Journal Article on Concrete Rebar Inhibitor

To Ascertain the Effectiveness, Dosage And Characterisation of Vappro (CRI) Concrete Rebar Corrosion Inhibitor in Wet and Dry Environments

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Abstract

The analysis of how Vappro CRI (Concrete Rebar Inhibitor) in short CI protects steel rebar under different environments and the critical concentration for it to perform under harsh environments is important. In order for corrosion to occur, it requires water and oxygen. Other factors such as harsh environment (3.5% sodium chloride) will accelerate the corrosion rate. In this experiment, different concentrations of Vappro concrete rebar corrosion inhibitor was used and added into the soil sample by two methods. The first method is by mixing the CI into the soil sample surrounding the porous film. The other method is direct mixing CI into the soil sample. The values of corrosion rate for the steel rebar under all environments will be determined by Electrochemical Impedance Spectroscopy (EIS). The environments include water, 3.5% sodium chloride, pH 4.0 buffer solution and dry condition as the control.

The objectives of this journal article are to find out the condition for CI to function, the estimated diffusion time required for CI to diffuse to the steel rebar and form a passive film and finally to determine the critical concentration of CI to perform under 3.5% sodium chloride environment.

One of the major experimental findings is that diffusion of CI does occur in all environments. However, it requires the presence of moisture to form a passive film around the steel rebar and protect it from further corrosion. Otherwise, the values of corrosion rate will still continue to increase, as seen in the steel rebar without any CI. Secondly, the estimated diffusion time for CI to diffuse to the steel rebar and form a passive film is approximately a period of 3 months. Lastly, it is assumed that the critical concentration of CI under harsh environments like 3.5% sodium chloride is 0.5% to be able to protect the steel rebar from severe corrosion.

Therefore, the importance for Vappro concrete rebar corrosion inhibitor to work under harsh environments like sodium chloride can be concluded to be an effective method to reduce corrosion rate of the steel rebar.

1. Introduction

1.1 Ions Present in Soil

Most of the underground pipelines in the developed world are used to transport water, natural gas, and also to contain electrical cables. Underground corrosion is of utmost importance where it results in significant pipeline failures and lead to the disruption of water supply or telecommunication service. Due to corrosion, these pipelines must be regularly inspected and maintained.

According to M. Ferreira and A.C Ponciano (2007), it is necessary to treat soil as a corrosive environment due to the massive corrosion of underground pipelines over the years. Soil can be defined as an electrolyte due to its corrosivity and ability to develop the phenomenon of corrosion. Robinson (1993) stated that soil corrosivity can be determined by physical and chemical characteristics such as the oxygen concentration, presence of sulphate and sulfide, the ions, resistivity, total acidity, redox potential and others.

To study the credibility cited above, M. Ferreira and A.C Ponciano (2007) carried out an experiment by collecting 16 soil samples from different areas near a duct in Brazil. The soil

samples were prepared as an aqueous solution by assuming that the dissolved substances are the factors of corrosion. Then, the soil samples undergo physic-chemical characterization to discover any metal ions and anions. The determination of anions and metal ions in the aqueous solution was performed using Liquid Ion Chromatography and Plasma Emission Spectrometry respectively.

The results of this discovery is that among the anions, nitrite (NO_2^-), bromide (Br^-) and phosphate (PO_4^{3-}) were present in small concentration that is lower than 0.05mg/L. Fluoride anions (F^-) was present in a slightly higher concentration of 0.18mg/L while the other ions consisting of chloride (Cl^-), nitrate (NO_3^-) and sulphate (SO_4^{2-}) were present in a greater concentration. Chloride, nitrate and sulphate ions are the main ions that affect the acidity of the soil by forming acids. On the other hand, the metals that can be found most abundantly in the soil samples are calcium (Ca), sodium (Na), potassium (K), iron (Fe) and strontium (Sr). Copper (Cu) and barium (Ba) were present in small concentration.

Most of the soil samples show an acidic pH ranging from 5 to 6. The amounts of anions were in small concentration hence making the soil moderately acidic. To sum up this study on corrosivity of the soil by chemical composition, the soil is a complex environment due to the availability of various ions. The analysis of this composition is important to develop a good design on minimizing the corrosion of underground pipes.

1.2. Background Information

According to Ho (2013), corrosion is the destruction or deterioration of a material due to reaction with its environment. The requirements for corrosion to occur include moisture, oxygen and the presence of elements such as hydrogen from the surroundings.

McCafferty (2010) wrote that corrosion potential, E_{corr}, is readily measured by determining the voltage difference between a metal immersed in a given environment and an appropriate reference electrode. According to the ASTM standard (C876), if the corrosion potential is -200mV or higher, there is a 90% probability that the rebar has not corroded. However, there might be corrosion if the potential range between -200mV and -350mV. If the corrosion potential is smaller than -350mV, it can be said that the rebar has underwent corrosion.

Iskandar (2012) mentioned that Microbiologically-Influenced Corrosion (MIC), which is also known as microbial or biological corrosion, is an electrochemical process. It is interpreted to show an increase in the corrosion activity or the deterioration of the rebar due to the presence of bacteria which feeds on nutrients and other elements found in water and soils with a pH ranging from 4-9 and temperature of 10-50˚C.

Corrosion can be classified by the forms in which it manifests itself. The basis for this classification is by visually observing the appearance of the corroded metal. In most cases, observing with a naked eye is sufficient but sometimes magnification is required. The eight forms of localized corrosion are unique but they are interrelated. According to Montana (2009), the eight forms are uniform or general attack, galvanic or two-metal corrosion, crevice corrosion, pitting, intergranular corrosion, selective leaching or parting, erosion corrosion and stress corrosion.

Corrosion leads to percentage section reduction meaning there is a change in the length and area of the specimen. It will be a hazard to people as structural failure of bridges, towers and buildings will cause injuries and even death. Furthermore, a corroded metal water pipe can

also be harmful to our lives. This is because the corroded metal may cause leakage of water; and more importantly the leaching of heavy metal substances such as lead and cadmium from the metal pipe. These heavy metals of lead or cadmium will produce a bitter and rusty taste to the water. If the water is consumed in the long run, it may give rise to health problems (National Physical Laboratory, UK).

Therefore, in order to ensure that the properties of metal rebar used in buildings, construction sites and concrete do not deteriorate erratically, CI must be used. In this experiment, soil was used instead as a representative of concrete and Vappro Concrete Rebar Corrosion Inhibitor will be added into the soil with different amounts. After which, the soil samples will be placed under four different environments namely dry, pH 4.0, 3.5% sodium chloride and water. Values of corrosion rate will then be determined using Electrochemical Impedance Spectroscopy (EIS) and results will be compared.

2. Objectives

The main objectives of the project are to find out the condition for CI to function, the estimated diffusion time required for CI to diffuse to the steel rebar to form a passive film in soil sample. In addition, to further prove that the CI used in this experiment requires a shorter time to diffuse from the admixture to steel rebar, as compared to the CI in concrete.

Furthermore, it is to determine the critical concentration of CI to perform under 3.5% sodium chloride environment. Another objective is to test the nature of CI, such as whether the alkalinity of the CI will affect pH values of the soil samples which will lead to an increase or decrease in corrosion rate of the steel rebar.

Besides that, some other general objectives are to determine which application method is the most effective for the CI to work in soil conditions and to perform characterisation of CI using FTIR.

3. Carbonation

According to Leuven (2000), carbonation occurs when there is presence of carbon dioxide in porous media like sand grains. There will be diffusion of carbon dioxide from the surroundings through the pores. After which, the diffused carbon dioxide will react with the moisture inside the sand and a humid environment is created inside the box.

Calcium carbonate is found in pebbles and sand. The mixture of cement that was added to the mixture of sand and pebbles will create an alkaline environment. The hydration product which is calcium hydroxide will also be found in cement. This calcium hydroxide will react with rock, which contains calcium carbonate, and carbon dioxide gas will be produced, as seen in equation 3 below.

$$Ca(OH)_2 + CaCO_3 \longrightarrow CO_2 + 2CaO + H_2O$$

$$CO_2 + H_2O \longrightarrow H_2CO_3 \text{ (Carbonic acid process is carbonation)}$$

Equation 1: Reaction between Alkaline and Carbonate, and the Formation of Carbonic Acid

Therefore, the presence of carbon dioxide in turn dissolves in the moisture from the surroundings and eventually, carbonation occurs. When this happens, there will be a build-up of corrosion products, causing surface cracks and stains on the surface of the soil and

within. The carbon dioxide produced also causes the pH to decrease and results in the layer of passive steel oxides breaking down. This leads to the widespread corrosion of the steel rebar and eventually bar corroded, spalling and exposed.

Carbonation is restricted to a thin surface layer, however as time goes by, carbon diffuses inward from the surface and the zone of carbonation extends gradually into the soil. Carbonation also results in lowering the pH values and lead to the production of free chloride ions.

4. Factors Affecting Corrosion

According to Philip (2009), atmospheric corrosion is a complicated electrochemical process taking place in corrosion cells which consists of rebar, surface electrolytes and the atmosphere. There are several factors that affect corrosion which are temperature, relative humidity, conductivity of electrolyte, chlorine content, dust, impurities in the air and the position of how the rebar was placed with the most significant factor being oxygen.

5. Characterisation Equipment

5.1 Electrochemical Impedance Spectroscopy (EIS)

According to William (1983), EIS is the measurement of impedance over a range of frequencies. It is an instrument that can be used to test the corrosion rate, electrochemical mechanism and reaction kinetics. During the measurement, small amplitude of current signal was used and applied to the part being tested.

By using an electrolyte solution, a voltage (electrical potential) is applied and the resulting impedance of a coating is then measured. NACE International (2000) also mentioned that impedance is defined as the ability of a circuit to resist the flow of alternating electrical current.

