Experimental Findings for Corrosion Inhibition Efficiency and its Effects on the Compressive Strength of the Concrete Based on the Optimum Dosage of Vappro Concrete Admixture Vapour Corrosion Rebar Inhibitor.

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Abstract

The primary purpose of this technical report relates to the experimental findings of the optimum dosage of Vappro 4030-Concrete Admixture Vapour Corrosion Rebar Inhibitor for its optimum corrosion inhibition efficiency, its effects on the compressive strength of the concrete and ascertaining amines and amino alcohols as chemical functional groups of VAPPRO CRI 4030 determined via FTIR

1.0 Introduction

The application of corrosion inhibitors is one of the many methods available for the protection of reinforcing steel in concrete. This study presents the results of an investigation of the effects of Vappro Concrete Rebar Inhibitor (VAPPRO CRI) 4030 as a concrete admixture on the corrosion of reinforcing steel. Ultimately, the optimum concentration of Vappro CRI 4030 to be used was determined. The investigation was divided into two main segments. The first part of the investigation consisted of primary indication of corrosion probability using half-cell potential measurements (ASTM C876-91) on single pieces of rebar embedded in the casted concretes after 90 days of ponding. Thereafter, scanning electron microscopy (SEM) was used to check if the inhibitors reacted with the rebar surfaces. The investigation ended with ferroxyl indicator and weight loss tests.

Secondly, it was planned to determine the chemical structure of Vappro CRI 4030 using FTIR. Compatibility of Vappro CRI 4030 with the concretes was also studied through compressibility strength test after a 28-days immersion in tap water. Results from this test were also discussed in accord with the chloride composition of concretes with similar dosage levels. The possible mechanisms of Vappro CRI 4030 were also proposed, namely: formation of vapour molecules

through migration and formation of complexes. They were then discussed with the tests' results obtained.

Key Words: amine, cathodic areas, chloride ions, compressive strength, corrosion inhibitor, half-cell potential, migration, phenolphthalein indicator, steel rebar, surface analysis, weight loss.

1.1   GENERAL

Steel corrosion in reinforced concrete costs European countries and the American to lose billions of dollars annually. This problem is widespread and affects all sectors of industry – construction, petrochemical, marine and transportation. Airports are no exception either. In the United States, there are about 583,000 bridges (1998). Of this figure, over 100,000 were structurally deficient and approximately 58.8% of the bridges are made of conventional reinforced concrete and prestressed concrete. Therefore, the annual induced cost of corrosion for the concrete used in the bridges mentioned above is around US$4.8 billion which is accounts for different areas such as maintenance cost, painting etc [1]. Elimination of all these bridge deficiencies was estimated to be from $78 billion to $112 billion, depending on how long it takes to make the repairs. While the corrosion of reinforcing steel is not the only cause of structural deficiencies in bridges in the United States, it is a significant contributor and therefore a matter of major concern (Virmani and Clemena 1998).

1.2   BACKGROUND

In the mid1970s, it was recognized that the deterioration of bridge deck concrete in snow belt states was caused by the corrosion of reinforcing steel which was in turn due to the ingress of chloride ions from these deicing salts. The benefits of deicing salt are too immense for its use to be ceased even though the cost of maintaining bridge decks is very high (Virmani and Clemena 1998); so, methods of effectively and economically protecting concrete from corrosion damage have received special attention since the early 1970s. The use of mild steel as a reinforcement for concrete structures is a well-established, practicable and economic solution for many civil engineering constructions. Many of such reinforced structures achieved decades of excellent service. However, over the past fifteen years there have been an increasing number of reports on

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[1] http://www.corrosioncost.com/infrastructure/highway/index.htm

corrosion failures. This is because common rebar is made of unfinished steel, making it susceptible to rusting. As rust takes up greater volume than the iron or steel from which it was formed, it causes severe internal pressure on the surrounding concrete, leading to cracking, spalling, and ultimately, structural failure. This is a particular problem where the concrete is exposed to salt water, as in bridges built in areas where salt is applied to roadways in winter, or in marine applications. The figure below showcases the corrosion process and total service life of the steel reinforcement.
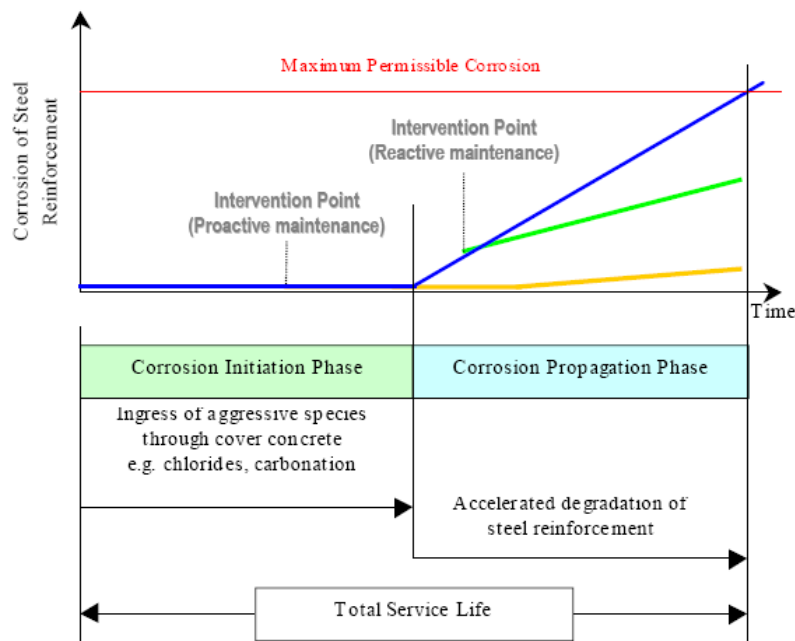

