosion protection methods was performed by Darwin et al. ([2011](#)) for a 46 m long, 11 m wide and 216 mm thick bridge deck. They determined repair times using experimental corrosion rates, with repair costs consistent regardless of protection method. The analysed corrosion protection methods included:

- conventional concrete with a cost of \$735.75/m³, with repairs occurring in years 19, 44, and 69
- conventional concrete with the organic CIA Rheocrete 222+, at a cost of \$6.08/L, increasing the concrete cost by \$30.40/m³, with repairs occurring in years 23, 48, and 73
- conventional concrete with the inorganic calcium nitrite CIA DCI-S, at a cost of \$1.32/L, increasing the concrete cost by \$19.80/m³, with repairs occurring in years 21, 46, and 71
- conventional concrete with the CIA Hycrete, at a cost of \$4.95/L, increasing the concrete cost by \$42.53/m³, with repairs occurring in years 38, and 63.

Using a discount rate of 2%, the authors determined that the conventional concrete with Hycrete had the lowest present cost at \$502/m², followed by the DCI concrete at \$670/m², then the Rheocrete 222+ concrete at \$690/m², and the conventional concrete at a rate of \$700/m².

5 DISCUSSION

5.1 Effectiveness of CIAs

The use of different types of CIAs has varying effects on the durability of concrete. The laboratory studies investigated in this report indicate that most of the CIAs produced longer corrosion initiation times, higher critical chloride thresholds, and the organic CIAs showed reductions in the chloride penetration. These properties generally result in an improved corrosion inhibition, as reported in the literature through accelerated laboratory testing.

Definitive conclusions regarding the long-term effectiveness of CIAs on bridge components were lacking due to the insufficient length of many of the field studies, though the presence of cracks seem to lead to increased corrosion regardless of the presence of CIAs. No benefits were seen for use of CIAs in repair patches on bridge components. Field studies with longer monitoring periods, therefore, are required for more definitive conclusions, which may provide additional clarity on the effectiveness of CIAs.

Varying effects of CIAs on the properties of concrete have been reported. Calcium nitrite-based CIAs cause a reduction in setting time and an increase in short-term compressive strength, while organic CIAs can reduce permeability and increase setting time, with amino-alcohol CIAs having little impact on compressive strength and amine and ester CIAs causing a reduction in compressive strength. These findings are in a general agreement with the properties of the currently available CIA products as reported by the local suppliers.

The addition of CIAs can provide effective corrosion resistance in uncracked reinforced concrete; however, variability in their effectiveness may exist for field applications. The effectiveness of the corrosion resistance provided by the CIAs, however, did not hold up in the presence of cracks or patch repairs. The laboratory testing showed dramatic increases in corrosion in the presence of cracks, regardless of the inclusion of CIAs, with the addition of the CIAs providing only slight or no improvements to corrosion resistance. These results were consistent with the field studies, where significant corrosion occurred in bridge and marine samples with cracking regardless of the presence of the CIAs. This is likely due to the direct exposure of the reinforcement to the aggressive chlorides caused by the cracks quickly overcoming the protective barriers developed by the CIAs. In applications where cracking is likely to occur, CIAs alone may not provide an effective corrosion protection system.

The studies on the effectiveness of the inhibitors seemed all to be only for the seawater chloride induced steel corrosion, whilst the concrete carbonation is also another cause for the corrosion of reinforcing steel. There are, however, a lack of studies available for the application of CIAs in concrete components that are high above seawater and subjected to carbonation and airborne chloride instead of salt water splashing. Also, no studies have been identified on how the CIAs work for components in salt containing soil.

5.2 CIAs Usage and Specifications

The following conclusions of CIA usage and specifications can be made:

- CIAs have been applied to projects throughout the world and in Australia, particularly in high chloride environments. There are, however, limited findings in quantifying and verifying their benefits in said applications.
- Domestic and international standards are available to cover the use of CIAs and the performance of concrete with CIAs. In Australia, products are tested mostly based on the ASTM standards. RMS and some other road agencies have their own specifications but also refer to the ASTM standards.

- There exist some environmental concerns about the use of some CIAs, such as inorganic nitrites. Concretes with these compounds are considered a hazardous waste, potentially leading to high disposal costs. There is an argument that once placed in mix the CIAs are encapsulated in concrete, and there are no post-hardening issues. Since CIAs have not been on the market for a long time, there are no instances where a disposal of concrete from an existing structure with CIAs has been assessed.
- There may be some economic benefit in using CIAs; however, real-life data is not sufficient to verify the potential benefits of CIAs over the lifespan of a structure.

6 CONCLUSION AND RECOMMENDATIONS

6.1 Conclusions

Effectiveness of different CIAs (findings from tests)

CIAs protect the reinforcing steel in concrete by assisting in the production of a passive film over the reinforcing steel, which suppresses the corrosion chemical reaction. They are purported to be able to elevate the critical chloride threshold, delay corrosion initiation, and reduce the rate of corrosion.

- Laboratory studies have supported the effectiveness of calcium nitrite and certain organic chemical CIAs to provide corrosion resistance for uncracked specimens.
- A lack of long-term field studies makes it difficult to draw definitive conclusions regarding the effectiveness of CIAs; however, the available results have shown some support of the benefits of CIAs in uncracked concrete. This may make these products more relevant for prestressed concrete.
- In the presence of cracks, the laboratory and field studies both demonstrated that the effectiveness of the CIAs was minor or negligible, and that corrosion occurs at significantly higher rates than for uncracked concrete irrespective of the presence of CIAs.
- The application of CIAs in repair patches was shown to provide negligible benefits in laboratory and field tests.