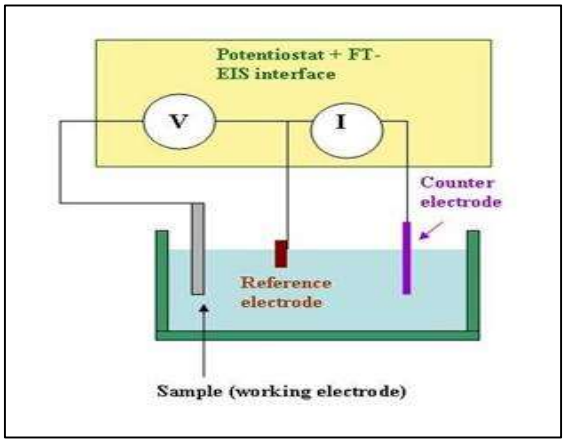
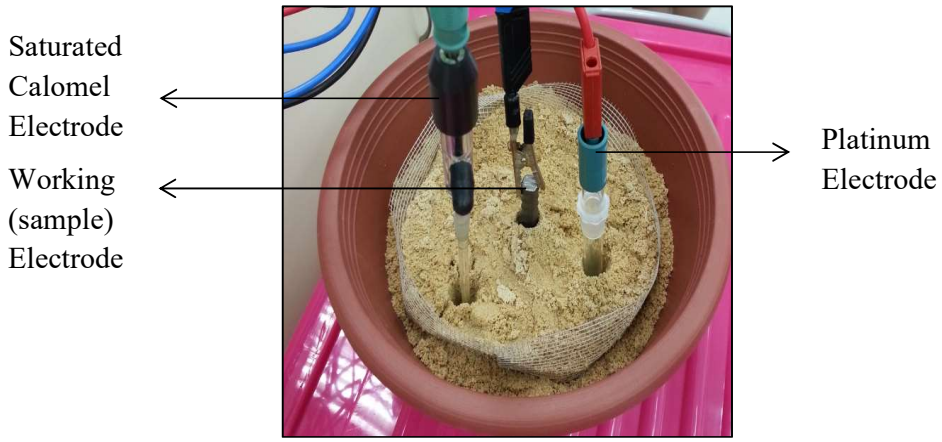


Diagram 1: Schematic Set-up of Overall EIS (Roy, 2007)

As seen from diagram 3 above and photograph 1 below, EIS uses three electrodes. They are reference (RE), working (WE) and counter electrodes (CE).



Photograph 1: EIS Set-up of Three Electrodes in Experiment

According to Bertolini (2005), perturbation is applied from the CE on the surface of the soil. The surface area of steel is assumed to be polarised when it lies beneath the CE. CE is used in the electrochemical cell by which electrical current is expected to flow. Hence, depending on how much the current is flowing, CE would need to be adjusted before starting the experiment. The CE will then be able to transport the current created by the circuit.

When operated in the potentiostatic mode, a potential is applied to the WE, with respect to the RE. For WE, it is the test sample that needs to be investigated. In the experiment, the test sample is the commercial steel rebar. It is important for the size of the test sample to stay constant during all experiments for easy calculation and data tabulation. Depending on whether the reaction on the electrode is reduction or oxidation, the WE can be referred to as either cathodic or anodic.

The main criterion for RE is that it must be stable and have a well-known electrode potential. Saturated Calomel Electrode is preferred because at standard conditions, the potential of SCE is +0.256V as compared to a standard hydrogen electrode (0.000V). The potential difference between the WE and the RE is actually being measured. Since RE has a fixed potential, the potential applied to the WE will be reproducible in every experiment. Also, the charge added or removed by the WE must be well balanced by the RE.

The equation for impedance is as follows:

$$Z = V_{ac} / I_{ac}$$

Where Z is impedance.

When a higher impedance value is obtained, this indicates a higher corrosion resistance of metals.

The advantages of EIS are as follows:

(1) EIS results have been found to correlate well to current test methods for corrosion resistance and it also generates quantitative results. This includes the rebar potential, polarization resistance and current density. The above information can determine whether the rebar is in the active or passive corrosion state.
(2) Non-destructive technique

(3) Useful on high resistance materials such as paints or coatings
(4) Fast analysis of results.

Robert Baboian (2005) mentioned that EIS has become a mature and important technique for electrochemical investigations to determine the corrosion rates of the steel rebar. It can detect whether the rebar is still able to withstand high load for a period of years by measuring the thickness loss of the commercial rebar. Robert Baboian (2005) also states that EIS measurement is a non-destructive method of evaluation for a wide range of materials including coatings, anodized films and CIs.

In this project, using EIS can help to monitor the corrosion rates of the steel rebar with different amounts of CI in different environments. From there, the results can be analyzed to see which environment will have a higher corrosion rate or the appropriate amount of CI to use in protecting the steel rebar. If the values (corrosion density of the rebar or corrosion rate of the rebar) obtained does not meet up to standards, certain actions will be taken to solve the problems.

5.2. X-Ray Fluorescence (XRF)

Amptek (2014) states that XRF is the emission of characteristic fluorescent x-rays from a material that has been excited by bombarding with high energy x-rays. According to XOS (2014), being an excellent quantitative and qualitative analytical tool, XRF is capable to analyze the elements of a material.

5.3. Fourier Transform Infrared Spectrometer (FTIR)

FTIR spectrometer uses infrared beam to pass through a sample. The sample will absorb some of the infrared radiation and the radiations that are not absorbed will be transmitted through and detected by a detector. The signal detected is then translated into a spectrum with the help of the computer. The resulting spectrum represents the molecular absorption and transmission, creating a unique molecular fingerprint which can be used for analysis. This can be seen in diagram 6 below.

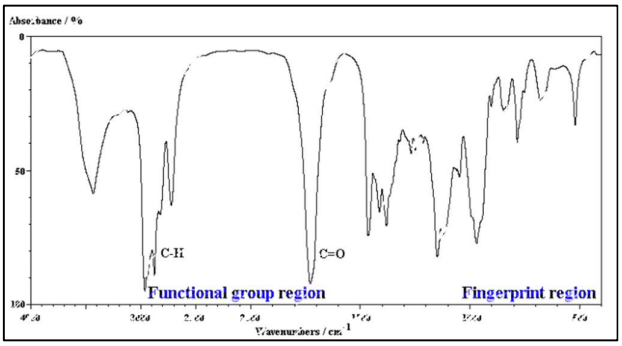


Diagram 2: Fingerprint Region of a Spectrum (Hynes, 2005)

As stated by Rees (2009), infrared radiation is used as a source for analysis in the instrument because a compound exhibits most of the characteristic properties in an infrared spectrum. For example, the peaks in the spectrum are corresponding to the vibrational frequency of functional groups present in the sample molecule. UC Davis (2005) mentioned that there are two important properties that a sample must acquire in order to be tested with infrared spectroscopy. Firstly, the stretching and bending vibrational frequencies of the

sample must correspond to the frequency of infrared radiation so that the sample is able to absorb the infrared radiation. Secondly, the sample must have dipole moment.

Photograph 2: FTIR

To carry this out, the CI powder will first be dissolved in water, and then a drop of the solution will be tested by using ATR, as seen in photograph 3 above. ATR (Attenuated Total Reflectance) is the most widely used FTIR sampling tool because it is convenient and simple to use. It measures the changes in total reflected infrared beam. ATR is used to study the interface of a solid or liquid sample.

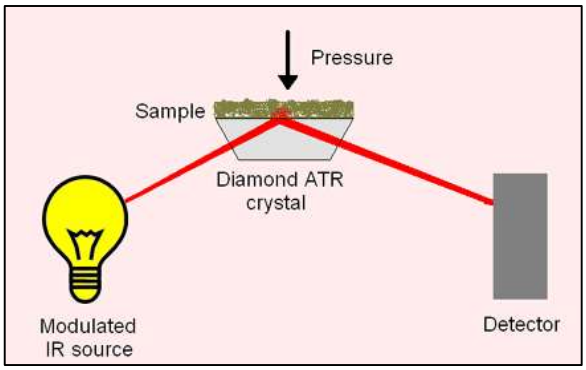


Diagram 3: ATR-FTIR Spectrometer

According to Piketech (2011), an ATR works with the infrared beam directed into a crystal of higher refractive index than air. The infrared beam reflects from the internal surface of the crystal and creates an evanescent wave which goes beyond the surface of the crystal. This evanescent wave protrudes only a few microns (0.5μ -5μ) into the sample. Perkin Elmer (2005) states that some of the energy of the evanescent wave is absorbed by the sample and the reflected radiation will be detected by the detector, as seen in diagram 7 above.

There must be good contact between the sample and the crystal surface. Besides that, the refractive index of the crystal must be significantly greater than the sample, or else internal reflectance will not occur. ATR enables analysis of solid and liquid samples. Unlike transmittance, it is not influenced by sample thickness.

In the project, ATR-FTIR is used to identify the characteristic peaks present in the CI. The unique peaks of the CI show the functional groups present in the CI.

6. Materials and Methods

This section describes the various testing methods, equipment and materials used.

6.1 Set-up of Samples in Different Environments

6.1.1 Materials & Equipment

- 16 Flower pots of equal diameter of 20mm each
- 240g cement
- 48kg Soil
- 1984g Pebbles
- 5g, 10g and 15g of Vappro Concrete Rebar Corrosion Inhibitor
- 16 Steel rebar
- 16 Porous films
- 4 Containers
- Tap water, pH 4.0 buffer solution and sodium chloride
- Analytical weighing balance

6.1.2 Procedure

1) For all samples without Cl, 2860g of soil, 15g of cement, and 124g of pebbles were weighed and mixed in a mixing plate and poured into a pot.

