



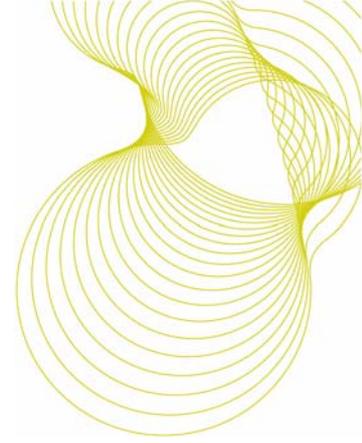
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**The use of surface  
applied FerroGard 903  
corrosion inhibitor to  
delay the onset of  
chloride induced  
corrosion in hardened  
concrete**

Prepared for: Sika Ltd

August 2005

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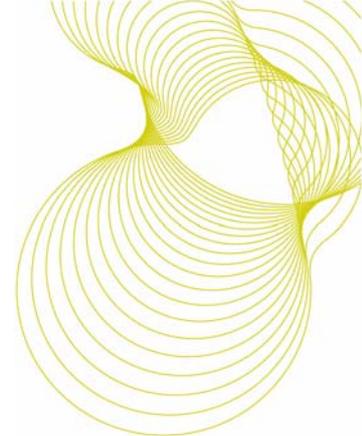
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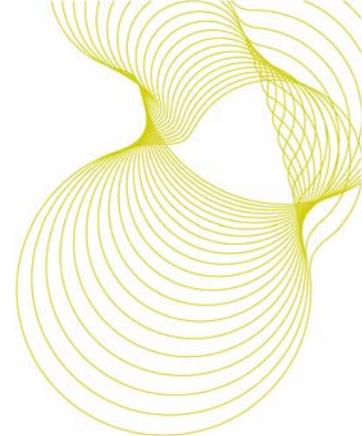
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## Contents

1	Synopsis	3
2	General Background Information	4
2.1	Types of Corrosion Inhibitor for Reinforced Concrete	4
2.2	Amino-alcohol Based Inhibitors	5
3	Experimental Overview: Delaying the Onset of Corrosion	7
3.1	Concrete Test Specimens	7
3.2	Accelerated Corrosion Testing (Chloride Ponding)	9
3.3	Electrochemical Corrosion Monitoring	10
4	Results - Delaying the Onset of Corrosion	13
4.1	Open Circuit Corrosion Potential (E <sub>corr</sub> )	14
4.2	Corrosion Current (I <sub>corr</sub> ) & Calculated Corrosion Rate	15
4.3	Cumulative Metal Loss of Mild Steel Reinforcement	17
4.4	Breakout and Visual Examination of Mild Steel Reinforcement	18
4.5	Chloride Depth Profile	20
5	Conclusions	21
	References	22
	Appendix I Experimental Details	



## 1 Synopsis

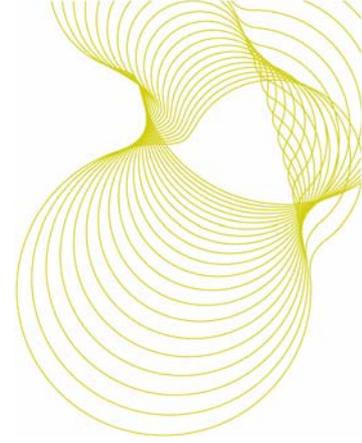
Concrete corrosion inhibitors have been used as a technique for both delaying the onset of mild steel reinforcement corrosion in new or early life concrete structures and also for controlling and/or reducing the rate of initiated reinforcement corrosion in existing structures.

BRE were appointed by Sika Ltd to perform independent laboratory testing of their surface applied concrete corrosion inhibitor product - 'Sika FerroGard 903'.

The objective of the laboratory testing was to investigate the effectiveness of the FerroGard 903 corrosion inhibitor to delay and/or suppress the onset of chloride induced reinforcement corrosion when the inhibitor product was applied directly to the surface of hardened reinforced concrete. In terms of this report the effectiveness of the inhibitor was assessed comparatively between specimens treated with the inhibitor and untreated control specimens subjected to the same accelerated corrosion regime

The ability of the Sika FerroGard 903 corrosion inhibitor to delay the onset of mild steel reinforcement corrosion in concrete test specimens was determined in the laboratory using standard electrochemical laboratory measurements of corrosion potential and corrosion rate (by measurement of linear polarisation resistance). In addition, visual inspection of the bars was conducted prior to the casting of the concrete specimens and also upon completion of the testing programme. This was done to assess the degree of visible chloride induced corrosion to the reinforcing bars as a result of the accelerated corrosion testing regime imposed during the laboratory testing programme.

This BRE report provides details of the test conducted and the results obtained from the electrochemical laboratory testing of surface applied Sika FerroGard 903 concrete corrosion inhibitor.



## 2 General Background Information

Steel embedded in concrete is effectively prevented from corroding in most, but not all, circumstances by the formation of a passive oxide layer on the steel surface. However, if the concrete becomes contaminated with chemical species that disrupt the passive layer or reduce the cement's alkalinity then, in the presence of sufficient concentrations of moisture and oxygen, corrosion of the steel could occur. Loss of steel passivity within concrete structures usually occurs through the action of two processes namely, carbonation of the concrete and chloride contamination. Corrosion of the steel reinforcement can occur through either process individually or through a combination of both.

Carbonation of concrete is brought about by the reaction of the alkaline phases of the cement matrix with acidic carbonaceous gases, particularly carbon dioxide, present in the atmosphere. This reaction leads to a reduction in alkalinity of the concrete pore solution and ultimately results in the depassivation of the steel reinforcement through general dissolution of the protective oxide film [1]. The contamination of concrete through the ingress of chloride ions, from a variety of sources such as de-icing salts and marine environments, results in a more localised breakdown of the passive oxide film leading to depassivation of the steel through pitting corrosion [2].

In an attempt to suppress and control the rate of steel corrosion, the use of corrosion inhibitors is just one of a variety of techniques that can be employed for reinforced concrete structures. The application of inhibitors is designated as one of the five "Principles" which are the basis of "Methods" known to control reinforcement corrosion (Method 11.3) in DD ENV 1504-9:1997 - "General principles for the use of products and systems"[3].

### 2.1 Types of Corrosion Inhibitor for Reinforced Concrete

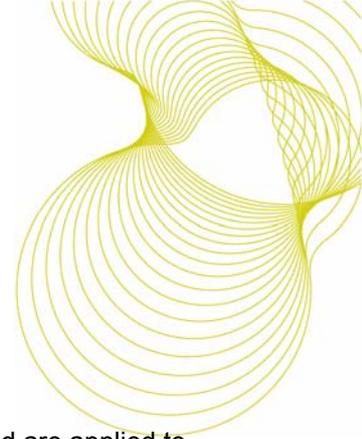
The corrosion process for steel reinforced concrete can be simplified into a two-stage process namely, the 'initiation phase' and the 'propagation phase'. By definition the initiation phase is the time taken for conditions to become conducive to corrosion of the reinforcement and the propagation phase is the period in which the accelerated corrosion of the steel reinforcement itself ultimately leads to rust staining, cracking and spalling of the cover concrete. Figure 1 shows a simplified model of the corrosion initiation and propagation phases during the service life of a hypothetical reinforced concrete structure.

Using this model it is easy to demonstrate how concrete corrosion inhibitor can be divided into two categories depending upon their primary use for either new or existing concrete structures.

#### **Admixture Inhibitors (cast-in inhibitors)**

Admixed inhibitors are primarily used as a preventative measure for new build structures and are designed to retard the onset of corrosion (i.e. increase the period of corrosion initiation shown in Figure 1).

They are generally added to the concrete mix in sufficient, but preferably small, concentrations prior to casting and should not significantly affect the physical properties of the concrete (e.g. compressive strength, setting time, microstructure etc.).



Admixed inhibitors have also been used in conjunction with concrete repair materials and are applied to existing structures as part of a rehabilitation strategy. However, some confusion still exists on how effective the application of inhibitors in this manner is in providing protection against the formation of incipient anodes.

### **Surface Applied (retro-applied inhibitors)**

Surface applied inhibitors are predominantly used as a rehabilitation or curative measure for reinforcement corrosion in existing structures, though their use as a proactive corrosion intervention measure to delay the onset of corrosion is increasing.

They are applied directly to the surface of existing concrete structures and are designed to penetrate the concrete matrix and suppress and/or control the corrosion rate of the embedded steel reinforcement. The mechanism by which the inhibitors ingress the concrete matrix and the exact concentration of inhibitor required at the steel/electrolyte interface in order to suppress corrosion depends primarily upon the type of inhibitor applied and its chemical composition.

The traditional reactive mode response to corrosion maintenance issues relies in part on the physical degradation of the steel reinforcement itself to indicate that the structure is exhibiting signs of distress and hence a degree of steel section loss, which can never be recovered (Figure 1 - reactive intervention point). The use of surface applied inhibitors at this intervention point is predominately to reduce or at least prevent an increase in the corrosion rate of the steel reinforcement, in order to achieve the required residual service life of the structure or component.

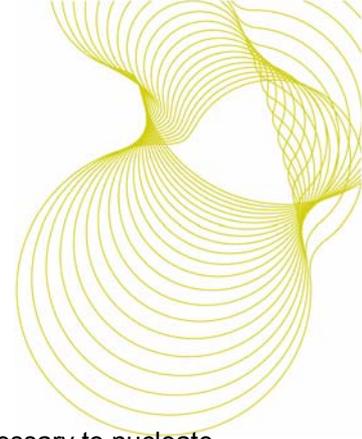
In the current climate of adopting a best value approach to the repair and rehabilitation of reinforced concrete structures, 'reactive' intervention alone may be insufficient if it limits the type, effectiveness and costs of the various repair and rehabilitation techniques available. Consequently the use of surface applied inhibitors as a proactive maintenance technique has recently been adopted in an attempt not only to increase the corrosion initiation period but also to limit the rate of corrosion in the propagation phase (Figure 1 - proactive intervention point).

## **2.2 Amino-alcohol Based Inhibitors**

The use of amino-alcohol and amine compounds, particularly their salts with inorganic and organic acids, as concrete corrosion inhibitors have been widely documented. Such compounds include ethanolamine, diethanolamine, triethanolamine and dimethylpropanolamine. These inhibitors are applied to the surface of existing structures within a water based carrier and have been reported to move within the concrete capillary network in both the liquid and vapour phases where they adsorb to the surface of the steel in order to retard corrosion.

In general the complexity of the inhibition process is primarily governed by whether uniform or pitting corrosion with chloride ions is predominant, though in both cases inhibition relies upon the adsorption of the active components occurring at both anodic and cathodic sites at the steel/electrolyte interface.

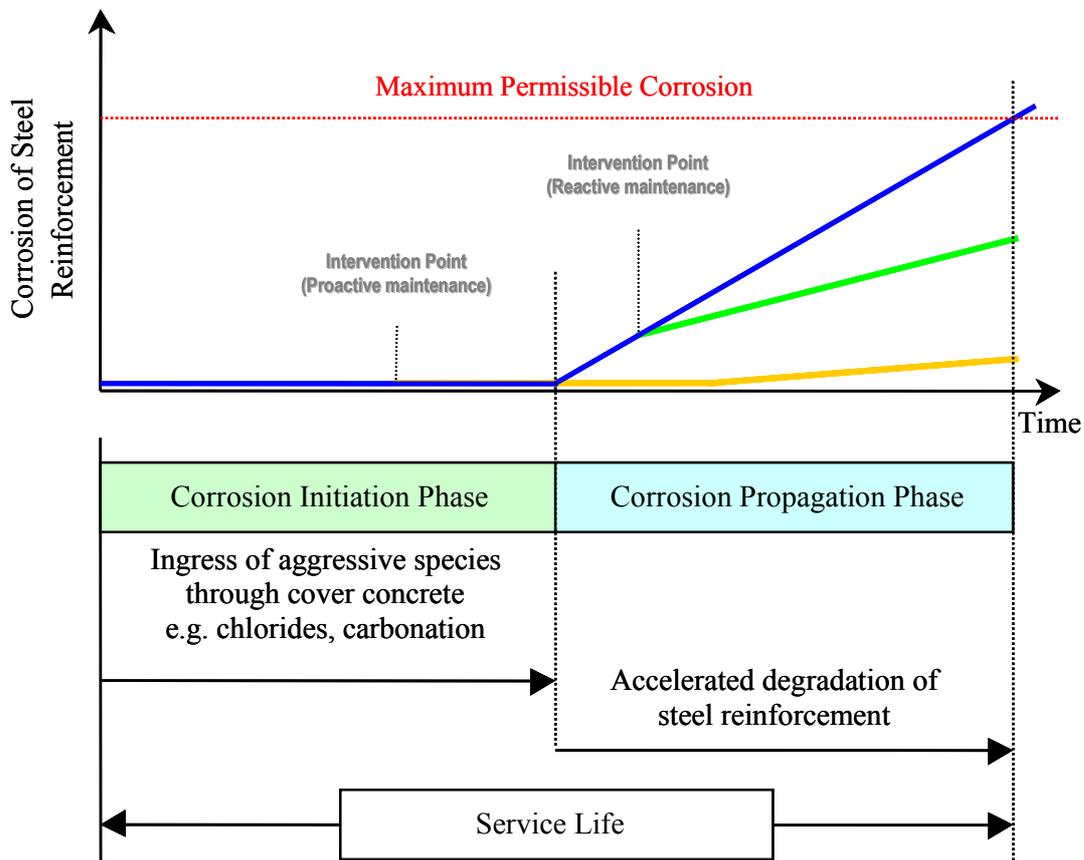
For conditions of uniform corrosion leading to a general reduction in bulk pH at the steel/electrolyte interface, the adsorption reaction is relatively uncomplicated. However, in the presence of chloride ions there may well be a competitive surface adsorption reaction between the inhibitor and chloride ions. This type of competitive displacement reaction may be responsible for reducing the effective chloride ion

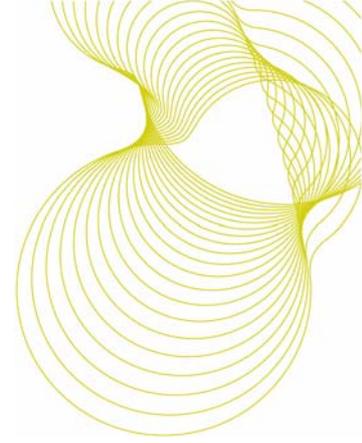


concentration at the steel/electrolyte interface thus, stifling the interfacial conditions necessary to nucleate pitting corrosion. Additionally, ingress of the inhibitor into the localised pitting environment may stifle the conditions required to sustain further pit growth.