While CIAs may provide benefits to corrosion resistance, they are not a substitute for good concrete designs.

In situations where the concrete is likely to crack, CIAs are not expected to be effective. They are considered to be more relevant for sections that are not likely to crack such as prestressed concrete elements.

Effects on concrete properties

From the review it was found that different CIAs have varying effects on the concrete properties. Calcium nitrite has been shown to accelerate the concrete setting time and early age compressive strength, whereas organic admixtures generally lengthen the setting time and cause either a negligible change or a reduction in compressive strength, depending on the chemical composition. Additional additives can be used to mitigate the adverse effects. Long-term data, however, are not available to assess the long-term impacts of CIAs on the properties of concrete.

Economic benefits

Some work has been presented which demonstrates CIAs may provide some reduced life-cycle costs in chloride rich environments. Real-life data, however, is not available to quantify the economic benefits of CIAs.

Environmental considerations

The toxicity of some inorganic CIAs, such as calcium nitrite, may present an environmental concern, with organic CIAs providing non-toxic alternatives. However, care should be taken in the handling of all CIAs. Long-term environmental impacts, such as high disposal costs, require further investigation.

Commercial supply

CIAs can be sourced from several commercial suppliers. TMR currently requires chemical admixtures used in its projects be registered with the Department ([TMR 2018](#)). Several CIAs are

currently registered chemical admixtures for TMR projects; however, there are no circumstances where CIAs have been approved to reduce or replace other products, mechanisms or specifications, commonly used to ensure adequate concrete performance. Long-term performance of these CIA products should be monitored to help inform TMR policy around the specification and use of CIAs.

6.2 Recommendations

It is recommended that:

1. With the durability and additional benefits provided by blended cements, CIAs should not be used as a substitute for blended cements in MRTS70. Regarding MRTS70's sections on *Chemical admixtures* and *Concrete mix – design and acceptance*, no changes are recommended based upon the work in this report.
2. TMR should maintain its current approach of allowing CIAs to be used in concrete but not allowing any proclaimed performance benefits to be considered in designing an adequately durable concrete.
3. If suppliers are interested in using CIAs as a substitute, TMR should request comparative performance testing to evaluate proposed mixes to triple-blended cement mixtures commonly used to prove equivalent performance.
4. TMR should investigate any issues that may arise related to disposing of concrete with CIAs added. This may change TMRs position on recommendation 2.
5. Develop a methodology to track the performance of current TMR structures where CIAs have been added to inform long-term policy of the specification and use of CIAs.

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APPENDIX A COMMERCIALLY AVAILABLE CORROSION INHIBITING ADMIXTURES

Table A 1 provides the details of a list of currently available commercial CIAs.

Table A 1: Commercially available admixtures

Name	Supplier	Chemical composition	Organic/ Inorganic	Protection mechanism	TMR registered admixture (Y/N) (1,2)	Product data sheet
DCI	GCP Applied Technologies	Calcium nitrite	Inorganic	Anodic inhibitor	N	(GCP Applied Technologies 2016)
DCI-S	GCP Applied Technologies	Calcium nitrite with retarding admixture	Inorganic	Anodic inhibitor	Y	(W.R. Grace & Co. 2013)
DCI-N	GCP Applied Technologies	Calcium nitrite	Inorganic	Anodic inhibitor	Y	(GCP Applied Technologies 2018 a)
CNI	Sika	Calcium nitrite	Inorganic	Anodic inhibitor	Y	(Sika 2009)
Ferrogard 901	Sika	Surfactants and amino alcohol	Organic	Mixed inhibitor	Y	(Sika 2012)
MasterLife CI 222/ Rheocrete 222+	BASF	Amines and esters	Organic	Mixed inhibitor with pore blocking	N	(BASF Australia 2019a)
MasterLife 2006	BASF	Silicic acid, disodium salt, and ammonia derivate	Inorganic	Mixed inhibitor	Y	(BASF Australia 2019b)
MasterLife CI 30/ Rheocrete CNI	BASF	Calcium nitrite	Inorganic	Anodic inhibitor	Y	(BASF UAE 2019)
Ad-Tek CNI	Ad-Tek Pty Ltd	Calcium nitrite	Inorganic	Anodic inhibitor	N	(Ad-Tek b)
Ad-Tek CI	Ad-Tek Pty Ltd	Amino-alcohol and amine	Organic	Mixed inhibitor	N	(Ad-Tek a)
Eucon CIA	Euclid Chemical Company	Calcium nitrite	Inorganic	Anodic inhibitor	N	(Euclid Chemical Company 2017)
MCI 2000	Cortec Corporation	Amino alcohol	Organic	Mixed inhibitor	N	(Cortec Corporation 2002)
MCI 2005	Cortec Corporation	Amine carboxylates	Organic	Mixed inhibitor	N	(Cortec Corporation 2018)
Hycrete X1000	Hycrete Inc	Proprietary	Unknown	Mixed inhibitor with pore blocking	N	(Hycrete 2017)
Hycrete MC1000+	Hycrete Inc	Proprietary	Unknown	Mixed inhibitor with pore blocking	N	(Hycrete 2019)

1 Accurate as of 01/04/2019.