2) For samples with 0.167% Cl, same amount of soil, cement and pebbles were weighed and mixed. 500g of the mixture was scooped out to mix with 0.167% of Cl. The admixture was then arranged at the side of the pot with the help of a porous film. A steel rebar was then set in the middle of the pot.

3) Step 2 was repeated for samples with 0.333% and 0.5% Cl by replacing the 0.167% Cl used.

4) Each of the samples with 0%, 0.167%, 0.333% and 0.5% Cl were repeated 4 times to create 4 sets of different environments such as dry, tap water, 3.5% sodium chloride solution and pH 4 buffer solution.

5) The pots were then placed in the container with different environment as stated above. Each container contained samples with 0%, 0.167%, 0.333% and 0.5% Cl.

6) Various tests were conducted to determine the corrosion rate, diffusion time of Cl and presence of foreign elements.

Photograph 3: Porous Film Used

Photograph 4: Fine Soil Used

Photograph 5: Pebbles Used

Photograph 6: Packing of the Sample

Photograph 7: Samples with Different Concentration Admixture

6.2 Determination of Corrosion Rate of New Commercial Steel Rebar

6.2.1 Materials & Equipment

- Zahner Zennium Electrochemical Impedance Spectroscopy
- Zahner Zennium Programme
- Counter Electrode - platinum electrode
- Reference Electrode - calomel electrode
- Working Electrode - commercial steel rebar
- Commercial steel rebar
- Glass Ware Container
- Ultra-Pure Water
- Retort Stands

6.2.2 Procedure

1) The red, green/black and blue/black wires were connected to the respective electrodes and were placed in the glassware.

2) Red wire was connected to the platinum electrode, green and black wire was connected to the Reference Electrode (RE), the Working Electrode (WE) was connected to the blue and black wire.

3) About 200-250ml of ultra-pure water was poured into the glassware. The commercial rebar was then clamped to the working electrode and submerged into the electrolyte together with the other electrodes.

4) Then ThalesZ software was started on the computer.

5) Maximum and minimum current in 'I/E' were set to 2A and -2A respectively, and the edge potentials were set to 4V and -4V respectively.

6) Scan mode was set at 10mV/s for this set-up.

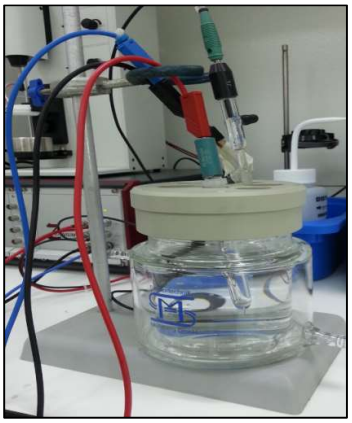
7) The setting for 'Potentiostat' in Current Potentiostat was chosen and 'OFF' button was pressed.

8) Three electrodes have been connected accurately by checking in 'Check cell connection'.

9) 'Calomel/sat.KCL' option was chosen when the 'Reference Electrode Potential' option popped up.

10) Once all settings have been configured, the test was started by clicking on 'Start Recording'.

11) After the test was completed, the graph was saved, printed and analysed.



Photograph 8: Set up for EIS

6.3 Determination of Corrosion Rate of Commercial Steel Rebar

6.3.1 Materials & Equipment

- Samples prepared in the pots
- Zahner Zennium Electrochemical Impedance Spectroscopy
- Zahner Zennium Programme
- Counter Electrode- A platinum electrode
- Reference Electrode- A calomel electrode
- Working Electrode- Commercial Steel Rebar

6.3.2 Procedure

1) Procedures under section 4.2.2 were carried out from steps 1 to 10 except for steps 3 and 6. Scan mode was set at 30mV/s for this set-up.

2) The three electrodes were immersed into the soil mixture (0% dry) with equal distance apart.

3) After the test was completed, the graph was saved, printed and analyzed.

4) Steps 1 to 3 were repeated with the remaining 15 samples.

Photograph 9: Set-up to Test Corrosion Rate of Commercial Rebar

6.4 Determination of Diffusion of Corrosion Inhibitor

6.4.1 Materials & Equipment

- 3 Equal size aluminium containers
- 5g, 10g and 15g of Concrete Rebar Corrosion Inhibitor
- 8580g of Soil
- 496g of Pebbles
- 60g of Cement
- Distilled water
- Analytical weighing balance
- Small plastic container
- Filter funnel
- Filter paper
- Retort stand
- Beakers
- Ruler
- Threads

6.4.2 Procedure

1) 2860g of soil, 124g of pebbles and 15g of cement were weighed and mixed in an aluminium tray.

2) 500g of the mixture was scooped out to mix with 0.167% of CI.

3) A porous film acting as a divider was placed 5cm away from 1 side of the aluminium tray. The admixture was placed in the 5cm wide space and soil mixture without CI was placed on the other side of the porous film.

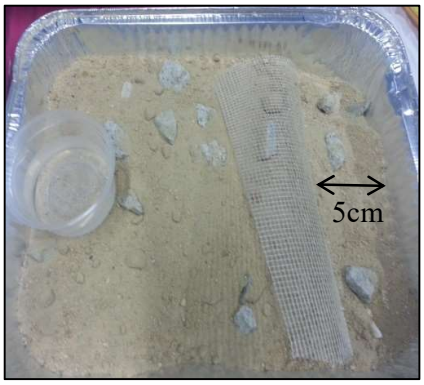
4). Threads were then placed at 5cm intervals from the porous film.

5) A small plastic container filled with water was placed at one end of the aluminium tray to facilitate the diffusion of CI as the environment is too dry.

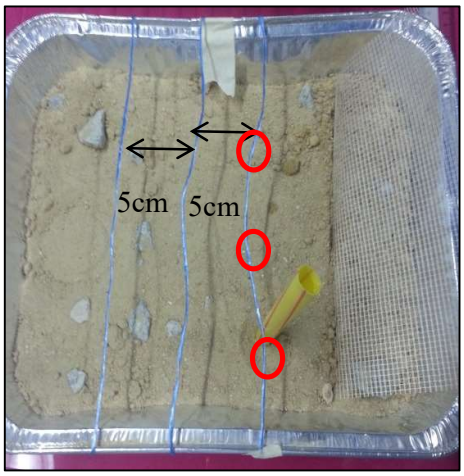
6) Steps 1 to 4 were repeated by replacing 0.167% CI with 0.333% and 0.5% CI.

7) A small amount of sample from each aluminium tray was taken by using a straw at the first 5cm from the porous film. The samples were randomly taken 3 times along the first thread.

8) The samples were soaked in distilled water for 30 minutes to allow certain molecules to dissolve in water. Then the samples were filtered and ready to be tested with FTIR. FTIR test was carried out to determine the presence of CI in the filtrate.



Photograph 10: Porous Film 5cm from one end and Water at the other end



Photograph 11: Thread Arranged at 5cm Intervals and Area Sample was taken

6.5 Determination of Peaks of Corrosion Inhibitor

6.5.1 Materials & Equipment

- Distilled water
- 5g Vappro corrosion inhibitor
- FTIR Equipment
- Dropper
- Kimwipes

6.5.2 Procedure

1) 0.167% of CI was added into 100ml of water and stirred. Stirring was to ensure a homogenised sample.

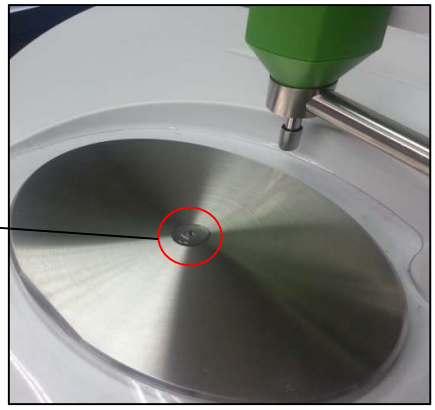
2) The wavenumbers for the start and end points were set as 4000cm^{-1} and 500cm^{-1} respectively. The number of scans was set as 16.

3) Kim wipe was used to clean the crystal region to prevent contamination. Background sample was collected by scanning the air.

4) A few drops of filtrate (enough to cover the surface of crystal region) were dripped onto the surface of the ATR crystal by using a dropper.

4) 'Scan' button was then clicked. However, no spectrum was collected first. 'Scan' button was clicked again to obtain the spectrum.

5) The spectrum obtained was printed and analysed.



Photograph 12: Surface of ATR Crystal must be Covered Completely by Sample

6.7 Determination of Elements Present in the Vappro Concrete Rebar Corrosion Inhibitor

6.7.1 Materials & Equipment

- X-Ray Fluorescence (XRF) Machine
- Vappro Concrete Rebar Corrosion Inhibitor
- 3525 Ultralene, 0.16 mil Thin Film for XRF
- Small Circular Containers

6.7.2 Procedure

1) XRF machine was calibrated analytically beforehand.

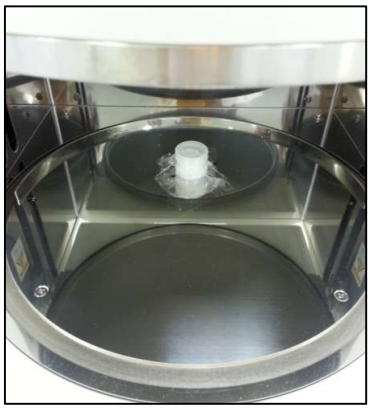
2) Vappro Rebar Corrosion Inhibitor was packed into a small container and covered tightly with a XRF thin film.

2) 'Open' button was pressed and the sample was placed in the chamber.

3) After 100 seconds of scanning the sample, graph was printed and result was analysed.

Photograph 13: XRF

Photograph 14: Sample Preparation for XRF



Photograph 15: Sample Placed in Chamber

6.8 Modification of Samples

An additional 50g of CI was added to the sample that contains 0.167% CI by direct mixing. The concentration of CI in soil sample becomes 1.83%. While an additional 40g of CI was added to the admixture for the sample that contains 0.333% CI, and this makes up to a concentration of 1.67% CI.