Since most of the commercially available amino-alcohol inhibitors are blends containing several active components, it is probable that more than one inhibition mechanism is operating in order to suppress corrosion. However, due to the commercial sensitivity of the inhibitor formulations, much of the manufacturer's published literature is restricted with regards to the degree of quantitative data concerning the mechanisms of inhibition, the concentration of inhibitor adsorbed or the minimum concentration of inhibitor required to be adsorbed in order to bring about an effective level of inhibition.

**Figure 1** Simplified model of 2-stage corrosion process for steel reinforced concrete structures (After Tutti).





### 3 Experimental Overview: Delaying the Onset of Corrosion

The objective of the laboratory testing was to investigate the effectiveness of the FerroGard 903 corrosion inhibitor to delay and/or suppress the onset of chloride induced reinforcement corrosion when the inhibitor product was applied directly to the surface of hardened reinforced concrete. In terms of this report the effectiveness of the inhibitor was assessed comparatively between specimens treated with the inhibitor and untreated control specimens subjected to the same accelerated corrosion regime.

The ability of the corrosion inhibitor to delay the onset of mild steel reinforcement corrosion in concrete test specimens was determined as a function of time in the laboratory using standard electrochemical laboratory measurements of corrosion potential and corrosion rate (using the linear polarisation method). In addition, visual inspection of the bars was conducted prior to the casting of the concrete specimens and also upon completion of the testing programme. This was done to assess the degree of visible chloride induced corrosion to the reinforcing bars as a result of the accelerated corrosion testing regime imposed during the laboratory testing programme.

The following section outlines the preparation of the test specimens, the accelerated corrosion testing regime, the application of the inhibitor material and the electrochemical corrosion monitoring of the concrete specimens. (Further specific details relating to the experimental conditions, procedures and concrete mix design are provided in Appendix I of this report).

#### 3.1 Concrete Test Specimens

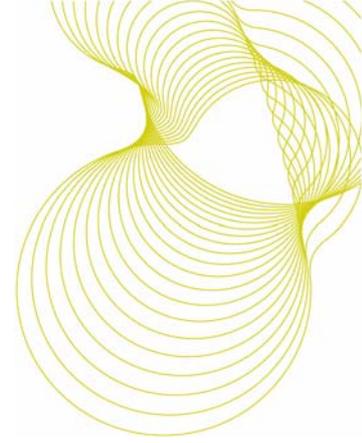
The concrete test specimens were prepared from standard 150 x 150 x 150 mm cube moulds (Details of the concrete mix design and curing regime is provided in Appendix I). Each test cube was prepared with a combination of 2 mild steel and 2 stainless steel reinforcement bars (as shown schematically in Figure 2). This arrangement was chosen to allow various combinations of electrochemical measurements to be taken in order to determine the corrosion rate of the mild steel reinforcement during the test programme (See section 3.5 - Electrochemical Corrosion Monitoring for further details).

##### Preparation of Concrete Specimens for Accelerated Corrosion Testing

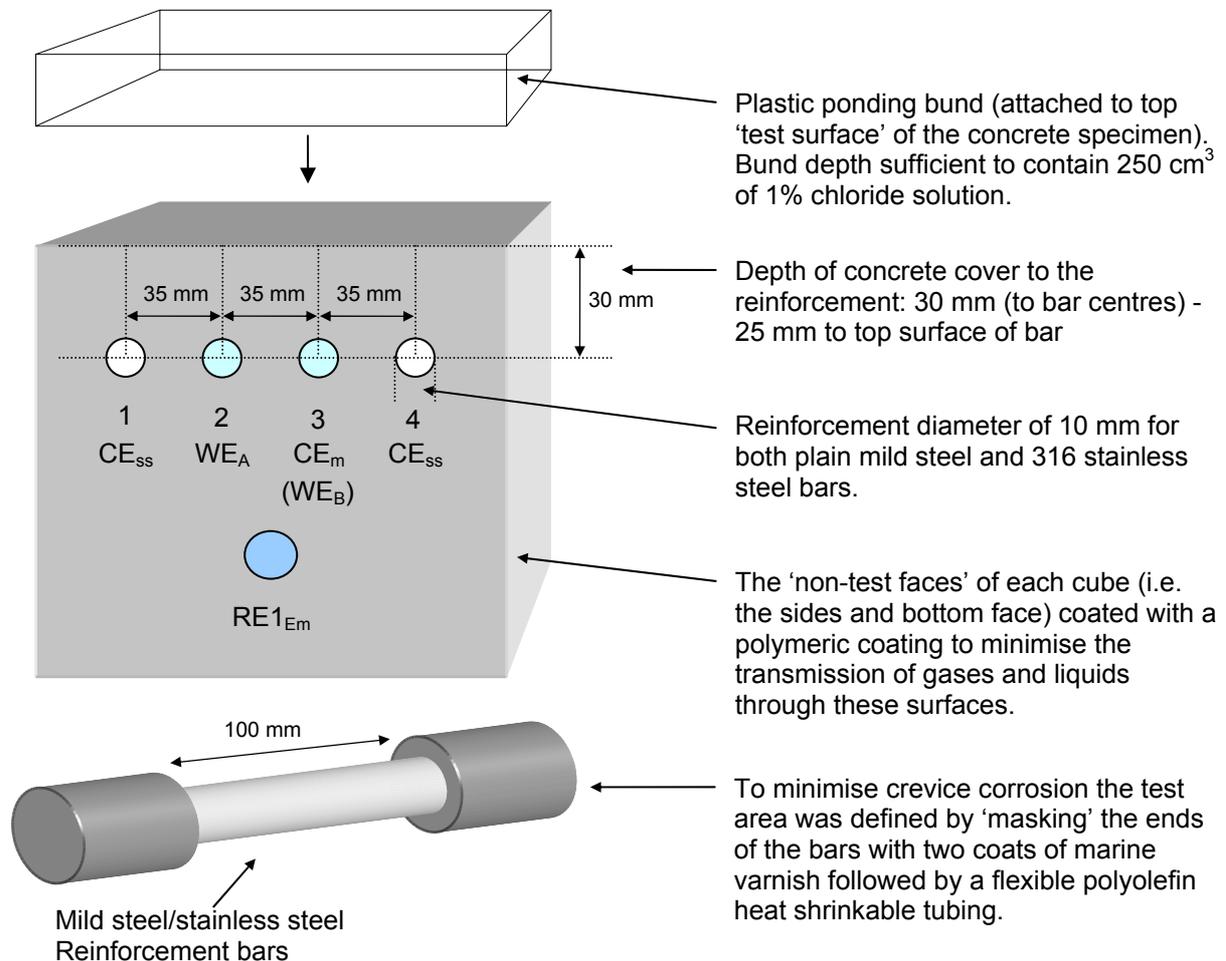
In order to simulate the specimens being a part of a larger concrete element, the 'non-test faces' of each cube (i.e. the side and bottom faces) were coated with a polymeric coating to minimise the transmission of gases and liquids through these surfaces. Care was taken to avoid any contamination of the top 'test face' of each specimen which was to be left exposed for the application of inhibitor material and/or chloride solution.

##### Preparation of Bund

A Perspex barrier was sealed to the sides of each concrete specimen with a neutral-cure silicone sealant. This barrier (or bund) extended sufficiently above the top 'test face' of the concrete specimen to contain the 250 cm<sup>3</sup> volume of chloride solution required for each ponding cycle.



**Figure 2** Schematic diagram of the concrete cube specimens.



Electrode Number	Label	Function
1	CE <sub>ss</sub>	Counter Electrode A (stainless steel)
2	WE <sub>A</sub>	Working Electrode A (mild steel)
3	CE <sub>m</sub> (WE <sub>B</sub> )	Counter Electrode (mild steel) [NB: Can be used as Working Electrode B (mild steel)]
4	CE <sub>ss</sub>	Counter Electrode B (stainless steel)
-	RE1 <sub>Em</sub>	Reference Electrode



### 3.2 Accelerated Corrosion Testing (Chloride Ponding)

The following section outlines the accelerated corrosion testing regime used to determine the effectiveness of the FerroGard 903 corrosion inhibitor to delay and/or suppress the onset of chloride induced reinforcement corrosion.

#### Accelerated Testing Programme

The accelerated testing programme was based upon a weekly conditioning cycle as detailed in Table 1. All specimens were initially subjected to conditioning Cycle A (ponding with deionised water only) to regulate the internal relative humidity of the concrete. The inhibitor material was applied in three stages over a 24 hour period ensuring that the product had been absorbed into the concrete before proceeding with each new application (see section below for details). Following the application of the inhibitor material to the test specimens, both the control and test specimens were subjected to conditioning Cycle B (two-day ponding with 1% chloride solution and five-day drying at laboratory room temperature and humidity) until the completion of the accelerated laboratory testing.

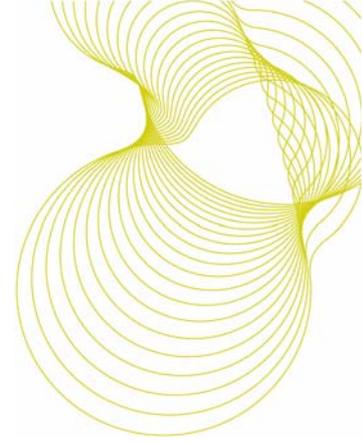
**Table 1** Accelerated corrosion testing programme.

Stage	Cycle Description	Duration
Cycle A	Deionised water (2 days wet - 5 days dry) Pond each cube with 250 cm <sup>3</sup> of solution	3 Cycles
Inhibitor Application	Sika FerroGard 903: Topically applied to the test specimens at a dosage of 1.0 kg m <sup>-2</sup> *  Control specimens left untreated	1 Cycle
Cycle B	1% chloride ion solution (by weight of chloride ion in AR Grade NaCl) (2 days wet - 5 days dry) Pond each cube with 250 cm <sup>3</sup> of solution	100 Cycles (Min) (Actual = 137)

\*See note on inhibitor application below.

#### Application of Inhibitor

The FerroGard 903 corrosion inhibitor was applied to the surface of the hardened concrete test specimens in three stages over a 12 hour period, ensuring that the product had been absorbed into the concrete before proceeding with each stage of the application. To reflect the aggressiveness of the accelerated chloride conditioning regime the manufacturers stated dosage level was exceeded in the laboratory testing programme and an inhibitor dosage of 1.0 kg m<sup>-2</sup> was applied to each test specimen (manufacturer's minimum inhibitor dosage for site applications = 0.5 kg m<sup>-2</sup>).



### Chloride Ponding Solutions

The 1% chloride ponding solution was prepared from AR grade sodium chloride (NaCl) and deionised water. Note: the 1% chloride solution was prepared by mass of chloride ions in solution and not by mass of dissolved NaCl in solution as follows:

$$\text{Mass of NaCl Required (g)} = \left( \frac{A_{\text{NaCl}_{(s)}}}{A_{\text{Cl}^{-}_{(aq)}}} \right) \times \left( \frac{V_{\text{H}_2\text{O}}}{100} \right) \times \% \text{Solution}_{\text{Cl}} \quad (\text{Equation 1})$$

Where:

(Atomic mass of sodium = 23.0 amu, Atomic mass of chloride = 35.5 amu)

$A_{\text{NaCl}} = 58.5$  amu,  $A_{\text{Cl}^{-}} = 35.5$  amu

$V$  = Volume of deionised water used for solution (ml)

$\% \text{Solution}_{\text{Cl}}$  = Desired concentration of chloride solution (e.g. 1.0%).