Figure 1-1. Schematic Representation of Corrosion Process and Total Service Life

1.3   CORROSION OF REINFORCING STEEL IN CONCRETE

Many metals, including iron, are found in their natural state as ores, natural oxides, sulfides, and other reaction products. These metals are usually derived from their ores by smelting, from which the metal absorbs and retains the energy needed to free it from the ore. This metallic state, however, is unstable because of its tendency to recombine with elements in the environment and return to its natural state and losing the extra energy in the process. Therefore, the process of a metal reverting to its natural state is called oxidation, or corrosion (Virmani and Clemena 1998).

Steel embedded in concrete is relatively prevented from corroding in most circumstances through the formation of a protective passive layer on the steel surface. This protective layer is stabilised

under highly alkaline concrete environment (pH 13-14). (Bentur et al. 1997). The passivation of the reinforcing steel in concrete is provided by the highly alkaline environment (pH 12.8) from the lime that was continuously produced from hydration reaction of cement. As long as the passive film on the reinforcing steel remains intact, the rate of corrosion is very low. However, if the oxide layer is broken, oxygen will be able to react with the steel and results in corrosion (Cathodic 1998).

Steel will remain corrosion resistant in concrete if the concrete cover prevents air and water from reaching the embedded reinforcement (Jones 1996). The ingress and reaction of carbon dioxide and sulphur dioxide will decrease the alkalinity to below a pH of 9.

Dissolved chloride ions are a big contributor to corrosion in concrete because they impair the passivity of the reinforcement and increase the active corrosion rate of steel. Oxidation is enhanced through the formation of an iron chloride complex, which is subsequently converted to iron oxide and chloride ions, which are then available to again combine with iron in the reinforcement. When corrosion products are deposited, they induce tensile stresses on the surrounding concrete, which cause cracking to occur (Jones 1996).

1.4   PREVENTIVE METHODS

It is since the late 1960s when corrosion of steel in reinforced concrete structures was first recognized as a problem in non-coastal areas. Thereafter, many methods have been developed with the intent of preventing corrosion from occurring. Generally, these methods can be divided into four different categories based on how they provide protection:

a. <u>Alternative reinforcement and slab design</u> includes materials that electrically isolate the steel from the concrete and create a barrier for chloride ions, materials that protect steel galvanically, and materials that have significantly higher corrosion thresholds than conventional reinforcing steel. Concrete slabs have been designed without any internal reinforcement.

b. <u>Barrier methods</u> protect reinforced concrete from corrosion damage by preventing water, oxygen, and chloride ions from reaching the reinforcement and initiating corrosion.

c. <u>Electrochemical methods</u> use current and an external anode to protect the reinforcement, even when the chloride ion concentration is above the corrosion threshold.

d. Corrosion inhibitors offer protection by raising the threshold chloride concentration level, by reducing the permeability of the concrete, or by doing both. There are a variety of generic types available, the principal ones being calcium nitrite and amino carboxylate.

1.5 OBJECTIVES AND SCOPE

It must be noticed that ever since the 1970s, many research projects and field studies have been conducted on different methods for protecting reinforced concrete bridge structures from corrosion damage. Good quality concrete is generally taken as the primary protection system for any structure, but in many situations, quality concrete must be combined with other corrosion protection methods to ensure sufficient durability. There is no single corrosion protection method that is totally effective under all circumstances.

Magna research team together Dr. Benjamin Valdez Salas and Dr. Michael Schorr Weiner of Autonomous University of Baja California (UABC) were tasked to look into the effectiveness of Vappro CRI 4030, a product of Magna International Pte. Ltd, in protecting the rebar in concrete against corrosion. It was aimed to:

a. study the effectiveness of the Vappro CRI 4030 in protecting the steel rebars against corrosion in concrete using different dosage levels (5, 10 and 15 grams).

b. propose the optimum amounts of Vappro CRI 4030 for maximum effectiveness in reinforced concrete.

c. observe the compatibility between Vappro CRI 4030 and the concrete by determining changes to the permeability of concrete (compressive strength).

d. determine the chemical structure of Vappro CRI 4030 and propose the possible mechanism of this corrosion rebar inhibitor.
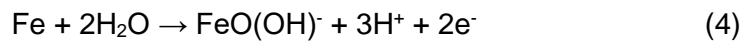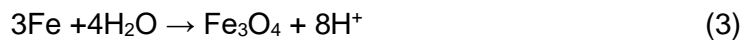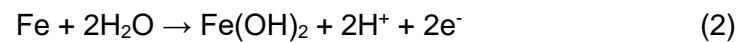
LITERATURE REVIEW

2.1   ELECTROCHEMICAL CORROSION OF STEEL IN CONCRETE

ASTM terminology (G 15-07 Standard Terminology) defines corrosion as "the chemical or electrochemical reaction between the material, usually a metal, and its environment that produces a deterioration of the material and its properties."