6.8.1 Materials & Equipment

- Analytical Weighing Balance
- Vappro Concrete Rebar Corrosion Inhibitor
- Samples with 0.167% and 0.333% of CI for all environments
- Spade

6.8.2 Procedure for 0.333% CI Sample

1) 40g of CI was weighed.

2) In sample with dry environment 0.333% CI, the admixture at the circumference of the porous film for was scooped out by using a spade.

3) 40g of CI was then added and mixed into the admixture scooped out.

4) The mixture was placed back into the pot surrounding the porous film.

5) The above steps were repeated for the remaining samples of 0.333% CI in all environments.

6.8.3 Procedure for 0.167% CI Sample

1) 50g of CI was weighed.

2) Steel rebar was removed. The CI was added slowly into the soil mixture which is within the circumference of the porous film and mixed homogeneously.

3) Steel rebar was placed back into the original position.

4) The above steps were repeated for the remaining samples of 0.167% CI in all environments.

Amount of CI/ Date	29 July mm/year	8 Aug mm/year	11 Sep mm/year	2 Oct mm/year
0g (0%)	$1.315x10^{-4}$	$7.176x10^{-4}$	$9.568x10^{-4}$	Error
5g (0.167%)	$2.3888x10^{-4}$	$7.176x10^{-4}$	$1.914x10^{-3}$	$2.153x10^{-3}$
10g (0.333%)	$1.196x10^{-3}$	$2.393x10^{-3}$	0.01435	2.39310^{-3}
15g (0.5%)	$2.393x10^{-5}$	$4.784x10^{-3}$	$9.568x10^{-3}$	0.01196

Photograph 16: Outer Region of Porous Film Modified for 0.333% Samples; Inner Region Modified for 0.167% CI Samples

7. Results and Calculations

In this section, the results obtained from the various tests were collated and tabulated.

7.1 Corrosion Rate of all Samples

Table 1: Results of EIS Corrosion Rate for pH 4.0 Environment from 29 July to 2 October

Amount of CI/ Date	18 July mm/year	8 Aug mm/year	11 Sep mm/year	7 Oct mm/year
0%	Error	$1.44×10^{-3}$	$7.18×10^{-5}$	$1.20×10^{-6}$
0.167%	$4.78×10^{-3}$	Error	$4.78×10^{-4}$	Error
0.333%	$7.18×10^{-3}$	Error	$2.15×10^{-3}$	$1.44×10^{-4}$
0.5%	$9.57×10^{-3}$	$9.57×10^{-3}$	$7.18×10^{-3}$	$1.67×10^{-4}$

Table 2: Results of EIS Corrosion Rate for Dry Environment from 18 July to 7 October

Amount of CI/ Date	22 July mm/year	8 Aug mm/year	11 Sep mm/year	7 Oct mm/year
0%	0.144	0.191	0.191	0.215
0.167%	0.167	0.239	0.478	0.478
0.333%	0.191	0.598	Error	0.431
0.5%	0.431	Error	1.67	1.20

Table 3: Results of EIS Corrosion Rate for Water Environment from 22 July to 7 October

Amount of Cl/Date	22 July mm/year	8 Aug mm/year	11 Sep mm/year	7 Oct mm/year
0%	1.91	Error	2.39	1.91
0.167%	2.39	5.98	6.69	4.31
0.333%	2.39	2.51	4.31	9.57
0.5%	Error	2.27	9.57	2.63

Table 4: Results of EIS Corrosion Rate for 3.5% Sodium Chloride Environment from 22 July to 7 October

Amount of Cl/Date	21 Oct mm/year	6 Nov mm/year	13 Nov mm/year
0%	Error	Error	Error
1.83%	0.02392	0.04784	0.03588
1.67%	1.914×10^{-3}	1.67410^{-3}	1.196×10^{-3}
0.5%	5.502×10^{-3}	4.784×10^{-3}	2.392×10^{-3}

Table 5: Results of EIS Corrosion Rate for pH 4.0 Environment from 21 October to 13 November

Amount of Cl/Date	21 Oct mm/year	6 Nov mm/year	13 Nov mm/year
0%	Error	2.15×10^{-4}	6.70×10^{-4}
1.83%	8.37×10^{-5}	1.20×10^{-4}	4.07×10^{-4}
1.67%	1.08×10^{-4}	1.22×10^{-4}	1.67×10^{-4}
0.5%	1.44×10^{-4}	1.67×10^{-4}	8.37×10^{-4}

Table 6: Results of EIS Corrosion Rate for Dry Environment from 21 October to 13 November

Amount of Cl/Date	21 Oct mm/year	6 Nov mm/year	13 Nov mm/year
0%	0.311	0.239	0.287
1.83%	Error	1.32	0.191
1.67%	0.191	0.108	0.0230
0.5%	1.03	0.909	0.669

Table 7: Results of EIS Corrosion Rate for Water Environment from 21 October to 13 November

Amount of Cl/Date	21 Oct mm/year	6 Nov mm/year	13 Nov mm/year
0%	Error	6.70	11.24
1.83%	7.66	9.09	6.46
1.67%	11.48	6.70	4.31
0.5%	2.39	2.39	5.26

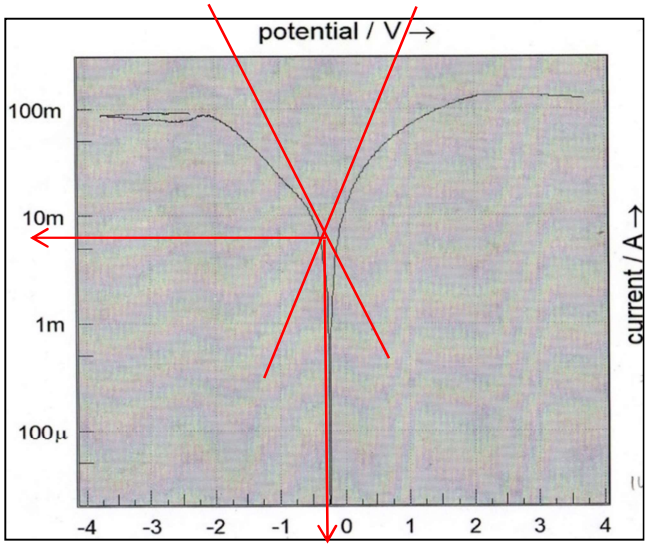
Table 8: Results of EIS Corrosion Rate for 3.5% Sodium Chloride Environment from 21 October to 13 November

7.2 pH Values of all Environments

Table 9: Results of pH value for all Environments.

Environment	Dry				Water				3.5% Sodium Chloride				pH4			
Sample	0%		0.5%		0%		0.5%		0%		0.5%		0%		0.5%	
Date	Aug	Nov	Aug	Nov	Aug	Nov	Aug	Nov	Aug	Nov	Aug	Nov	Aug	Nov	Aug	Nov
pH value	7.52	8.56	7.64	9.40	7.61	7.71	7.61	8.90	7.62	7.55	7.54	8.67	7.45	7.04	7.36	9.02

7.3 Sample Calculations for Determining the Corrosion Rate of Steel Rebar



Graph 1: Tafel Plot obtained from 3.5 % Sodium Chloride Environment

As seen from graph 1 above, the graph is plotted as current (A) versus potential (V). The value of either the anodic or cathodic current is called the Corrosion Current. Once the tangents were drawn for cathodic and anodic curve, the value for current can be obtained. In order to determine the value for corrosion density before corrosion rate is calculated, for area of the metal, it must be measured before the experiment and should be included in the table to find corrosion density. This is because the corrosion density value is not determined by the graph generated from EIS machine.

For instance, under 3.5% sodium chloride environment, 0% and 0.5% CI were compared by referring to the values of corrosion rate. Sample calculations for both concentrations of inhibitor are shown in table 13 below.

Environment	Material	Atomic weight (a) (g/mol)	Corrosion current density ($\mu A/cm^2$) / icorr	Area of steel rebar (cm^2)	Valency charge on iron (n)	Density, g/cm^3 of iron (D)	Constant of corrosion rate mm/yr (K)	Corrosion rate (mm/yr)
3.5% Sodium Chloride (0% CI)	Iron	56	$28x10^3\mu A$ / $48.695cm^2$ = 575.0077	48.695	2	7.86 (obtained from physics hypertextbook; 2015)	0.00327	6.70
3.5% Sodium Chloride (0.5% CI)	Iron	56	$10x10^3\mu A$ / $48.695cm^2$= 205.3598	48.695	2	7.86	0.00327	2.39

Table 9: Guideline on the Calculation for Rate of Corrosion

As seen from table 13 above, it is set up to guide users when finding the value for corrosion rate. The atomic weight, valency charge and density depend on what metal was used. In this experiment, the metal used was iron. The corrosion rate of the steel rebar can be obtained by the following equation:

$$\text{Corrosion rate} = k\ (a.\ icorr\ /\ nD)$$

Equation 2: Relationship between Corrosion Rate and Corrosion Density

Corrosion rate for 0% CI for 3.5% sodium chloride environment
= 0.00327mm/year [(56g/mol x 575.0077 $\mu A/cm^2$) / (2 x 7.86g/cm^3)]
= 6.70mm /year.

As seen from table 13 above, by comparing the values of corrosion rate of steel rebar for 0% and 0.5% CI, it can be observed that with the presence of inhibitor, the value of corrosion rate decreases from 6.70mm/yr to 2.39mm/yr. Thus, this highlights the importance of CI in protecting the rebar from severe corrosion under harsh environments like 3.5% sodium chloride. Further analysis of the project will be discussed in the discussion section.

After the corrosion rate is obtained, we will then show the relationship between the life expectancy of rebar and loss of cross section in table 14 below.