Hence, for a 1% chloride solution a mass of 16.48g of  $\text{NaCl}_{(s)}$  was dissolved in 1 litre of deionised water. (approximately 0.3M NaCl solution).

## 3.3 Electrochemical Corrosion Monitoring

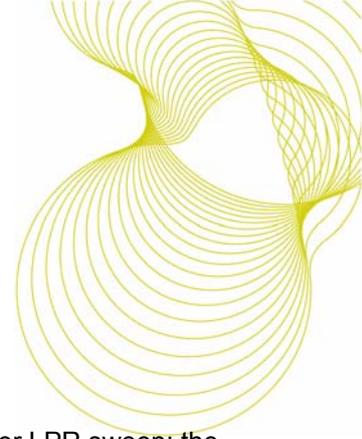
### Half-Cell Potential Measurement

All half-cell potential measurements were taken using a high input impedance ( $100\text{M}\Omega$ ) digital voltmeter with a resolution of 0.1 mV. Measurements were taken immediately after the deponding of each concrete specimen (i.e. after removal of the chloride solution) and prior to the use of any other electrochemical monitoring techniques that may otherwise have disturbed the potential of the mild steel electrodes. For each half-cell potential measurement, a saturated silver/silver chloride (Ag/AgCl) electrode, with a typical rest potential of  $194 \text{ mV} \pm 10 \text{ mV}$  vs. a standard hydrogen electrode, was used as the reference half-cell. All half-cell measurements were scaled against the saturated calomel electrode (SCE) rest potential (see appendix I for details).

### Linear Polarisation Resistance Measurement

Linear polarisation resistance (LPR) measurements of the concrete test specimens were obtained using a standard laboratory potentiostat and sweep generator. The mild-steel bar was used as the working electrode with an adjacent 316 stainless-steel reinforcing bar being used as a counter electrode and a cast-in Ag/AgCl reference electrode (see Figure 2).

Potentiodynamic LPR measurement of the corrosion current ( $I_{\text{corr}}$ ) was conducted using a 10mV perturbation in both directions away from the open circuit corrosion potential ( $E_{\text{corr}}$ ) at a potential sweep rate of  $10 \text{ mV min}^{-1}$  ( $0.1667 \text{ mV sec}^{-1}$ ), with data being acquired every 0.1667 mV.



Performing the LPR measurement in this manner resulted in a total of 240 data points per LPR sweep; the first 120 data points representing the anodic behaviour of the reinforcing bar and the second 120 data points representing the cathodic behaviour of the reinforcing bars.

The polarisation resistance ( $R_p$ ) was calculated using the Stern-Geary relationship (Equation 2) and the equivalent metal loss calculated from Faraday's Law (Equation 3). The equivalent metal loss between each monitoring interval was calculated and the cumulative metal loss plotted to represent the degree of corrosion to the mild steel reinforcement.

### Stern-Geary Relationship

Through the measurement of induced changes in potential and current, the corrosion potential, concrete resistance ( $R_p$ ) and corrosion current may be ascertained simultaneously by means of the Stern - Geary relationship [4]:

$$i_{\text{Corr}} = \frac{B\Delta I}{\Delta E} = 2.303 \frac{(\beta_a \cdot \beta_c)}{(\beta_a + \beta_c)} \cdot \frac{\Delta I}{\Delta E} = \frac{B}{R_p} \quad (\text{Equation 2})$$

Where:

$i_{\text{Corr}}$  = Corrosion Current.

B = The Stern-Geary Coefficient.

$\Delta I$  = Change in Current.

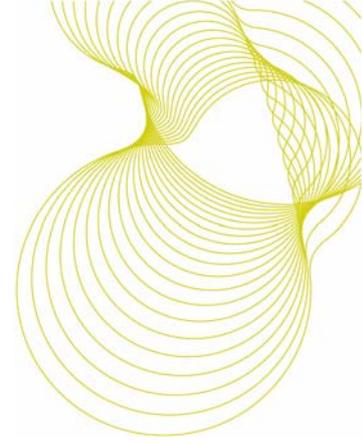
$\Delta E$  = Change in Potential.

$\beta_a$  = Anodic Tafel Coefficient.

$\beta_c$  = Cathodic Tafel Coefficient.

$R_p$  = Polarisation Resistance.

Values for the Stern-Geary coefficient for mild steel in concrete are generally assumed to be 26mV for actively corroding steel and 52mV for passive conditions, correlating to the Tafel slopes obtained for actively corroding and passive steel respectively. However, it must be noted that these values may not always be appropriate [5].



### Calculation of Corrosion Rates

The term corrosion current density is often confused with corrosion rate. Corrosion rates in relation to reinforced concrete, by definition, are concerned with metal loss per unit time. This metal loss is normally quoted in terms of microns of metal lost per year (microns per year or grams per year), whereas, corrosion current density is simply the measured cell current per unit area i.e.  $\mu\text{A cm}^{-2}$  or  $\text{mA m}^{-2}$ , measured at a specific instance. Faraday's law can be used to convert current density to corrosion rate and is illustrated below for iron, Fe being oxidised to ferrous ions,  $\text{Fe}^{2+}$ . The consumption rate,  $w$ , can be calculated according to the following equation:

$$w = \frac{(Mit)}{(z\rho F)} \quad \text{(Equation 3)}$$

where:

$w$  = the mass of steel consumed

$M$  = the atomic weight of metal (in this case iron 56 amu)

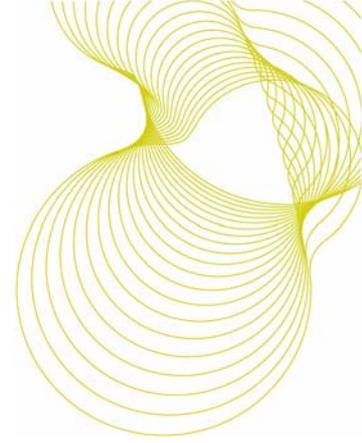
$I$  = the current in amperes (A),

$t$  = the time in seconds

$Z$  = the number of electrons (2 when  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ )

$\rho$  = the density of iron ( $7860 \text{ Kg m}^{-3}$ )

$F$  = the Faradays constant =  $96\,500 \text{ C mol}^{-1}$ .



## 4 Results - Delaying the Onset of Corrosion

The figures in the following section relate to the results from the electrochemical corrosion monitoring of the concrete test specimens. In terms of this report the effectiveness of the FerroGard 903 corrosion inhibitor to delay the onset of chloride induced corrosion was assessed comparatively between specimens treated with the inhibitor and untreated control specimens subjected to the same accelerated corrosion regime

For each cycle of the accelerated corrosion testing regime, the potentiodynamic measurement of the corrosion current ( $I_{corr}$ ) was conducted using a 10mV perturbation in both directions away from the open circuit corrosion potential ( $E_{corr}$ ) at a potential sweep rate of  $10 \text{ mV min}^{-1}$  ( $0.1667 \text{ mV sec}^{-1}$ ), with data being acquired every 0.1667 mV.

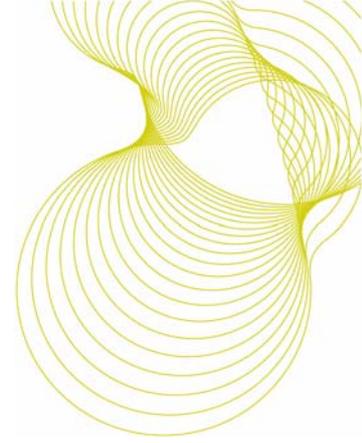
The figures relating to the measurement of corrosion current ( $I_{corr}$ ) use the following labelling convention. The solid line represents measurements recorded on the forward sweep of the potentiodynamic polarisation sweep (from -10mV to +10mV). The dashed line represents measurements recorded on the reverse sweep (sweep from +10mV to -10mV).

### Interpretation of LPR Results.

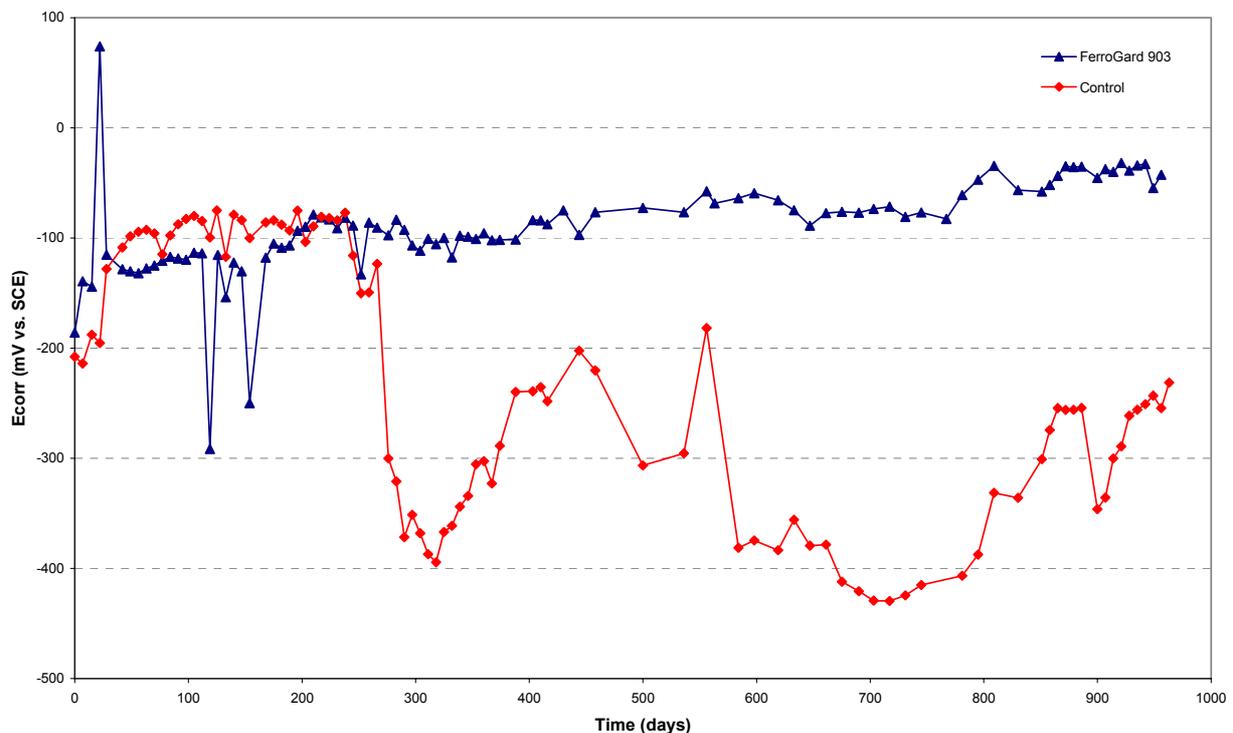
In this report the LPR readings obtained have been interpreted using empirically derived guidelines established from the corrosion of mild steel reinforcement in concrete [1,6] (Table 2).

**Table 2** Interpretation of corrosion current measurements ( $I_{corr}$ ) obtained from LPR readings of corroding mild steel in reinforced concrete [1,6].

<b>Corrosion current density</b>	<b>Corrosion Level</b>
$< 0.1 \mu\text{A cm}^{-2}$	Negligible.
$0.1 - 0.5 \mu\text{A cm}^{-2}$	Low to moderate
$0.5 - 1.0 \mu\text{A cm}^{-2}$	Moderate to high.
$> 1.0 \mu\text{A cm}^{-2}$	High.



#### 4.1 Open Circuit Corrosion Potential ( $E_{corr}$ )

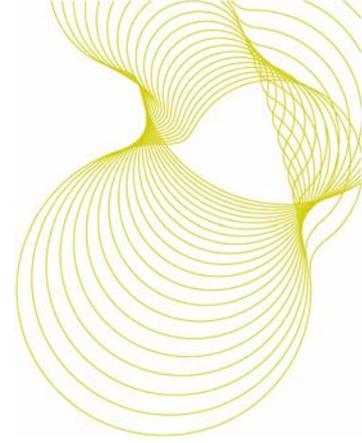


**Figure 3** Change in measured open circuit corrosion potential ( $E_{corr}$ ) versus SCE for inhibitor treated and control concrete specimens exposed to accelerated chloride ponding regime.

From the commencement of the accelerated chloride testing to approximately 250 days (36 ponding cycles), the measured corrosion potential ( $E_{corr}$ ) of both the control and the FerroGard 903 treated specimens was similar with the majority of measured potential readings falling within the range of -75 mV to -125 mV versus a standard calomel electrode (SCE) (Figure 3). This behaviour was not unexpected as it reflects the time taken for chlorides to ingress the concrete to the depth of the steel reinforcement in sufficient concentration before corrosion is likely to be initiated (See section 2 - Figure 1).