Life expectancy	Corresponding loss of cross-section in (mm/year)
< 0.5 μa/cm2 – no corrosion damage expected	<0.006 mm/year
0.5 – 2.7 μa/cm2 – corrosion damage possible after 10 to 15 years	0.006-0.030 mm/year
2.7 – 27 μa/cm2 – corrosion damage expected in 2 to10 years	0.030-0.310 mm/year
>27 μa/cm2 – corrosion damage expected in 2 years or less Hence, after the machine measured the thickness of the specimen, the readings were then matched against the corresponding loss of cross section in (mm/yr). The severity of damage will then be determined.	>0.31 mm/year

Table 10: Relationship between Life Expectancy of Metals and Corresponding Loss of Cross Section (K. Clear,1986)

Since the corrosion rate obtained for the steel rebar under 3.5% sodium chloride environment is 6.70mm/year, from table 14 above, it can be estimated that corrosion damage is expected in 2 years or less, due to the presence of the aggressive chloride ions from the surroundings. Further explanations will be discussed under the subsequent sections.

8. Discussions

In this section, the results obtained from the various tests were analyzed and discussed.

8.1 Explanations on Corrosion Rate for Dry Environment with respect to EIS

It was seen from table 9 above that at the end of the experiment on 13 November, it was found that the pot with 0.5% CI has the highest corrosion rate, followed by the pot with 0% CI, then the pot with 0.167% IC and lastly the pot with 0.333% CI. Throughout this experiment, some results showed error which could be due to the fact that the pots are in a dry environment where it is difficult for electrons to flow in the dry soil.

Theoretically, the pot with 0% CI should have the highest corrosion rate, followed by the pot with 0.167% CI, then the pot with 0.333% and the pot with 0.5%. However, the results were not as expected. This could be due to the fact that the CI was only placed around the pot, far from the steel rebar, where the movement of CI to the steel rebar is still unknown and unpredictable.

It is also uncertain if the amount of CI deposited around the pot will be used completely to prevent the corrosion of steel rebar, thus leading to unexpected results. Hence, modifications were made by increasing the amount of CI. The values of corrosion rate do not show any significant drops immediately but it did help in reducing the corrosion rate eventually. This can be seen by comparing the results from the first and last test, which is on 18 July and 13 November, it can be seen that the CI did help in reducing the corrosion rate

but requires a longer time due to the dry environment. Hence, it can be assumed that in dry environment, the medium to transport the Cl is very important.

The corrosion rates in the dry environment were the lowest as compared to the other environments. In the dry environment, only air and limited water (moisture in the air) is present. Ferrous materials like steel tend to be protected by promoting oxidation or a protective oxidation layer. When oxygen comes into contact with the steel rebar, a protective oxide layer forms around the metal and slows down the rate of corrosion. In addition to the Cl reducing the corrosion rate, the oxide layer also helps in further reducing it. That is why the corrosion rates in the dry environment are the lowest.

8.1.1 Comparison of Corrosion Rate between Dry Environment and 3.5% Sodium Chloride Environment

Comparing the pots in a dry environment with the 3.5% sodium chloride environment, the pots in the 3.5% sodium chloride environment experience a higher corrosion rate. This is mainly due to the fact that there are presence of air, water and electrolytes in the 3.5% sodium chloride environment where corrosion depends on these factors. Another important factor is that the 3.5% sodium chloride environment contains the aggressive chloride ions which aid in the increase in corrosion rate. With the presence of air, water, and chloride ions, the steel rebar will rust and corrode at a faster pace resulting in higher corrosion rate.

8.1.2 Comparison of Corrosion Rate between Dry environment and Water Environment

By comparing the pots in a dry environment and the water environment, the pots in the water environment have a higher corrosion rate. The presence of air, water and electrolytes in the water environment allows the steel rebar to corrode easily and quickly. In contrast, the dry environment only has air and limited water present. The steel rebar will still corrode but slower since lesser factors are influencing the rate of corrosion. Therefore, the corrosion rate for dry environment will be slower as compared to the pots in the water environment.

8.2 Explanations on Corrosion Rate for pH 4.0 Buffer Environment with respect to EIS

Based on table 8 above, it shows that sample with 0.167% Cl has the highest corrosion rate at the end of the experiment, followed by sample with 0.5% and 0.333% Cl. Sample with 0% Cl was unable to be detected by EIS due to the soil being very dry. Electrons were unable to flow through the soil due to the lack of electrolyte, hence results were not obtained. However, in the beginning, the sample can be detected because the soil was moist. In samples with 0.167%, 0.333% and 0.5% Cl, the corrosion was slow in the beginning because the rebars were not rusted yet. Due to the inconsistency in the results for the first 4 tests, samples with 0.167% and 0.333% Cl were modified.

According to theory, sample without Cl should have the highest corrosion rate followed by 0.167%, 0.333%, and 0.5% sample due to acidic environment. However, results obtained were not as expected. This may be due to several reasons. Firstly, the acidic environment was created by using buffer solution due to safety and health concern. Buffer solution is a solution that consists of a mixture of weak acid and its conjugate base. A buffer solution is very stable as its ions will not break down and diffuse into the soil sample to cause acidic environment to the sample.

As it did not mimic the real acidic environment in daily live, it is assumed that this set-up is not representative. Besides that, the sample did not have direct contact with the pH 4.0 buffer solution. This is to prevent the chemical reaction or corrosion between flower pots with the pH 4.0 buffer solution. As the pH 4.0 buffer solution did not seep through the flower pot, the samples were not as damp as samples in water and 3.5% sodium chloride, and the samples in pH 4.0 buffer solution lack of acidity.

8.3 Explanations on Corrosion Rate for Water Environment with respect to EIS

Amount of Cl/Date	22 July mm/year	8 Aug mm/year	11 Sep mm/year	7 Oct mm/year	21 Oct mm/year	6 Nov mm/year	13 Nov mm/year
0%	0.144	0.191	0.191	0.215	0.311	0.239	0.287
0.167%	0.167	0.239	0.478	0.478	Error	1.32	0.191
0.333%	0.191	0.598	Error	0.431	0.191	0.108	0.0230
0.5%	0.431	Error	1.67	1.20	1.03	0.909	0.669

Table 11: Table Adapted from Results Section on Corrosion Rate for Water Environment, highlighting on 0% Cl sample

As seen from table 12 above, at the end of the experiment, soil sample with 0.333% Cl has the lowest value corrosion rate of 0.0230mm/year, this is then followed by 0.167%, 0% and then 0.5% of Cl, with values of 0.191mm/year, 0.287mm/year and 0.669mm/year respectively.

From table 12 above, it can be observed that the values of corrosion rate for steel rebar in 0% Cl are increasing from 22 July to 21 October with values from 0.144mm/year to 0.311mm/year. However, the values of corrosion rate started to decrease at 6 November with a value of 0.239mm/year and increased again at 13 November with value of 0.287mm/yr. The explanation is as follows.

Normally, for steel, the typical anodic oxidation reaction is Fe $\rightarrow$ $Fe^{2+} + 2e^-$. All liquids containing water contain at least two kinds of free ions carrying electric charges. They are hydrogen ions which are positively charged, and the hydroxyl ions which are negatively charged. The result from the electrolytic dissociation of some of the water molecules represented by the reversible action is $H_2O \rightleftharpoons H^+ + OH^-$ Therefore, the production of OH^- ions and Fe^{2+} will react to become ferrous hydroxide.

The reaction is $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$. The ferrous hydroxide will then combine with the presence of oxygen and water from the surroundings to produce ferric hydroxide, $Fe(OH_3)$, which becomes common iron rust when dehydrated to Fe_2O_3. Hence, this rust will act as a protective layer but rust at the same time. As long as the rust does not undergo external stress, this would inhibit the steel rebar from further corrosion. On the other hand, if the rust was to be removed, it means that the protective layer will not be present anymore.

8.3.1 Comparison of 0% Cl Sample in 3.5% Sodium Chloride Environment and Water Environment

Environment	Amount of Cl/Date	22 July mm/yr	8 Aug mm/year	11 Sep mm/yr	7 Oct mm/yr	21 Oct mm/yr	6 Nov mm/yr	13 Nov mm/yr

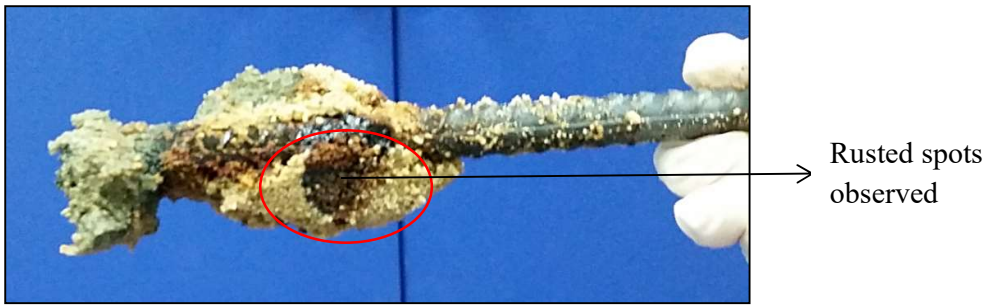
3.5% Sodium Chloride	0%	1.91	Error	2.39	1.91	Error	6.70	11.24
Water	0%	0.144	0.191	0.191	0.215	0.311	0.239	0.287

Table 12: Comparison of 0% Cl in 3.5% Sodium Chloride Environment and Water Environment

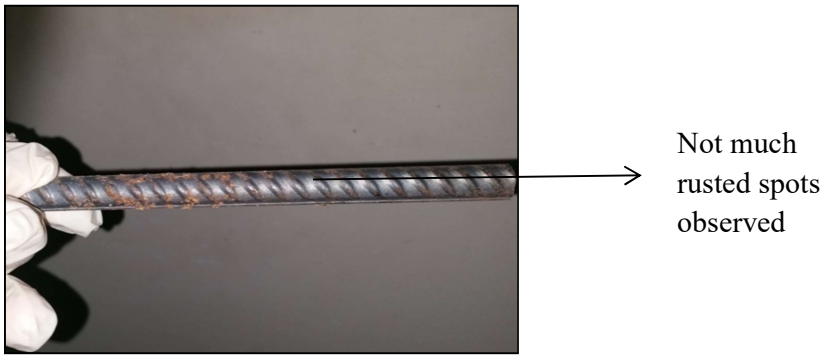
3.5% sodium chloride environment is harsher than water environment. As seen from table 13 above for 0% Cl in 3.5% sodium chloride environment, the corrosion rate on 22 July and 13 November are 1.91mm/yr and 11.24mm/yr respectively. While for water environment, the corrosion rate on 22 July and 13 November are 0.144mm/yr and 0.287mm/yr respectively. The corrosion rate in 3.5% sodium chloride environment increased by tenfold without any Cl. If Cl was not added to the other soil samples in 3.5% sodium chloride environment, the rate of corrosion would be even more severe. Hence, it is crucial to add Cl in harsh environment to reduce severe corrosion from taking place.