##### *Control Specimen*

With further accelerated chloride testing cycles (>36 cycles), the control specimen exhibited a significant but fluctuating shift in corrosion potential to more negative values than had been observed during the initial 36 cycle period, with measured values falling within the range -200 mV to -400 mV versus SCE. The erratic nature of the measured shift in corrosion potential was not unexpected as the chloride induced corrosion of mild steel in concrete is dynamic in nature and is related to the nucleation, development, and growth of pits. The observed trend continued until the cessation of the testing programme after 137 cycles. The measured potential shift was indicative of an increased risk of corrosion to the steel reinforcement (and hence a increased rate of corrosion of the mild steel reinforcement\*). \*See note on next page

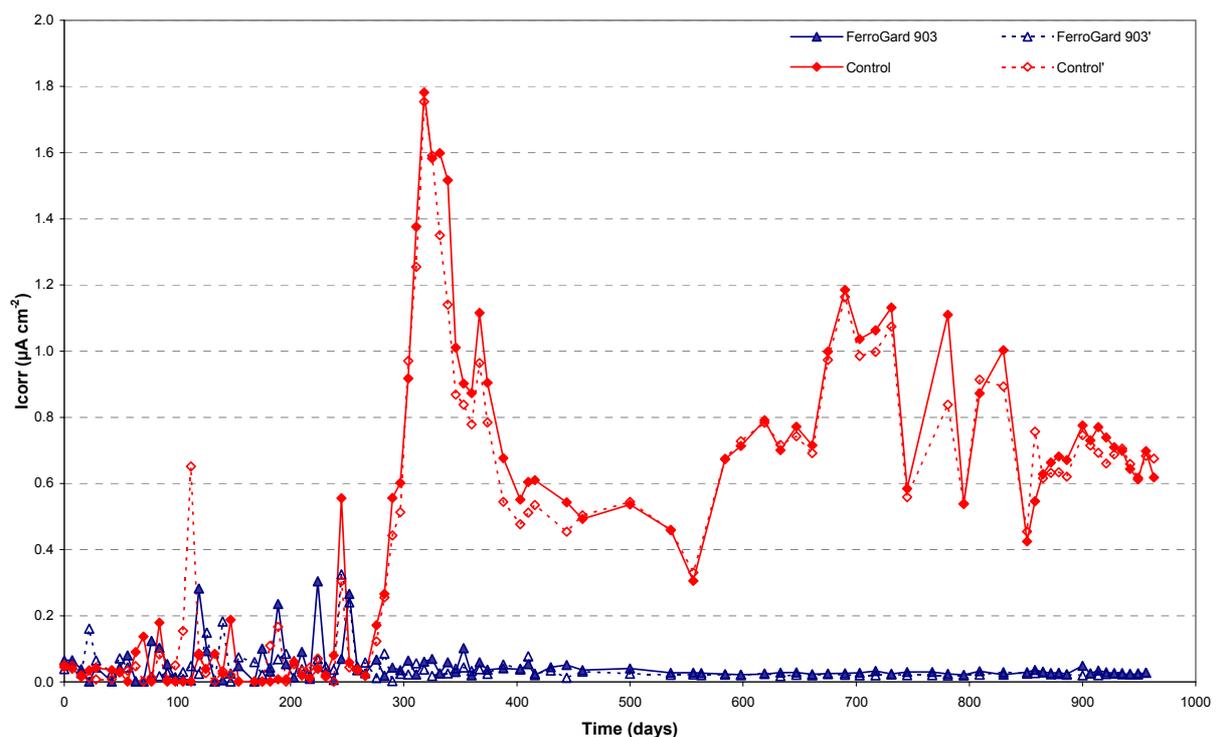


### FerroGard 903 Specimen

The general trend in measured corrosion potential for the specimen treated with FerroGard 903 corrosion inhibitor was for a shift to more positive values over the duration of the accelerated testing period (137 cycles). Generally this type of positive shift in potential is indicative of a lower risk of corrosion to the mild steel reinforcement (and hence an lower rate of corrosion of the mild steel reinforcement\*).

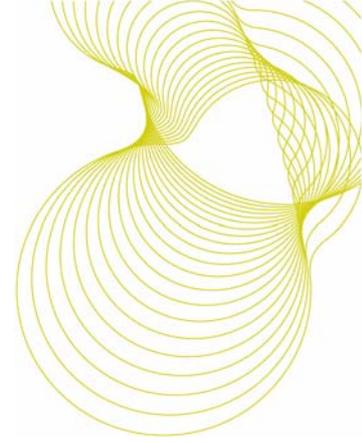
\*Measurement of the open circuit potential ( $E_{corr}$ ) can be used to give an indication of the condition of steel with regard to the 'risk' of corrosion activity. No direct kinetic information is gained regarding the rate of corrosion, although, in many cases the rate of corrosion of steel in concrete generally increases as the corrosion potential becomes more negative [1].

## 4.2 Corrosion Current ( $I_{corr}$ ) & Calculated Corrosion Rate



**Figure 4** Change in measured corrosion current density ( $I_{corr}$ ) for inhibitor treated and control concrete specimens exposed to accelerated chloride ponding regime.

From the commencement of the accelerated chloride testing to approximately 250 days (36 ponding cycles) the measured corrosion current ( $I_{corr}$ ) of both the control specimen and that treated with FerroGard 903 corrosion inhibitor was similar, with the majority of measured current readings falling below  $0.20 \mu\text{A cm}^{-2}$ . Over this period the corrosion rate of the mild steel was considered to be low (Figure 4). As stated previously, this period reflects the time taken for chlorides to ingress the concrete to the depth of the steel reinforcement in sufficient concentration before corrosion is likely to be initiated (See section 2 - Figure 1).

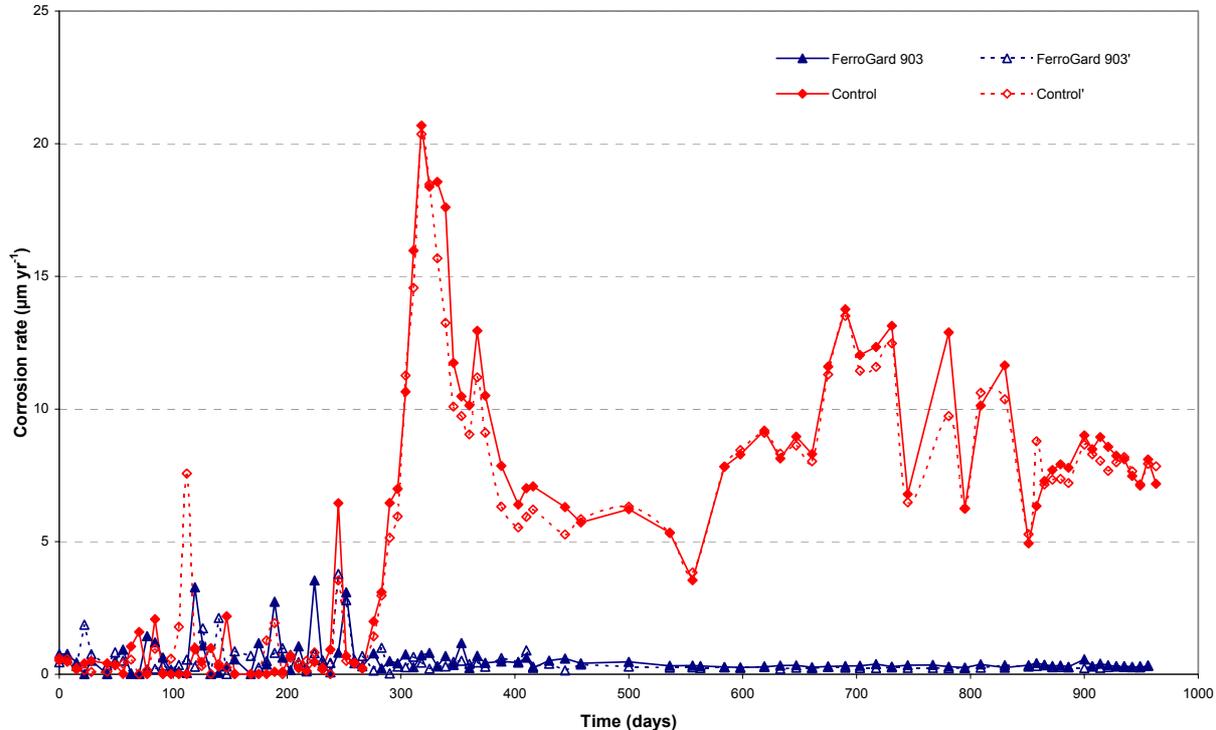


### Control Specimen

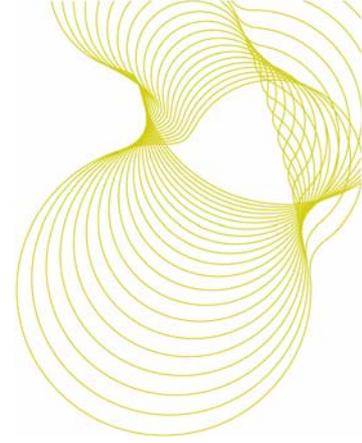
As stated previously, the observed negative shift in corrosion potential ( $E_{corr}$ ) - (Figure 3) was reflected in a corresponding increase in the measured corrosion current ( $I_{corr}$ ) after 250 day (36 cycles) (Figure 4). With further accelerated chloride testing cycles the control specimen exhibited a significant but fluctuating increase in corrosion current and hence corrosion rate (Figure 5). The observed trend continued until the cessation of the testing programme after 137 cycles. An increase in measured corrosion current with continued accelerated testing was expected since chloride ions will inevitably ingress through the concrete matrix and reach the depth of the mild steel reinforcement in sufficient concentrations to nucleate, and sustain the development and growth of pits in the presence of sufficient concentrations of moisture and oxygen. The erratic nature of the measured shift in corrosion current was not unexpected as the chloride induced corrosion of mild steel in concrete is dynamic (as discussed earlier).

### FerroGard 903 Specimen

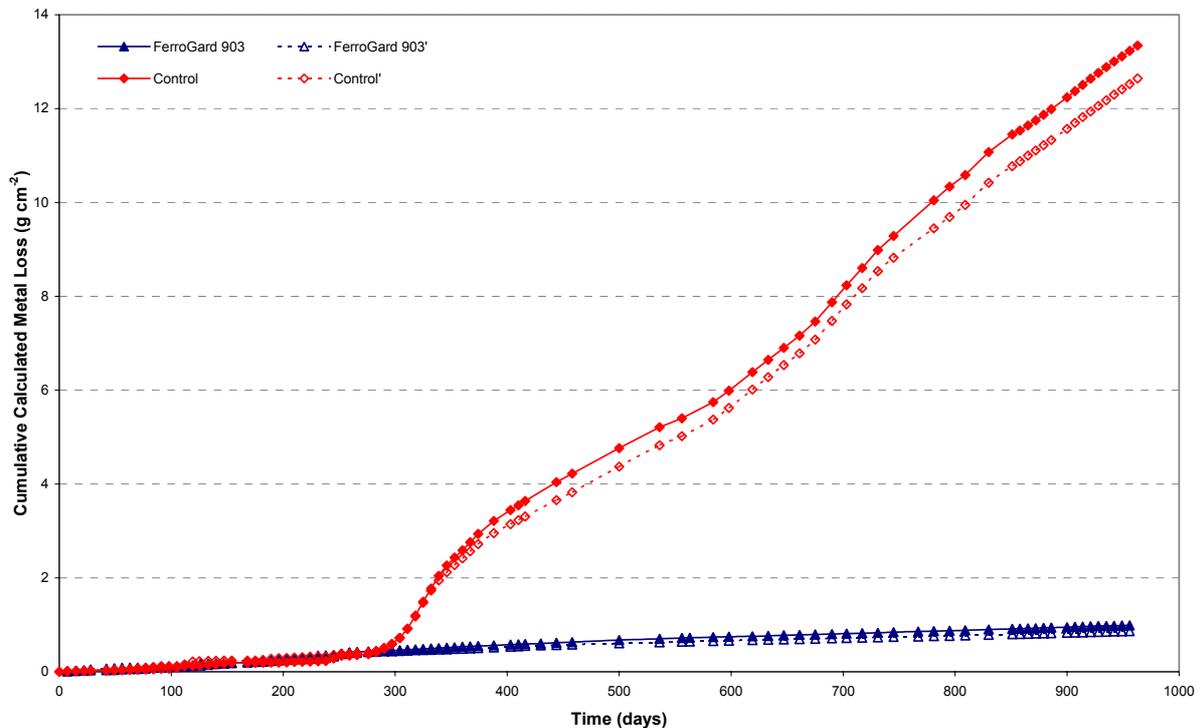
With regard to the specimen treated with FerroGard 903 corrosion inhibitor, there was little variation in the measured corrosion current over the duration of the accelerated testing period (137 cycles). The majority of the current readings were below  $0.1 \mu\text{A cm}^{-2}$  ( $\sim 1 \mu\text{m yr}^{-1}$ ) which is generally considered to be indicative of a low rate of corrosion to the mild steel reinforcement.



**Figure 5** Change in calculated corrosion rate of the mild steel reinforcement for inhibitor treated and control concrete specimens exposed to accelerated chloride ponding regime.



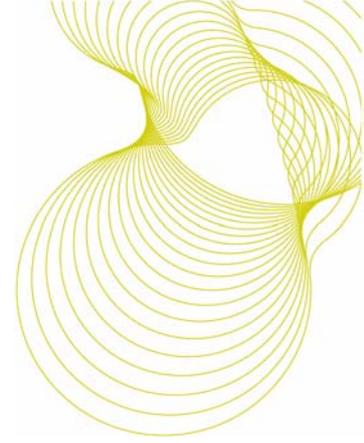
### 4.3 Cumulative Metal Loss of Mild Steel Reinforcement



**Figure 6** Cumulative metal loss of the mild steel reinforcement calculated from measured corrosion current ( $I_{corr}$ ) for inhibitor treated and control concrete specimens exposed to accelerated chloride ponding regime.

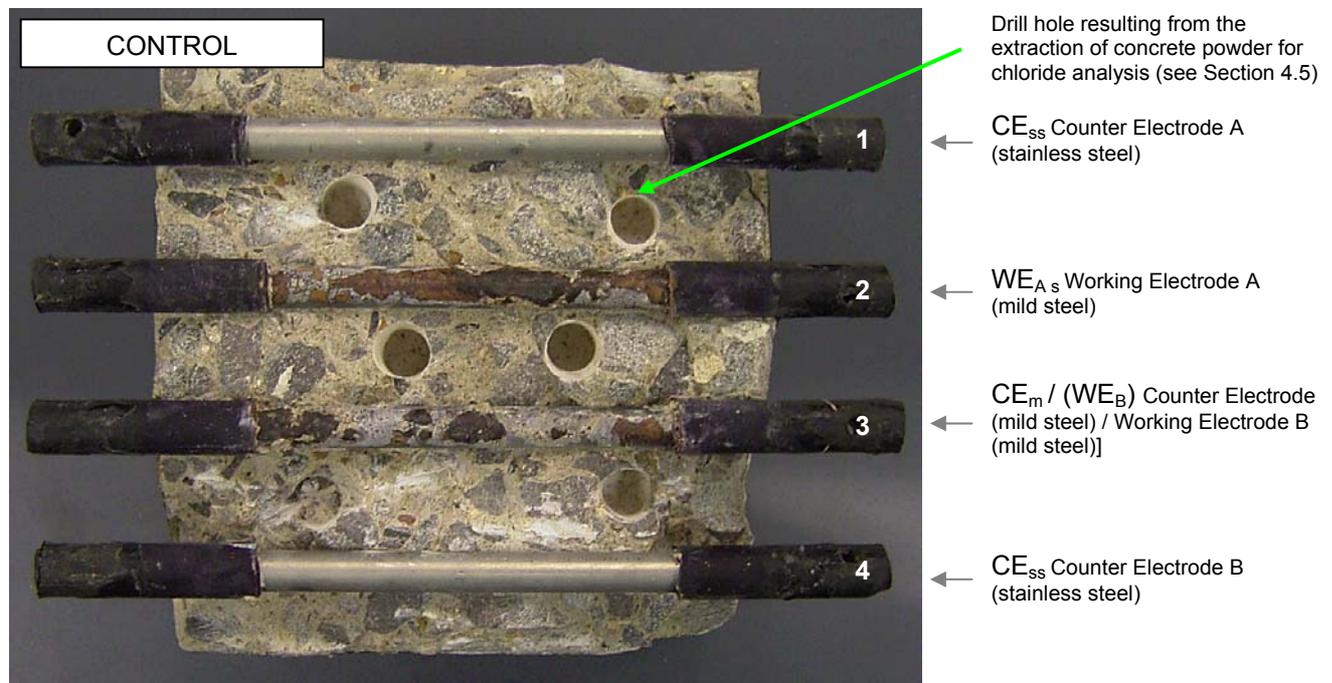
The measured corrosion current was used to calculate the equivalent metal loss of the mild steel reinforcement over the duration of the accelerated chloride ponding regime (Figure 6). This calculation was based upon the following assumptions; 1) iron (Fe) is being oxidised to ferrous ions ( $Fe^{2+}$ ) and 2) The metal consumption rate is determined by a linear current (charge) flow characteristic between consecutive LPR measurements.

Based upon the calculated equivalent metal loss (Figure 6), the time to corrosion initiation in the control specimens was approximately 250-300 days (36-43 chloride ponding cycles). With subsequent ponding cycles there was a marked increase in the calculated equivalent metal loss in the control specimens based upon the measured corrosion current ( $I_{corr}$ ). However, the test specimens treated with the corrosion inhibitor maintained a relatively uniform rate of metal dissolution for the duration of the accelerated corrosion conditioning (137 cycles) thus suggesting that the degree of corrosion to the mild steel reinforcement was low compared with the untreated control specimens. Breakout and visual examination of the mild steel reinforcement bars revealed that this was indeed the case (See section 4.4).



#### 4.4 Breakout and Visual Examination of Mild Steel Reinforcement

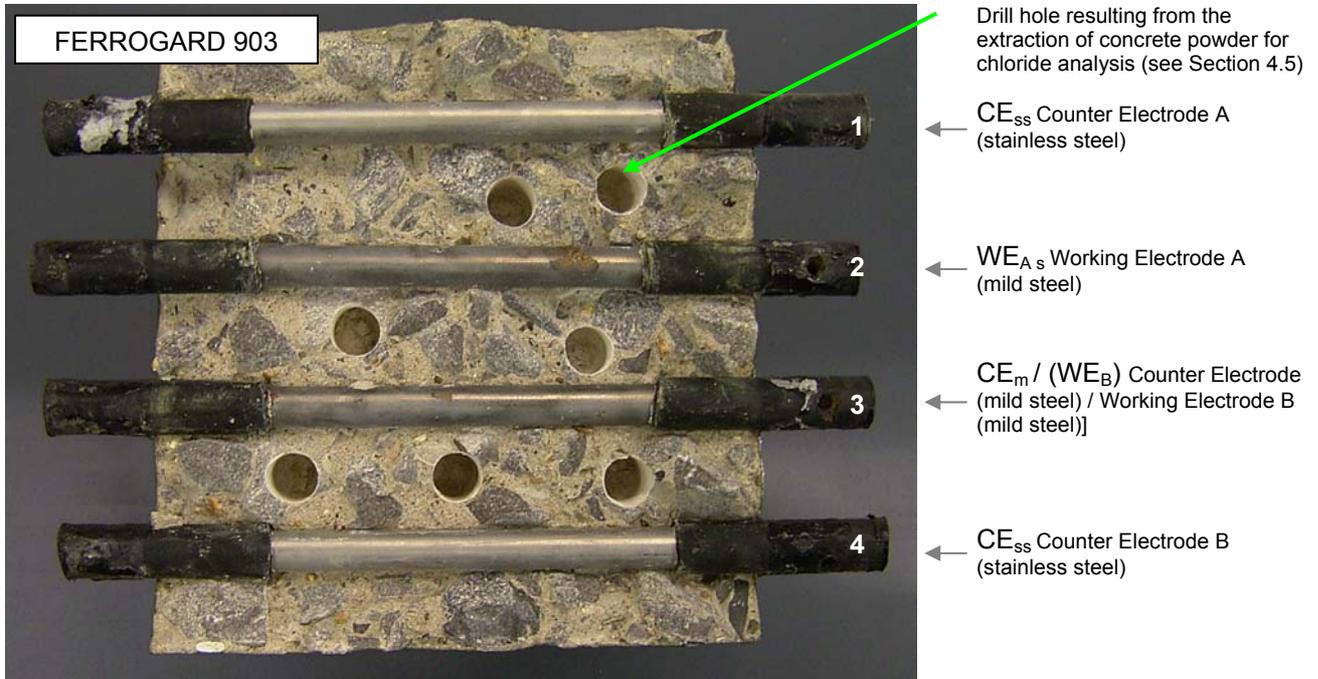
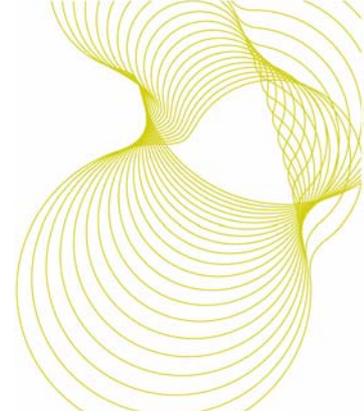
Breakout and visual examination of the steel bars revealed the cumulative degree of chloride induced corrosion to the mild steel reinforcement over the duration of the accelerated chloride corrosion testing programme. All mild steel reinforcement bars were initially polished to a bright surface finish and degreased prior to casting. This included the removal of any mill scale from the surface of the bars with silicon carbide paper.



**Figure 7** Breakout and visual inspection of the reinforcement bars from control specimen after completion of the accelerated corrosion testing regime (137 ponding cycles with 1% chloride solution).

##### Control Specimen

Electrode Number	Label	Visual Inspection after 137 chloride ponding cycles
1	CE <sub>ss</sub>	n/a (Stainless steel counter electrode).
2	WE <sub>A</sub>	Heavily corroded bar - some indication of deep pitting and significant loss of cross sectional area in localised regions.
3	CE <sub>m</sub> (WE <sub>B</sub> )	Heavily corroded bar - some indication of deep pitting and significant loss of cross sectional area in localised regions.
4	CE <sub>ss</sub>	n/a (Stainless steel counter electrode).

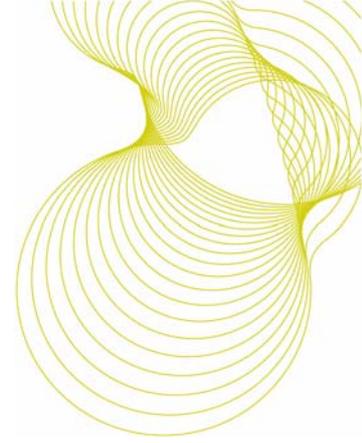


**Figure 8** Breakout and visual inspection of the reinforcement bars from FerroGard 903 specimen after completion of the accelerated corrosion testing regime (137 ponding cycles with 1% chloride solution).

**FerroGard 903 Test Specimen**

Electrode Number	Label	Visual Inspection after 137 chloride ponding cycles
1	CE <sub>ss</sub>	n/a (Stainless steel counter electrode).
2	WE <sub>A</sub>	Some areas of localised corrosion observed - little evidence of heavy/deep pitting corrosion. Majority of the bar surface area appeared to be free from chloride pitting corrosion.
3	CE <sub>m</sub> (WE <sub>B</sub> )	Some areas of localised corrosion observed - little evidence of heavy/deep pitting corrosion. Majority of the bar surface area appeared to be free from chloride pitting corrosion.
4	CE <sub>ss</sub>	n/a (Stainless steel counter electrode).

The mild steel reinforcement bars removed from the specimens treated with the FerroGard 903 corrosion inhibitor showed little evidence of deep pitting corrosion compared to the untreated control specimens which were observed to be heavily corroded after the completion of the accelerated corrosion testing regime. The visual corrosion condition of the bars supports the data obtained from the electrochemical corrosion monitoring and suggests that the application of the inhibitor increased the time to corrosion initiation of embedded mild steel bars subjected to the ingress of chloride ions.