In contrast, the corrosion rate in water environment does not show any significant change in corrosion rate for sample with 0% Cl. Thus, it means that even if Cl was not added, it will not have any drastic effect in corrosion values. This may be the nature of the rust formation, which was mentioned above. Even though the rust produced can protect the corrosion, the corrosion will still occur but at a slower rate as the rust is not fully adhered to the surface of the steel rebar.

As a result, if Cl was to work under water environment, it may not contribute any significance in the lowering of corrosion rate. Hence, even with the presence of Cl, it does not show significant improvement in the corrosion rate.



Photograph 17: Severe Degree of Corrosion for 3.5% Sodium Chloride Environment



Photograph 18: Lowest Degree of Corrosion for Dry Environment

At the end of the experiment, it was found that the corrosion rate in 3.5% sodium chloride environment is the highest with a value of 11.24mm/year, followed by the steel rebar in water with a value of 0.669mm/year, pH 4.0 with a value of 0.03588mm/year and dry environment with a value of $8.37x10^{-4}$mm/year . As seen in photograph 23 above, under 3.5% sodium chloride environment, pitting attack of the steel rebar may penetrate the deepest and fastest. Furthermore, the fastest corrosion rate for steel occurred in 3.5% sodium chloride environment, where there is an abundant supply of oxygen that is required for corrosion to take place. On the other hand, looking at photograph 24 above, the degree of corrosion for steel in dry environment is the lowest.

As a result, we will then base our findings on 3.5% sodium chloride which is the best medium and most suitable environment to analyze the corrosion rate of steel rebar, and the effectiveness of the CI in this environment. CI is important to work under harsh environment such as 3.5% sodium chloride as it is more meaningful to compare with sample that uses CI in water as environment. Apart from that, with CI working under 3.5% sodium chloride environment, it also reflects the nature of concrete in sea water or at the seaside.

8.4 Explanations on Corrosion Rate for 3.5% Sodium Chloride Environment with respect to EIS

Amount of CI/Date	22 July mm/year	8 Aug mm/year	11 Sep mm/year	7 Oct mm/year	21 Oct mm/year	6 Nov mm/year	13 Nov mm/year
0%	1.91	Error	2.39	1.91	Error	6.70	11.24
0.167%	2.39	5.98	6.69	4.31	7.66	9.09	6.46
0.333%	2.39	2.51	4.31	9.57	11.48	6.70	4.31
0.5%	Error	2.27	9.57	2.63	2.39	2.39	5.26

Table 13: Table Adapted from Results Section on Corrosion Rate for 3.5% Sodium Chloride Environment, highlighting on Modification done for 0.167% and 0.333% Sample

As seen from table 14 above, at the end of the experiment, 13 November, it was found that the corrosion rate of steel rebar in soil sample with 0% CI was the highest with a value of 11.24mm/year, followed by soil sample with 0.167%, 0.5% and 0.333% CI, with values of 6.46mm/year, 5.26mm/year and 4.31mm/year respectively. From table 14 above, it can be seen that the corrosion rate for the steel rebar with 0% CI increases throughout the experiment and there is a significant increase of 4.54mm/year from 6 November to 13 November. However, even if there is a layer of oxide coated on the steel surface, the aggressive chloride ions will also damage the layer of oxide coating. Due to the inconsistency in the results for the first 4 tests, samples with 0.167% and 0.333% CI were modified after 7 October.

Looking at the period from 22 July to 7 October, it can be observed that the corrosion rate of steel rebar in soil sample with 0.333% of CI is the highest with a corrosion value of 9.57mm/yr. This is followed by the soil sample with 0.167%, 0.5% and 0% CI with corrosion values of 4.31mm/year, 2.63mm/year and 1.91mm/year respectively. Theoretically, as the amount of CI increases, the corrosion rate should show a significant decrease as the function of CI is to protect the rebar by coating with a passivation layer around it. However, the results show otherwise. Some possibilities are as follows.

8.4.1 Presence of Aggressive Chloride ions

As mentioned previously, 3.5% sodium chloride acts as a seaside environment, the presence of chloride ions in the surroundings will lead to the acceleration of the localized attack in steel rebar. According to PCA (2002), chloride ion is classified as the most aggressive ions as it will cause de-passivation with the creation of the active sites on the metal surface, thus increasing the corrosion process. Also, when a sufficient amount of chlorides reaches the steel reinforcement, it permeates the passivating layer and the chloride ions will eventually reach the steel, accumulating to a certain level. The protective film will start to undergo corrosion and protection film is lost. This further explains the reason why even 0.333% CI in soil sample shows the highest value of corrosion rate at 7 October. In addition, the amount of chloride ions present in the soil from the 3.5% sodium chloride environment was tested using XRF. This was done to further determine that the presence of chloride ions contributed to a higher corrosion rate.

8.4.2 Microbial Activity

Photograph 19: Fungi and Mould Observed on the Soil Surface

Photograph 20: Microorganisms

Apart from the presence of chloride ions, another reason for the significant changes in the corrosion rate of steel rebar is due to the presence of microbial activity. It can be observed from photographs 25 and 26 above. It is predicted that the thickness of the passive films on steel samples may be lowered due to the mutual attack by these bacteria and ions. Furthermore, the main triggers of corrosion of steels are due to Sulphate Reducing Bacteria (SRB). Researchers have found that the degree of microbiologically induced corrosion of

carbon steel is directly proportional to the bacterial resistance to the metal ions. For instance, the corrosion rate increases with an increase in the microbial activity that take place in the environment.

Furthermore, as stated by Olivia (2009), an example of other bacteria such as SRB can be found in seawater which is anaerobic and is responsible for the accelerated corrosion process promoting damages to steel structures near shore sites and reservoir. Hence, these biological activities will vary the pH of the environment, change the temperature of the surrounding and then accelerate the rate of anodic and cathodic corrosion reaction in rebar, while leaving the corrosion mechanism more or less unchanged. These microorganisms are commonly subdivided into fungi, algae, diatoms and bacteria.

Therefore, in order to further propose that the bacteria is involved in the reduction of iron, confirmation can be done by conducting experiment on the presence of bacteria on steel surfaces. However, this will be mentioned under recommendations.

8.5 Reasons for Modifications

From the start of the experiment set up, for 0.167% and 0.333% Cl, they were added into soil sample around the circumference of the porous film without direct mixing. It was realised that the corrosion rate obtained for 0.167% and 0.333% of Cl does not work effectively before 7 October.

There are a few assumptions to it. It may be due to the concentrations of Cl from the admixture being insufficient to diffuse to the surface of steel rebar to form a passive film, or the diffusion of Cl has yet to reach the surface of steel rebar. To further interpret the results and confirm the assumptions, modifications were carried out for these two concentrations (0.167% and 0.333% Cl) after 7 October.

An additional 50g of Cl was added to the sample that contains 0.167% Cl by direct mixing. The concentration of Cl in soil sample becomes 1.83%. While an additional 40g of Cl was added to the admixture for the sample that contains 0.333% Cl, and this makes up to a concentration of 1.67% Cl.

After 21 October, all samples with 1.67% Cl have a lower corrosion rate as Cl will form a passive film on the steel rebar mainly by diffusion. In contrast, for samples with 1.83% Cl, the values of corrosion rate increases. This further verified that diffusion of Cl does take place in soil sample but it takes time to diffuse from the admixture to steel rebar, and that direct mixing is not a preferred preparation method. Further reasons on why direct mixing is not a preferred method will be mentioned under section 6.7.1 of this report.

8.5.1 Relationship between Amount of Cl and the Corrosion Rate

Amount of Cl/Date	22 July mm/yr	8 Aug mm/yr	11 Sep mm/yr	7 Oct mm/yr
0.167%	2.39	5.98	6.69	4.31
0.333%	2.39	2.51	4.31	9.57
0.5%	Error	2.27	9.57	2.63

Table 14: 0.167%, 0.333% and 0.5% before modifications in 3.5% sodium chloride environment

Amount of Cl/Date	21 Oct mm/year	6 Nov mm/year	13 Nov mm/year
1.83%	7.66	9.09	6.46
1.67%	11.48	6.70	4.31
0.5%	2.39	2.39	5.26

Table 15: 0.5%, 1.67% and 1.83% after modifications in 3.5% sodium chloride environment

Referring to the highlighted results from table 15 and 16 above, in the experiment set-up for both concentrations of Cl that were added to the soil sample, the Cl was added into the admixture not direct mixing. The Cl will mainly diffuse from the admixture to the steel rebar. Hence, these two different concentrations of Cl can be compared and analysed.