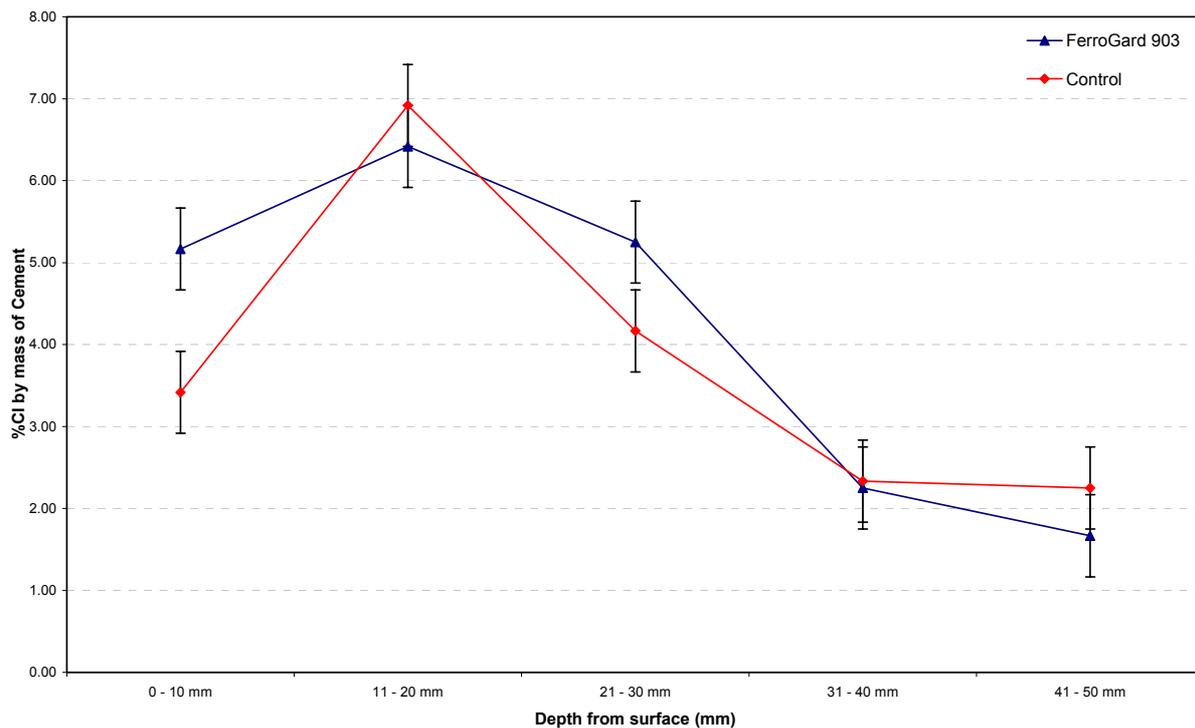


#### 4.5 Chloride Depth Profile

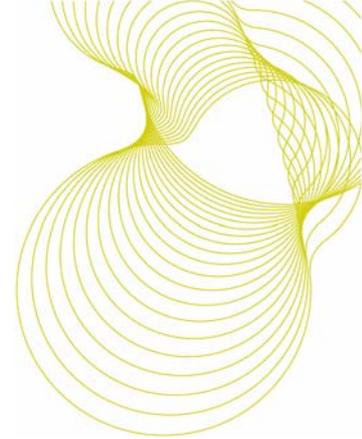
In order to determine the chloride content of the concrete at the depth of the steel reinforcement as a result of the ingress of chloride ions from the accelerated corrosion testing regime, samples of concrete adjacent to the mild steel bars were extracted by drilling (See Figures 7 & 8).

The analysis of the chloride content of concrete powder removed by drilling was determined by acid extraction and wet chemical methods in accordance with British standard BS EN 196-21:1992 (Methods of Testing Cement - Part 21 : Determination of the Chloride, Carbon Dioxide and Alkali Content of Cement).

The measured chloride profiles indicated that the concentration of chloride ions (by %wt of cement) at the depth of the reinforcement for both the control and the FerroGard 903 treated specimens was in excess of 4% (by mass of cement). At this chloride ion concentration corrosion of the reinforcement would normally be expected provided there were sufficient concentrations of moisture and oxygen to nucleate and sustain pit growth.



**Figure 9** Analysis of the chloride content of concrete powder (expressed as %Cl by mass of cement) removed from inhibitor treated and control concrete specimens (Assumed cement content 12% by mass).



## 5 Conclusions

The objective of the laboratory testing was to investigate the effectiveness of the FerroGard 903 corrosion inhibitor to delay and/or suppress the onset of chloride induced reinforcement corrosion when the inhibitor product was applied directly to the surface of hardened reinforced concrete. In terms of this report the effectiveness of the inhibitor was assessed comparatively between specimens treated with the inhibitor and untreated control specimens subjected to the same accelerated corrosion regime.

Based upon the results obtained during the 2.5 year test programme it is possible to conclude that:

- 1) Electrochemical measurement of corrosion potential and corrosion rate using liner polarisation resistance indicated that application of the FerroGard 903 to the surface of hardened concrete delayed/reduced the onset of chloride induced corrosion of mild steel reinforcement in the laboratory tests conducted compared with untreated control specimens.

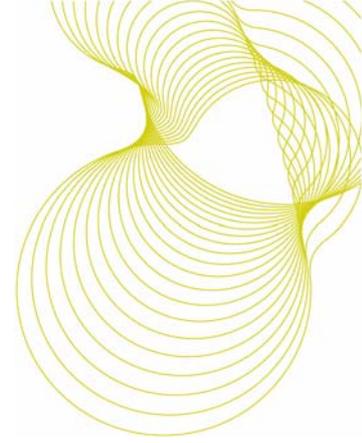
Specimens treated with FerroGard 903 corrosion inhibitor, exhibited little variation in the measured corrosion current over the duration of the accelerated testing period (137 cycles ~ 32 months). The majority of the current readings were below  $0.1 \mu\text{A cm}^{-2}$  (corrosion rate  $\sim 1 \mu\text{m yr}^{-1}$ ) which is generally considered to be indicative of a low rate of corrosion of the mild steel reinforcement.

Conversely, after 36 cycles (8 months) of the accelerated corrosion testing the untreated control specimens exhibited a significant but fluctuating increase in measured corrosion current to values in excess of  $0.5 \mu\text{A cm}^{-2}$  (corrosion rate  $\sim 6 \mu\text{m yr}^{-1}$ ), a degree that is generally considered to be indicative of a moderate to high rate of corrosion of the mild steel reinforcement.

- 2) Breakout and visual examination of the steel bars from the concrete specimens revealed the cumulative degree of chloride induced corrosion to the mild steel reinforcement over the duration of the accelerated chloride corrosion testing programme (137 cycles ~ 32 months).

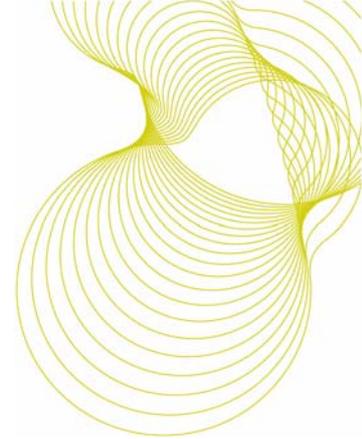
The mild steel reinforcement bars removed from the concrete specimens treated with FerroGard 903 corrosion inhibitor showed little evidence of chloride pitting corrosion compared to the untreated control specimens which were observed to be heavily corroded after the completion of the accelerated corrosion testing regime.

- 3) Upon completion of the accelerated corrosion testing the measured concentration of chloride ions at the depth of the reinforcement bars for both the control specimens and the FerroGard 903 treated specimens was in excess of 4% (by mass of cement). At this chloride ion concentration corrosion of the reinforcement would normally be expected to occur provided there were sufficient concentrations of moisture and oxygen to nucleate and sustain pit growth.
- 4) Based upon the comparative experimental results obtained, the 'proactive' use FerroGard 903 was assessed as effective at delaying the onset of chloride induced reinforcement corrosion when applied directly to the surface of hardened mild steel reinforced concrete.



## References

1. BRE DIGEST 434, "*Corrosion of Reinforcement in Concrete: Electrochemical Monitoring*",(1998).
2. QUILLIN, K., "*Modelling degradation processes affected concrete*", BR434, (2001).
3. DD ENV 1504-9:1997 - "*General principles for the use of products and systems*"
4. STERN, M. & GEARY, A.L., "*Electrochemical Polarization I. A Theoretical Analysis of the Shape of Polarization Curves*", J. Electrochem. Soc., Vol. 104, pp 56-63, 1957.
5. GODDIN, J.R.J., *Development of a Multi-functional Electrochemical Monitoring Probe for the Prediction of Steel Reinforcement Corrosion*, PhD Thesis, BRE, (2005).
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## Appendix I Experimental Details

### Laboratory Concrete Mix Details

#### Concrete Mix Design

Mix design based upon a nominal 40 MPa concrete (target free water/cement ration 0.65\*).

Material	Kg/m <sup>3</sup>
Ordinary Portland Cement	285.0
20 - 10 mm Cheddar Limestone Aggregate	855.3
10 - 5 mm Cheddar Limestone Aggregate	426.0
5 - 0 mm Cheddar Limestone Aggregate	656.3
Water	197.4

\*Free w/c ratio 0.65 (Total w/c ratio = 0.693)

#### Mixing of Concrete

All concrete was mixed under laboratory conditions in compliance with the British Standard, BS 1881-125 : 1986 (Testing Concrete - Part 125: Methods for Mixing and Sampling Fresh Concrete in the Laboratory).

#### Moulds Used (Standard 150 x 150 x 150 mm)

All steel moulds used for casting concrete specimens were calibrated and in compliance with the British Standard, BS EN 12390-1 : 2000 (Testing Hardened Concrete - Part 1 : Shape, Dimensions and Other Requirements for Specimens and Moulds).

#### Curing of Concrete Specimens

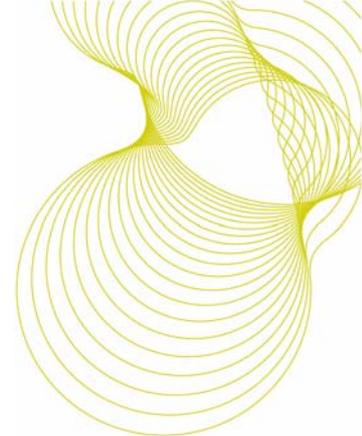
All concrete specimens were “normally cured” in accordance with British Standard BS 1881-111 : 1983 (Testing Concrete - Part 111 : Method of Normal Curing of Test Specimens 20°C Method).

All concrete specimens were cured under damp sacking and polythene at approximately 20°C and 65% relative humidity for 72 hours after being cast and were de-moulded at 24 hours. The samples were then allowed to cure for a further 25 days under the same laboratory conditions but without the damp sacking and polythene.

#### Concrete Workability

Concrete mix tested for slump type and value in accordance with British standard BS 1881-102 : 1983 (Testing Concrete - Part 102 : Method for Determination of Slump).

Measured True Slump = 85 mm



### **Concrete Density**

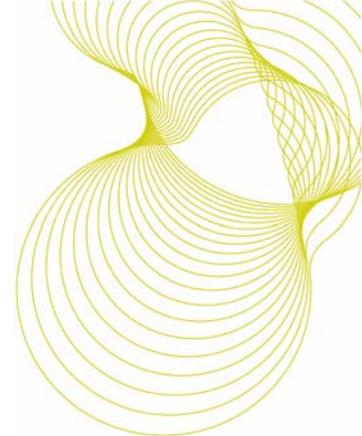
The wet density was measured in accordance with British Standard BS 1881-107 : 1983 (Testing Concrete - Part 107 : Method for Determination of Density of Compacted Fresh Concrete).

Wet Density = 2420 kg m<sup>-3</sup>

### **Concrete Compressive Strength**

The development of compressive strength during the 28-day curing cycle was determined in accordance with British Standard BS 1881-116 : 1983 (Testing Concrete - Part 116 : Method for Determination of Compressive Strength of Concrete Cubes).

Age at test (days)	Compressive Strength (MPa)		
	Sample A	Sample B	Sample C
1	14.0	12.5	13.5
3	23.0	23.5	24.5
14	36.0	36.0	35.0
28	41.0	40.5	41.0



## Electrochemical Specimen Design

The concrete test specimens were prepared from standard 150 x 150 x 150 mm cube moulds (Details of the concrete mix design and curing regime is provided in Appendix I of this report).

Each test cube was prepared with a combination of 2 mild steel and 2 stainless steel reinforcement bars (as shown schematically in Figure 2). This arrangement was chosen to allow various combinations of electrochemical measurements to be taken in order to determine the corrosion rate of the mild steel reinforcement during the test programme (See section on Electrochemical Corrosion Monitoring for further details).

**Table A1** Test specimens for test programme

Delaying the Onset of Corrosion	Specimen Identification		
Control Specimens	Control D1	Control D2	Control D3
FerroGard 903 Treated Specimens	F903D1	FG903D2	FG903D3

### ***Preparation of Concrete Specimens for Accelerated Corrosion Testing.***

In order to simulate the specimens being a part of a larger concrete element, the 'non-test faces' of each cube (i.e. the sides and bottom face) were coated with a polymeric coating to minimise the transmission of gases and liquids through these surfaces. Care was taken to avoid any contamination the top 'test face' of each specimen which was to be left exposed for the application of inhibitor material and/or chloride solution.

### ***Preparation of Bund.***

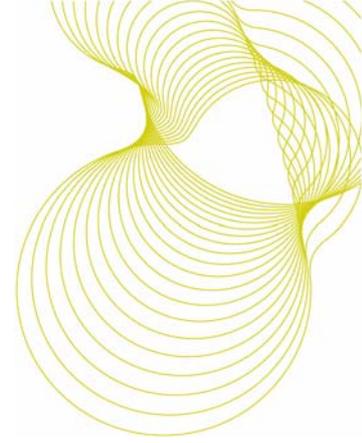
A Perspex barrier was sealed to the sides of each concrete specimen with a neutral-cure silicone sealant. This barrier (or bund) extended sufficiently above the top 'test face' of the concrete specimen to contain the 250 cm<sup>3</sup> volume of chloride solution required for each ponding cycle.

### ***Protection of Reinforcing Bar Protruding from Specimens.***

It was necessary to provide a means of avoiding/minimising the corrosion of the reinforcement steel protruding from the sides of the concrete which could otherwise have lead to misleading corrosion results. Every steel bar that was cast in this manner was therefore masked beforehand using a 0.5mm thick coating of epoxy adhesive followed 24 hours later by a 1mm thick adhesive-lined shrink-wrap.

### ***Application of Inhibitor Materials (Delaying the onset of corrosion)***

The FerroGard 903 corrosion inhibitor was applied topically to the hardened concrete test specimens in three stages over a 12 hour period, ensuring that the product had been absorbed into the concrete before proceeding with each stage of the application. To reflect the aggressiveness of the accelerated chloride conditioning regime the manufacturers stated dosage level was exceeded in the laboratory testing programme and an inhibitor dosage of 1.0 kg m<sup>-2</sup> was applied to each test specimen (manufacturer's minimum inhibitor dosage of 0.5.kg m<sup>-2</sup>).



### **Chloride Ponding Solutions**

The 1% chloride ponding solution was prepared from AR grade sodium chloride (NaCl) and deionised water. Note: the 1% chloride solution was prepared by mass of chloride ions in solution and not by mass of dissolved NaCl in solution as follows:

$$\text{Mass of NaCl Required (g)} = \left( \frac{A_{\text{NaCl}_{(s)}}}{A_{\text{Cl}^{-}_{(\text{aq})}}} \right) \times \left( \frac{V_{\text{H}_2\text{O}}}{100} \right) \times \% \text{Solution}_{\text{Cl}} \quad (\text{Equation 1})$$

Where:

(Atomic mass of sodium = 23.0 amu, Atomic mass of chloride = 35.5 amu)

$A_{\text{NaCl}} = 58.5$  amu,  $A_{\text{Cl}^{-}} = 35.5$  amu

$V$  = Volume of deionised water used for solution (ml)

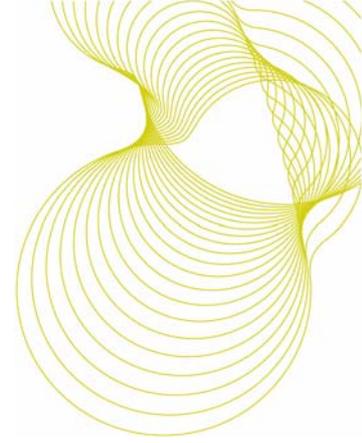
$\% \text{Solution}_{\text{Cl}}$  = Desired concentration of chloride solution (e.g. 1.0%).

### **Laboratory Conditions.**

Throughout the ponding and monitoring of the concrete specimens, the samples were stored in a laboratory with a mean temperature of  $20 \text{ }^{\circ}\text{C} \pm 5^{\circ}\text{C}$ .

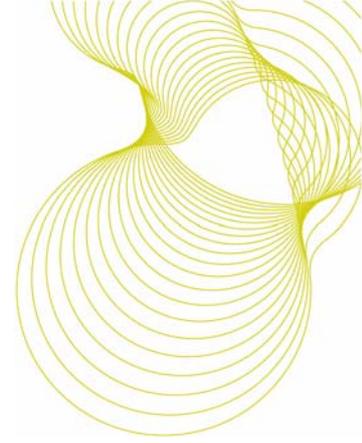
### **Determination of the Chloride Content of Concrete Specimens.**

The analysis for chloride content of concrete powder obtained from drillings of concrete specimens was conducted in accordance with British standard BS EN 196-21:1992 (Methods of Testing Cement – Part 21: Determination of the Chloride, Carbon Dioxide and Alkali Content of Cement).



### **Cube Specimens**





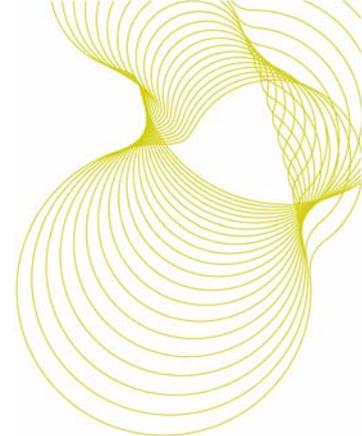
## Electrochemical Corrosion Monitoring

### Reference Electrodes

Electrode type	Electrode reaction	Potential at 25°C (V)		Electrode name
		vs.NHE	vs.SCE	
Hydrogen	(Pt)/H <sub>2</sub> , H <sup>+</sup> (a=1)	0	-0.2412	Normal Hydrogen Electrode (NHE)
Silver / silver chloride	Ag/AgCl, KCl (0.1 M)	0.2881	0.0470	
	Ag/AgCl, KCl (3.5 M)	0.2050	-0.0360	
	Ag/AgCl, KCl (saturated)	0.1970	-0.0450	
		0.1988	-0.0420	
Ag/AgCl, NaCl (saturated)	0.1940	-0.0470		
Calomel	Hg/Hg <sub>2</sub> Cl <sub>2</sub> , KCl (0.1M)	0.3337	0.0925	Normal Calomel Electrode (NCE)
		0.3360	0.0950	
	Hg/Hg <sub>2</sub> Cl <sub>2</sub> , KCl (1 M)	0.2801	0.0389	
		0.2830	0.0420	
	Hg/Hg <sub>2</sub> Cl <sub>2</sub> , KCl (3.5M)	0.2500	0.0090	
	Hg/Hg <sub>2</sub> Cl <sub>2</sub> , KCl (saturated)	0.2412	0	Saturated Calomel Electrode (SCE)
0.2440				
Hg/Hg <sub>2</sub> Cl <sub>2</sub> , NaCl (saturated)	0.2360	-0.0052	Sodium Saturated Calomel Electrode (SSCE)	

### Half-Cell Potential Measurements

All half-cell potential measurements were taken using a high input impedance (100MΩ) digital voltmeter with a resolution of 0.1 mV. Measurements were taken immediately after the deponding of each concrete specimen (i.e. after removal of the chloride solution) and prior to the use of any other electrochemical monitoring techniques that may otherwise have disturbed the potential of the mild steel electrodes. For each half-cell potential measurement, a saturated silver/silver chloride (Ag/AgCl) reference half-cell, with a typical rest potential of 194 mV ± 10 mV vs. a standard hydrogen electrode, was used as the reference half-cell. All half-cell measurements were scaled against the saturated calomel electrode (SCE) rest potential (see appendix I for details).



### **Linear Polarisation Resistance Measurements**

When a metal corrodes it does so with a steady state potential with respect to its environment. This potential is defined as the corrosion potential. This is measured against a reference electrode (half-cell). By using an externally applied force, for example current or voltage, it is possible to polarise the steel (i.e. change the corrosion potential with respect to the environment). In the region close to the rest (or equilibrium) corrosion potential ( $E_{\text{Corr}}$ ) and corrosion current ( $I_{\text{Corr}}$ ), it is assumed that the relationship between small changes in the overpotential and changes in the corrosion current is almost linear and therefore approximates Ohms law.

The slope of the current/potential response then equates to the resistance of the concrete between the measuring electrodes, which is generally found to be inversely proportional to the rate of reinforcement corrosion.

A potential shift,  $\Delta E$ , may be applied as a single step or as a potential ramp (i.e. the potential changed at a constant rate until a target shift is achieved). This is described as potentiostatic LPR. Conversely in galvanostatic LPR a small current is applied and the potential shift is measured. The polarisation resistance is equal to the ratio of the potential shift to the current flow,  $\Delta I$ . A corrosion current,  $I_{\text{corr}}$ , can then be calculated using the Stern-Geary equation (Equation 2).

Linear polarisation resistance (LPR) measurements for mild-steel reinforcing bars in concrete were taken using a calibrated Solartron 1287 potentiostat controlled using CorrWare Version 2.80. The mild-steel bar was used as the working electrode with an adjacent 316 stainless-steel reinforcing bar being used as a counter electrode and a cast-in Ag/AgCl reference electrode.

Potentiodynamic LPR measurement of the corrosion current ( $I_{\text{corr}}$ ) was conducted using a 10mV perturbation in both directions away from the open circuit corrosion potential ( $E_{\text{corr}}$ ) at a potential sweep rate of  $10 \text{ mV min}^{-1}$  ( $0.1667 \text{ mV sec}^{-1}$ ), with data being acquired every  $0.1667 \text{ mV}$ .

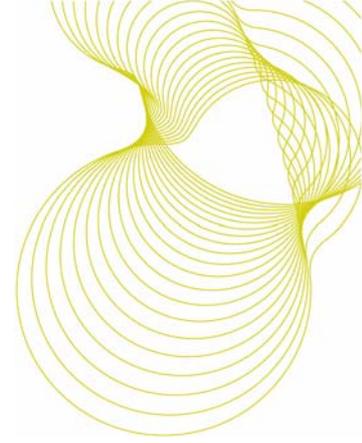
Performing the LPR measurement in this manner resulted in a total of 240 data points per LPR sweep, the first 120 data points representing the anodic behaviour of the reinforcing bar and the second 120 data points representing the cathodic behaviour of the reinforcing bars.

The polarisation resistance ( $R_p$ ) was calculated using the Stern-Geary relationship (Equation 2) and the equivalent metal loss calculated from Faraday's Law (Equation 3). The metal loss for each monitoring interval could then be calculated and the cumulative metal loss plotted to represent the degree of corrosion to the mild steel reinforcement.

LPR Measurement I    ELECTRODE No. 2 – Mild steel working electrode A ( $WE_A$ )  
                                   ELECTRODE No. 1 – Stainless steel counter electrode A ( $CE_{ss}$ )

LPR Measurement II    ELECTRODE No. 2 – Mild steel working electrode A ( $WE_A$ )  
                                   ELECTRODE No. 3 – Mild steel counter electrode A ( $CE_{ms}$ )

- Minimum of 4 hour between LPR measurement I and II.
- Record corrosion potential ( $E_{\text{corr}}$ ), corrosion current ( $I_{\text{corr}}$ ) and polarisation resistance ( $R_p$ ).
- Monitor all 6 cubes using LPR measurement I & II configuration.



### **Stern-Geary Relationship**

Through the measurement of induced changes in potential and current, the corrosion potential, concrete resistance ( $R_{pol}$ ) and corrosion current may be ascertained simultaneously by means of the Stern - Geary relationship [4]:

$$i_{Corr} = \frac{B\Delta I}{\Delta E} = 2.303 \frac{(\beta_a \cdot \beta_c)}{(\beta_a + \beta_c)} \cdot \frac{\Delta I}{\Delta E} = \frac{B}{R_p} \quad (\text{Equation 2})$$

Where:

$i_{Corr}$  = Corrosion Current., B = The Stern-Geary Coefficient.

$\Delta I$  = Change in Current.,  $\Delta E$  = Change in Potential.

$\beta_a$  = Anodic Tafel Coefficient.,  $\beta_c$  = Cathodic Tafel Coefficient.,  $R_p$  = Polarisation Resistance.

Values for the Stern-Geary coefficient for mild steel in concrete are generally assumed to be 26mV for actively corroding steel and 52mV for passive conditions, correlating to the Tafel slopes obtained for actively corroding and passive steel respectively. However, it must be noted that these values may not always be appropriate with there being an observed dependence upon the condition of the reinforcing steel.

### **Calculation of Corrosion Rates**

The term corrosion current density is often confused with corrosion rate. Corrosion rates in relation to reinforced concrete, by definition, are concerned with metal loss per unit time. This metal loss is normally quoted in terms of microns of metal lost per year (microns per year or grams per year), whereas, corrosion current density is simply the measured cell current per unit area i.e.  $\mu A \text{ cm}^{-2}$  or  $\text{mA m}^{-2}$ , measured at a specific instance. Faraday's law can be used to convert current density to corrosion rate and is illustrated below for iron, Fe being oxidised to ferrous ions,  $\text{Fe}^{2+}$ . The consumption rate, w, can be calculated according to the following equation:

$$w = \frac{(Mit)}{(z\rho F)} \quad (\text{Equation 3})$$

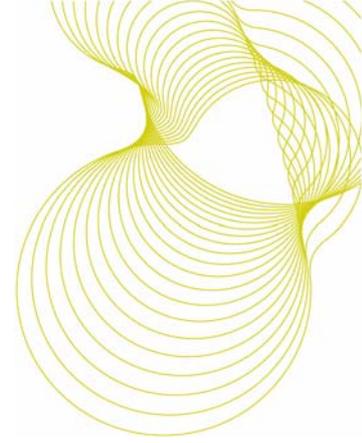
where:

w is the mass of steel consumed, M is the atomic weight of metal (in this case iron 56 amu)

I is the current in amperes (A), t is the time in seconds

Z is the number of electrons (2 when  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$ ),  $\rho$  is the density of iron ( $7860 \text{ Kg m}^{-3}$ )

F is the Faradays constant =  $96\,500 \text{ C mol}^{-1}$ .