As seen from table 15 above, for 0.333% Cl, the corrosion rate of steel rebar started increasing from 2.39mm/year to 9.57mm/year, from 22 July to 7 October. However, even after modifications have been made to the 0.333% Cl in soil sample to become 1.67% after 7 October, the corrosion rate on 21 October was 11.48mm/year which still increase since it requires time to diffuse. This shows that the amount of Cl that was added from the start was insufficient to be able to diffuse and protect the steel rebar from further corroding. However, since modifications have been made, from 6 November to 13 November, the values of corrosion rate started decreasing slowly.

For the initial 0.167% Cl, the corrosion rate does not show any significant changes or improvement on the degree of corrosion. However, after modifications took place where the amount of concentration inhibitor increases to 1.83%, the corrosion rate decreases from 6 November to 13 November by 2.63mm/yr. Even though direct mixing is not a preferred application method, with an increase in the amount of inhibitor it will still lead to an improvement in the value of corrosion rate.

This indicates that the additional Cl that was added to the soil sample during modification was sufficient to diffuse from the admixture to the steel rebar and form a passive film. In other words, when there is an increase in the concentration of Cl used, the diffusion rate increases, thereby contributing to a lower corrosion rate after the critical concentration, which is 0.5%. This statement truly fits into the diffusion law, where the diffusion rate is faster with an increase in the concentration of Cl.

This can be further proven by table 16 above, after the modification of adding additional 40g of Cl into the admixture, the corrosion rate decreases significantly from 21 October to 6 November with a value of 4.78mm/year, and decreases by 2.39mm/year from 6 November to 13 November within only 1 week after the EIS measurement was carried out.

By looking at the values from tables 15 and 16 above, for sample with 0.5% Cl in 3.5% sodium chloride environment, the corrosion rate obtained was not as high as compared to the values obtained for 0.333% from the start. Hence, this means that 0.5% of Cl may be the desired concentration as it contains a sufficient amount to allow diffusion to take place from admixture to steel rebar.

8.6 Effect of pH values on the Corrosion Rate in Water and 3.5% Sodium Chloride Environments

At the start of the experiment, the pH of pure CI was measured and it was found to be a pH value of 10.3, which shows a high alkalinity value. At the end of the experiment, pH values of the soil were taken around the steel rebar in sample with 0% and 0.5% CI. Results are shown in table 12 above. At the end of the experiment, the alkalinity of the soil increases due to the presence of corrosion inhibitor. This also indicates that diffusion of CI occurs as it diffuses from the side of the pot to the center of the pot.

Based on the results obtained, samples in 3.5% sodium chloride environment has the lowest pH value followed by samples in water, pH 4.0 buffer solution and then dry environment. The lower the pH value obtained for the soil sample, the higher the corrosion rate. This is because having a lower pH means that the environment in the soil sample is more acidic. Acidic condition is one of the factors that affect corrosion.

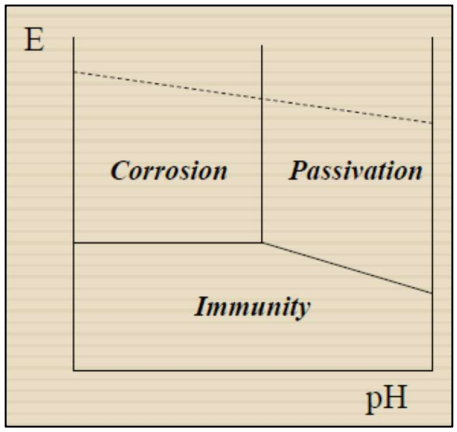


Diagram 4: Pourbaix Diagram

Having a higher pH means that the environment in the soil sample is more alkaline. Hence, based on the Pourbaix diagram in diagram 8 above, an increase in pH indicates passivation occurs which then moves the iron into a region of passivity where the most stable species is an insoluble iron hydroxide or hydrated oxide to be formed. Since there is a reduction in the corrosion rate, we can make assumptions that the iron hydroxide film may be coated onto the steel rebar. The film will tend to separate the iron from its corrosive environment, acting as a protective layer. However, it cannot be assumed that an insoluble film will always behave in a protective manner. The explanation is that if the film produced is not uniform, and is conducting and permeable to ions, or if it is damaged by flow of electrolyte across the surface or by mechanical means, then corrosion is likely to continue. Indeed, the local rate may well be accelerated because the exposed anode area is smaller.

8.7 Discussions and Analysis on the Overall Experiment

8.7.1 Method of Application

Photograph 21: Agglomeration of Cl

After 7 October, modifications were made on samples with 0.167% and 0.333% Cl. For 0.167% of Cl in soil sample, additional 50g of Cl was added by direct mixing with the soil. For 0.333% Cl in soil sample, additional 40g of Cl was added into the admixture. Theoretically, with higher amount of Cl and direct mixing method, sample with 1.83% Cl should have a lower corrosion density and a decrease in corrosion rate. The possible reasons may be due to the agglomeration of Cl due to the moisture from the surroundings and soil sample. This can be referred to photograph 27 above. Therefore, with the agglomeration, this will hinder the Cl from diffusing to the steel rebar preventing the formation of the passive film.

On the other hand, for sample with 1.67% Cl, direct mixing was not carried out. Hence, there was no agglomeration of Cl around the soil sample. This will create an easier pathway for the Cl to undergo diffusion, since there will be lesser hindrance. As a result, this explains the reason for sample with 1.67% Cl showing a lower corrosion rate as a whole. For instance, by comparing samples with 1.83%, 1.67% and 0.5% for 3.5% sodium chloride and water environments, the results can be further proven as shown below.

Amount of Cl/Date	21 Oct mm/year	6 Nov mm/year	13 Nov mm/year
1.83%	Error	1.32	0.191
1.67%	0.191	0.108	0.0230
0.5%	1.03	0.909	0.669

Table 16: Values of Corrosion Rate after Modification for Water Environment

Amount of Cl/Date	21 Oct mm/yr	6 Nov mm/yr	13 Nov mm/yr
1.83%	7.66	9.09	6.46
1.67%	11.48	6.70	4.31
0.5%	2.39	2.39	5.26

Table 17: Values of Corrosion Rate after Modification for 3.5% Sodium Chloride Environment

As seen from table 17 above, 1.83% Cl in soil sample using direct mixing shows only a small decrease from 6 November to 13 November by 1.129mm/yr for water environment. While for

3.5% sodium chloride, from table 18 above, it actually shows an increase in the value of corrosion rate from 21 October to 6 November by 1.43mm/yr.

The modifications made for the initial 0.333% Cl in soil sample for water and 3.5% sodium chloride environments were to add 40g of Cl into the admixture. Thus, the Cl will be forming the protective layer mainly by diffusion, because direct mixing was not carried out in these samples. For water environment, both 1.67% and 0.5% Cl shows a trend of decreasing in corrosion rate. For 3.5% sodium chloride environment, both 1.67% and 0.5% also shows a trend whereby smaller values of corrosion rate were obtained, except for the 0.5% Cl, where the values of corrosion rate increased from 6 November to 13 November. The reason for the increase in corrosion rate will be further elaborated under section 6.7.2. Hence, as seen from the values obtained with and without direct mixing for two environments, it can be assumed that Cl actually works better via diffusion from the admixture to steel rebar.

However, this is different from the concrete sample, as concrete is more densely packed. As a result, direct mixing must be carried out for the concrete sample. Otherwise, it would be difficult for the Cl to diffuse to the steel rebar, unlike the Cl in soil sample.

8.7.2 Critical Concentration of Cl for 3.5% Sodium Chloride Environment

Amount of Cl/Date	22 July mm/year	8 Aug mm/year	11 Sep mm/yr	7 Oct mm/year	21 Oct mm/yr	6 Nov mm/year	13 Nov mm/year
0.333%	2.39	2.51	4.31	9.57	-	-	-
1.67%	-	-	-	-	11.48	6.70	4.31
0.5%	Error	2.27	9.57	2.63	2.39	2.39	5.26

Table 18: 0.333%, 1.67% and 0.5% Cl in 3.5% Sodium Chloride Environment

From table 19 above, the sample with 0.5% Cl for 3.5% sodium chloride environment possessed the most stabilised results and there were no modifications made to the soil sample. Therefore, results can be interpreted. The corrosion rate from 8 August to 11 September increased from 2.27mm/year to 9.57mm/year, and then shows a drastic drop at 7 October, with a value of 2.63mm/yr. After which, from 7 October to 6 November, the values of corrosion rate almost remained constant. However, at 13 November, it started to increase from 2.39mm/year to 5.26mm/yr. This might be due to the following assumption.

It is assumed that 0.5% Cl is the critical concentration for 3.5% sodium chloride environment till 6 November. This can be explained as since the corrosion rate increased at 13 November, the Cl might have been used up after 6 November. The mechanism is that for example, if the passive film was formed but incomplete, corrosion will still occur. Instead, if passive film is completely formed on the steel rebar, corrosion will not continue so corrosion rate will decrease. Since the corrosion rate still increases by 2.87mm/yr from 6 November to 13 November, this shows that there was no excess Cl to diffuse to the steel rebar to form passive film and to prevent steel rebar form further corroding.

Besides that, 0.5% Cl also serves as a critical pot life for the Cl to be able to protect the rebar. For instance, if the experiment was carried out after 13 November and the corrosion rate shows a higher value, this means that the Cl is already used up. This proves that the Cl has a timeframe whereby Cl needs to be replenished to further protect the steel rebar from corroding.

Hence, this explains the possible reasons why 0.5% Cl is the critical concentration for 3.5% sodium chloride environment. In addition, the critical concentration of 0.5% Cl relies on the surface area of rebar used in this experiment and the harsh environment set-up. If a greater surface area of steel rebar was used instead and 3.5% sodium chloride as the environment, a greater amount of Cl must be used so as to form a complete layer of passive film. Hence, the critical concentration of Cl would increase to protect the rebar from greater degree of corrosion due to the harsh environment.

By referring to table 19 above, the corrosion rate for the 0.333% Cl shows an increase from 2.39mm/yr to 9.57mm/yr from 22 July to 7 October. Despite modifications having been made after 7 October, it can be observed on 21 October that the corrosion rate continue to increase from 9.57mm/yr to 11.48mm/yr. Thus, this further explains the reason for 0.5% to be the critical and minimum concentration of Cl able to protect the rebar, and not 0.333% Cl.

8.7.3 Time Taken for Cl to Diffuse

Environment	Amount of Cl/Date	22 July mm/year	8 Aug mm/year	11 Sep mm/year	7 Oct mm/year	21 Oct mm/year	6 Nov mm/year	13 Nov mm/year
3.5% Sodium Chloride	0.5%	Error	2.27	9.57	2.63	2.39	2.39	5.26
Water	0.5%	0.431	Error	1.67	1.20	1.03	0.909	0.669
pH 4.0	0.5%	2.393×10^{-5}	4.784×10^{-3}	9.568×10^{-3}	0.01196	5.502×10^{-3}	4.784×10^{-3}	2.392×10^{-3}
Dry	0.5%	9.57×10^{-3}	9.57×10^{-3}	7.18×10^{-3}	1.67×10^{-4}	1.44×10^{-4}	1.67×10^{-4}	8.37×10^{-4}

Table 19: Corrosion Rate of Samples with 0.5% Cl in all Environments

As seen from table 20 above, it was observed that the corrosion rates for all environments showed an increase in value from 22 July and then decreased from 7 October to mid of October and became relatively constant after November. This shows that the Cl requires a particular time to diffuse, and to lower the corrosion rate. Thus, we can make assumptions that the Cl requires approximately 3 months (90 days) to diffuse and form a passive film on steel rebar.

This can be further supported by the duration of the migration of Cl in concrete to the rebar. For instance, using concrete as the substrate, Cl usually requires around 4 months (120 days), to diffuse to the rebar. As concrete is more densely packed and less porous than soil, it requires more time for Cl to reach the steel rebar and form a protective film. In contrast, soil sample is more porous than concrete, so it requires less time for Cl to diffuse to steel rebar and form the layer of passive film.

8.7.4 Presence of Moisture to Form Passive Film

Environment	Dry				Water			
Sample	0%		0.5%		0%		0.5%	
Date	Aug	Nov	Aug	Nov	Aug	Nov	Aug	Nov
pH value	7.52	8.5	7.64	9.40	7.61	7.71	7.61	8.90

		6						

Table 20: pH values for 0% and 0.5% CI in Dry and Water Environments

As mentioned previously, the pH value of pure CI was found to be 10.3. From table 21 above, the pH values actually increased from August to November for 0.5% CI in soil for all environments. This means that diffusion does occur under all environments.

Referring to the highlighted results from table 21 above, since the pH value for water environment increased at the end of the experiment, this indicates that diffusion of CI occurs. From the corrosion rate of rebar obtained from water and dry environments, the increase in corrosion rate for water environment is actually smaller compared to the corrosion rate in dry environment.

This shows that the degree of corrosion of steel rebar was better controlled in water environment. Therefore, we can infer that CI does work for water environment due to the presence of moisture to form a passive film on steel rebar, thereby controlling the degree of corrosion in water environment. However, CI did diffuse to the steel rebar but did not work in dry environment, due to the absence of moisture to form a passive film to lower the corrosion rate of rebar.

8.8 Vappro Concrete Rebar Corrosion Inhibitor

8.8.1 Nature of CI

The nature of CI is in powder form. It requires the presence of moisture from the surroundings to form the passive film on the steel rebar by diffusion and thus protecting the rebar from further corrosion. This was mentioned previously under section 8.7.4. It is alkaline, containing a pH value of 10.3. When there is an increase in the concentration of CI, it increases the pH of soil sample and in turn lowers the values of corrosion rate, due to the high alkalinity.

8.8.2 Critical Concentration

In order to reduce the corrosion in 3.5% sodium chloride environment, it actually requires 0.5% CI in the soil sample to work. Hence, 0.5% CI is the minimum and critical concentration for 3.5% sodium chloride environment to enable it to form a complete passive film.

8.8.3 Diffusion Time

CI in soil sample requires only 3 months (90 days) to diffuse from the side of the pot to steel rebar lowering the corrosion rate by a forming passive film around steel rebar. This can be seen from the trend analyzed.

8.8.4 Best Application Method

Mixing the CI around the circumference of the porous film is a better application method as compared to adding CI in soil sample by direct mixing. This is because it was observed that the trend for the corrosion rates for all environments showed an improvement on the degree of corrosion whereby the CI protects that rebar mainly by diffusion. Hence, CI functions better by diffusion in soil sample in this project.

8.9 Functional Groups of CI

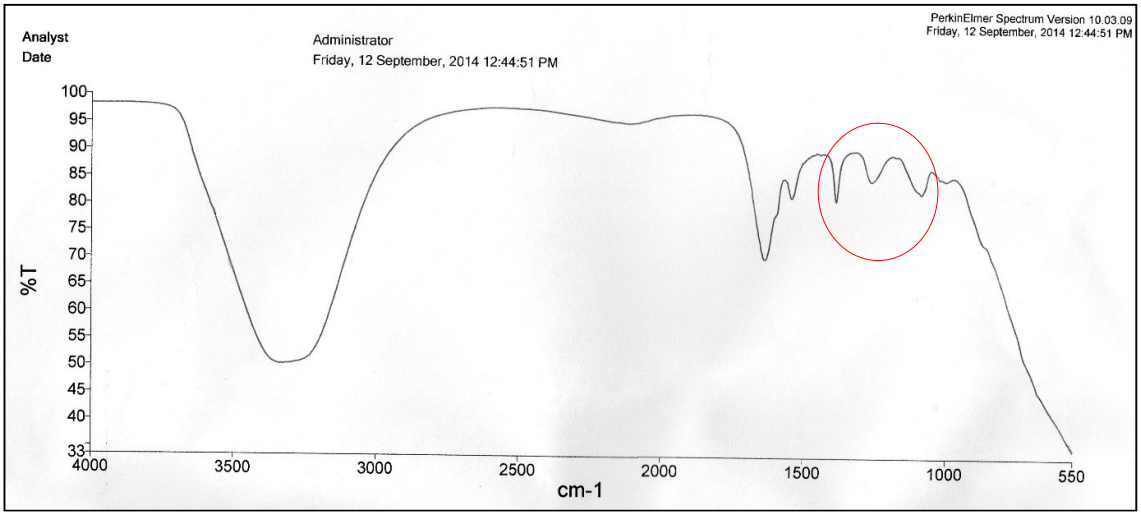


Figure 1: FTIR Spectrum of Pure CI

Wavenumber (cm^{-1})	Functional group	Types
1350-1000	Amines	C-N stretch
1000-1300	Carboxylate	C-O stretching

Table 21: Correlated Functional Groups of Characteristic Peak found in Pure CI

As shown from figure 1 above, the circled part of the characteristic peak was found to have a wavelength of around $1030cm^{-1}$. Referring to table 25 above, the characteristic peak at $1030cm^{-1}$ could be due to the presence of amine C-N or carboxylate C-O stretching.

Hence, the characteristic peak obtained from the spectrum above shows that Vappro concrete rebar corrosion inhibitor contains presence of amino carboxylate, which is an organic compound. This was further verified by the description in its MSDS which also stats that Vappro concrete rebar corrosion inhibitor contains amino carboxylate.

9. Conclusion

This section will describe the major experimental findings with concluding statements about the experiments.

In conclusion, it was found that CI works under all environments except for dry, because of the increased values of corrosion rate at the end of experiment. This shows that CI requires moisture to form a passive film on surface of steel rebar.

3.5% sodium chloride environment is the best to compare the effectiveness of CI under all environments. Even in water environment, the difference of corrosion rate is not significant. Hence, the presence of CI is important under harsh environment due to the significant values of corrosion rate obtained for 3.5% sodium chloride environment.

For instance, under 3.5% of sodium chloride environment, in order to inhibit the corrosion rate, it actually requires 0.5% CI in the soil sample to work. Hence, 0.5% CI is the minimum and critical concentration for 3.5% sodium chloride environment to be able to form a complete passive film. It also means that there may be a limited life time on how long it can protect the steel rebar from corroding for 0.5% of CI.

It was realized that 0.167% and 1.83% CI does not work as effectively. For example, by comparing the modified set-up for 1.83% and 1.67% CI in soil sample at the end of the experiment, sample with 1.67% CI shows a lower value of corrosion rate than 1.83%, which is the direct mixing. Hence, the best application method for CI in soil sample is by diffusion instead of direct mixing.

By comparing the trend for the values of corrosion rate under all environments, CI in soil sample requires only 3 months to diffuse from the pot surrounding to the steel rebar so as to lower the values of corrosion rate by forming passive film around steel rebar. The rate of diffusion of CI in soil (90 days) is faster than in concrete (120 days), according to Bavarian (2004)

It was mentioned that 0.5% CI in 3.5% sodium chloride environment was the critical and minimum concentration for CI to work, as the value of corrosion rate of steel rebar was observed to increase again after 13 November due to some reasons. Hence, to further confirm whether there is data inaccuracy or the CI has been used up, it is recommended to lengthen the timing for EIS experiment to December so as to observe the trend more clearly and determine the pot life of CI.

In order to further confirm the presence of SBR on steel rebar which will affect the values of corrosion rate especially under wet environments, this can be further analyzed with the help of SEM to detect SBR and verify if our findings are correct.

It is recommended to use the SEM to check the adhesion of the passive film on the steel rebar and further check the elements used for the formation of the passive film.

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