### Potentiostatic and Galvanostatic LPR.

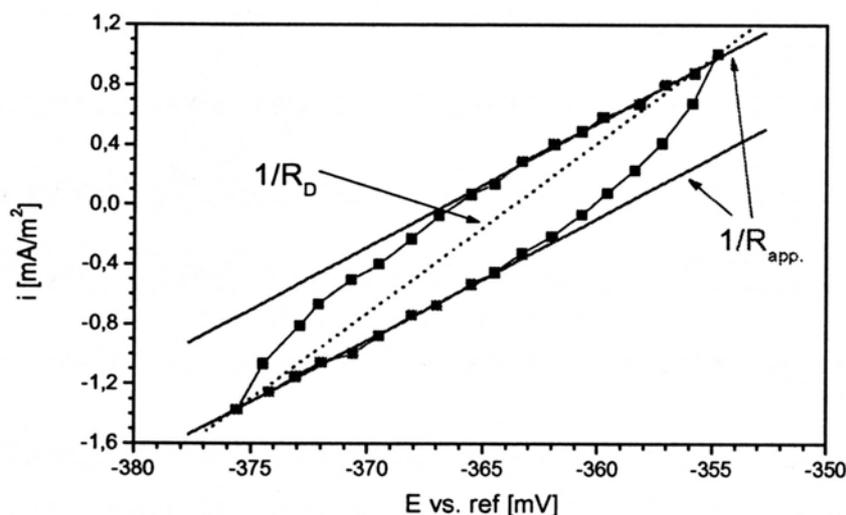
LPR measurements may be taken by applying a known shift in potential away from the equilibrium potential between the counter electrode and the working electrode and measuring the resulting current response, this is known as potentiostatic LPR. LPR measurements may also be taken by applying a known shift in current away from the equilibrium current between the counter electrode and the working electrode and measuring the resulting potential response, known as galvanostatic LPR.

Both potentiostatic and galvanostatic LPR techniques are in theory equally effective. However, as the corrosion current ( $i_{Corr}$ ) tends to be inversely proportional to the concrete resistance ( $R_P$ ), if galvanostatic LPR is used to measure a low corrosion current then considerable time may be required in order to achieve a steady potential response whereas, for potentiostatic measurements, the period required is generally much less<sup>1</sup>. It is for this reason that potentiostatic LPR is favoured in the majority of corrosion studies involving concrete reinforcement.

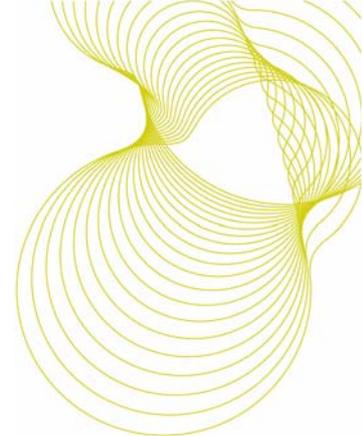
### LPR Hysteresis Loops.

Ideally, an LPR plot of current against time would result in a perfectly straight line. In practice when a polarisation curve is repeated between the values  $E_{Corr} + \Delta E$  and  $E_{Corr} - \Delta E$  it is generally observed that the arches belonging to the anodic and cathodic polarisations are not superimposed. Instead, the plot of polarisation vs. current can be seen to create a deformed parallelogram, or hysteresis loop, due to shifts in the equilibrium potential resulting from the applied potential perturbation.

The hysteresis loop can however be interpreted to provide a good approximation to the actual resistance of the concrete by the fitting of lines to the data gathered. The calculated apparent polarisation  $R_{app}$  – made by applying the potential in increments – tends to provide a more realistic resistance value than the so-called diagonal resistance  $R_D$  which is the gradient of the line joining the endpoints of the voltammogram (see Figure A1).



**Figure A1** LPR Voltammogram for Steel in Concrete Illustrating the Apparent Polarisation Resistance  $R_{app}$  and the Diagonal Polarisation Resistance  $R_D$ .



### ***Two and Three Electrode LPR Techniques.***

Both two electrode and three electrode LPR systems exist and are available commercially. However, the three-electrode system tends to be favoured for concrete corrosion studies as the inclusion of a reference electrode allows for the change in current ( $\Delta I$ ) and the change in potential ( $\Delta E$ ) to be measured through separate circuits. The circuit used for measuring  $\Delta E$  can then have a high input impedance reducing the risk of the concrete resistance effecting the value of the applied potential shift.

### ***Influence of Potential Perturbation Magnitude on LPR Results.***

If the perturbation to the system being monitored is excessive the corroding system may be changed irreversibly<sup>i</sup>. It is therefore important to set an appropriate limit to the disruption this perturbation may cause whilst maintaining a sufficient signal for the LPR measurement and analysis.

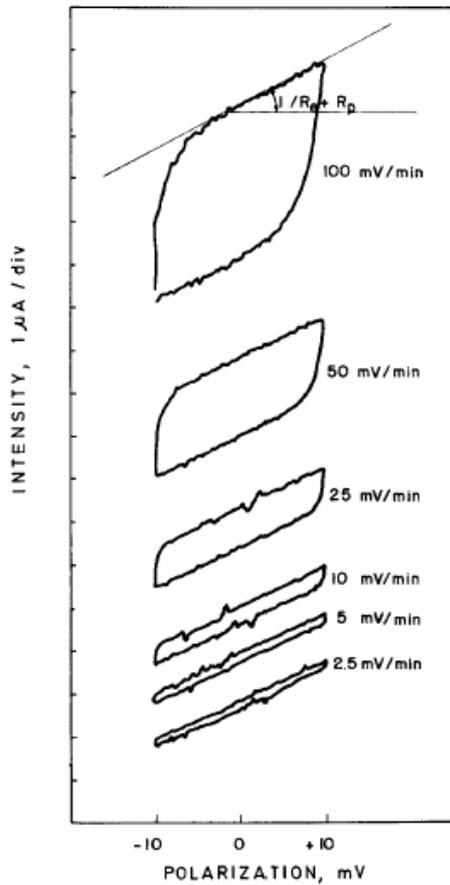
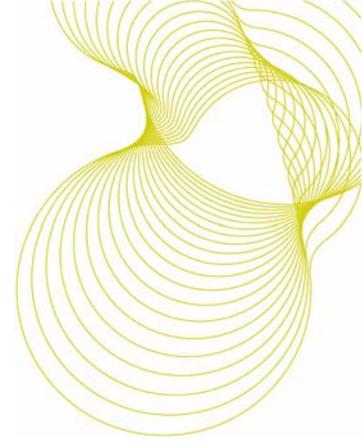
In practise, an applied potential shift of between 10 and 30 mV from the corrosion potential  $E_{\text{Corr}}$  has been recommended as an appropriate range for measuring reinforcing steel in concrete.

### ***Influence of Sweep Rate on LPR Results.***

As mentioned previously, the area of an LPR hysteresis loop may be reduced by lowering the rate at which the potential is applied to the system, resulting in a closer approximation to the ideal linear result<sup>ii</sup>, A2. One problem with using such slow potential sweep rates is that the electrochemical system may be changing during the span of the measurement. Also, as the monitoring and assessment of concrete structures requires many measurements to be taken, the time required to perform a complete assessment is greatly increased. The increase in required monitoring time for slow potential sweep rates will also lead to an increase in cost for systems in which a skilled operator is required to be present throughout each measurement.

In practise, an ideal potential sweep rate exists at which the measurement time is kept to a minimum and the polarisation resistance measured approximates the actual resistance of the concrete<sup>i</sup>.

For measurements in concrete a potential sweep rate of 5-10 mV min<sup>-1</sup> has been suggested as an appropriate LPR parameter for concrete approaching saturation. It is also suggested that a slower potential sweep rate might be required for very dry concrete due to the larger electrochemical relaxation times resulting from the reduced volume of concrete pore water<sup>i</sup>.



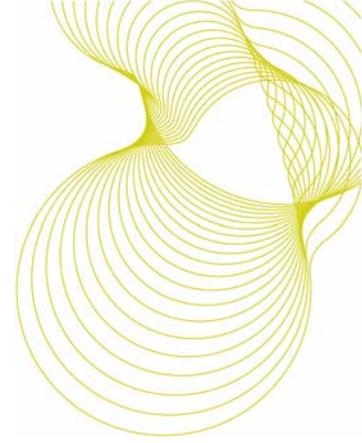
**Figure A2** The response of an electrical circuit to a triangular wave of potential applied at different sweep rates<sup>i</sup>.

**Interpretation of LPR Results.**

LPR readings obtained for reinforcing steel in concrete may be interpreted directly according to general guidelines that have been established empirically, Table A2 and Table A3.

Corrosion "Rate"* ( $\mu\text{A cm}^{-2}$ ) (*current density)	Corrosion Level
< 0.1	Negligible.
0.1 – 0.5	Low.
0.5 – 1.0	Moderate.
> 1.0	High.

**Table A2** Guidelines for the interpretation of concrete corrosion current measurements obtained from LPR readings<sup>iii</sup>.



Resistivity ( $k\Omega\text{-cm}$ )	Classification of Corrosion
>100 – 200	Corrosion Rate very low even if carbonated to steel or high amounts of chloride.
50 – 100	Low corrosion rate where steel is active.
10 – 50	Moderate to high corrosion where steel is active.
<10	Resistivity is not the parameter controlling the corrosion rate.

**TableA3** Guidelines for concrete resistivity measurements with respect to predicted corrosion levels<sup>iv</sup>.

However, a direct interpretation of LPR results using the guidelines from Table A2 & A3 yields little information about the expected time to failure of the concrete component. LPR measurements are typically converted into an equivalent metal loss for the steel being measured prior to interpretation by means of the equation<sup>iii</sup>:

$$P_x = 0.0115 * I_{Corr} * t_p \quad \text{(Equation 4)}$$

Where:

$P_x$  = The corrosion penetration depth – or cross-sectional loss from reinforcing bar (mm).

0.0115 = A conversion factor from  $\mu\text{A cm}^{-2}$  to  $\text{mm year}^{-1}$ .

$t_p$  = The time since corrosion was initiated (years).

And it is assumed that, for the period of each measurement, the corrosion current  $I_{Corr}$  does not change.

The time required before cracking of the cover concrete can be expected as a direct result of the calculated loss of reinforcement cross-section will, of course, depend upon the strength of the concrete and the force generated by the expansion of the corrosion products.

One possible method to estimate of the time to concrete cracking is based upon the empirical assumption that  $100\mu\text{m}$  of metal loss will be sufficient to result in concrete cracks of 0.1 – 0.2 mm across<sup>Error! Bookmark not defined.</sup><sup>v</sup>. This results in the equation:

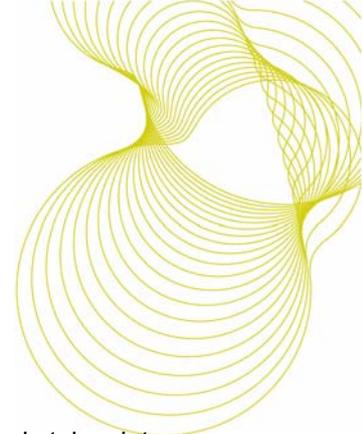
$$T_P = \frac{100}{C_r} \quad \text{(Equation 5)}$$

Where:

$T_P$  = The duration of the propagation stage, or time since corrosion initiation.

$C_r$  = The corrosion rate in  $\text{mm year}^{-1}$ .

The limitation of this analysis is that takes no account of the concrete cover depth or the bar diameter or geometry.



Another perhaps more reliable, but still empirical, method has been developed that not only takes into account bar size and geometry but also accounts for the fact that corrosion products may be more easily accommodated in a poor quality concrete<sup>vi</sup>:

$$X_c = 83.8 + \left( 7.4 * \frac{C}{\phi} \right) - (22.6 * f_{ST}) \quad \text{(Equation 6)}$$

Where:

$X_c$  = The loss of steel ( $\mu\text{m}$ ).

$C$  = The concrete cover depth (mm).

$\phi$  = The diameter of the reinforcing bar (mm).

$f_{ST}$  = The splitting tensile strength of the concrete (MPa).

## References

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- <sup>ii</sup> ANDRADE C. & ALONSO C., “Corrosion Rate Monitoring in the Laboratory and On-Site”, *Construction and Building Materials*, Vol. 10, No. 5, pp. 315 – 328.
- <sup>iii</sup> ANDRADE, C. & ALONSO, C., “On-site Measurements of Corrosion Rate of Reinforcements”, *Construction and Building Materials*, 15, 2001, 141-145.
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- <sup>v</sup> PARROTT, L., “Carbonation and Corrosion”, Presented at SCI Meeting: “Preventing Chloride and Carbonation Induced Corrosion of Reinforced Concrete”, 1998.
- <sup>vi</sup> EDVARSEN, C. & MOHR, L., “Duracrete – A Guideline for Durability-based Design of Concrete Structures”, *Procs. FIB Symposium “Structural Concrete – The Bridge Between People”*, Prague, Oct. 1999.