[2] Corrosion of steel in concrete is an electrochemical process in which the moist concrete forms the electrolyte. The followings are the reactions involved:

The Anodic Reaction

The reactions of iron in aqueous solutions can be described by a potential-pH diagram. The following were the only four primary anodic reactions to be considered generally:

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad\qquad (1)$$
$$Fe + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ + 2e^- \qquad\qquad (2)$$
$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H^+ \qquad\qquad (3)$$
$$Fe + 2H_2O \rightarrow FeO(OH)^- + 3H^+ + 2e^- \qquad\qquad (4)$$

A simplified potential-pH diagram (Figure 2.1) below, can be divided into regions representing immunity, corrosion (reactions 1 and 4) and passivity (reactions 2 and 3, which can form a protective layer of corrosion product on the surface). The basis of the passivity of iron and steel in an alkaline concrete environment therefore become apparent.

The Cathodic Reaction

The two principal cathodic reactions available for the corrosion of steel in concrete are indicated on the potential-pH diagrams:

$$2H^+ + 2e^- \rightarrow H_2 \qquad\qquad \text{line (a)}$$

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[2] N.J.M. Wilkins and P.F. Lawrence, AERE Harwell, Oxon, UK. *Chapter 8: The Corrosion of Steel Reinforcements in Concrete Immersed in Seawater*. Adopted from book: Corrosion of Reinforcement in Concrete Construction.

$$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^- \qquad \text{line (b)}$$
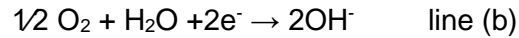
However, oxygen reduction is regarded as the cathodic reaction in most cases of significant corrosion of steel reinforcement.
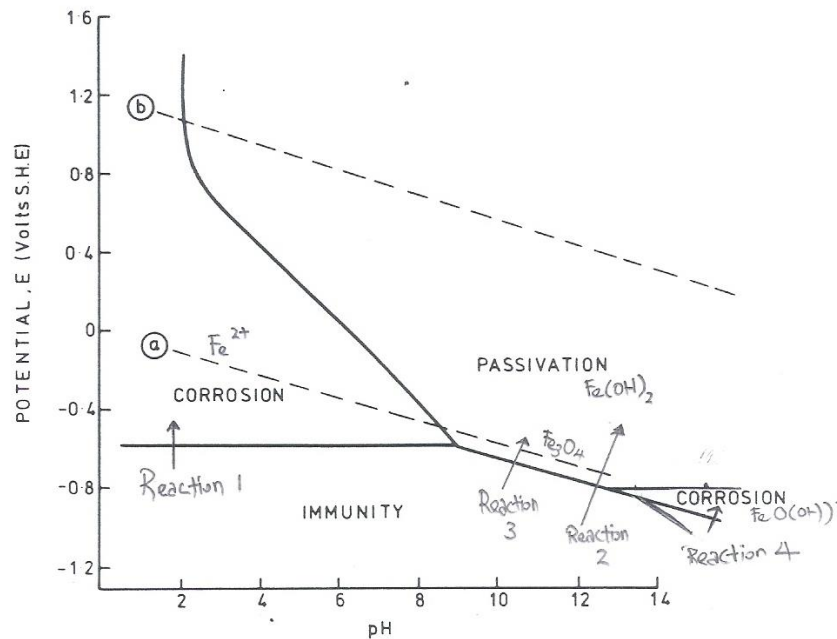

Figure 2-1. Potential-pH Diagram: Theoretical Conditions for Corrosion and Passivation of Iron

2.1.1 THE FOUR STATES OF CORROSION OF STEEL IN CONCRETE [3]

It may be useful now to define the four states (of protection or corrosion), in which the steel in concrete in concrete may find itself. The first state to be mentioned is:

a. The Passive State

Passive state is the protected state of steel in concrete, brought about by the high pH and the availability of oxygen. In this state, the corrosion rate is always insignificantly low at about 0.1m/year. In aerated concrete, the steel rebar will normally exhibit a potential in the range of +100 to -200 mV SCE.

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[3] H. ARUP, Korrosionscentralen, Glostrup, Denmark. *Chapter 10: The Mechanisms of the Protection of Steel by Concrete.* Adopted from book: Corrosion of Reinforcement in Concrete Construction.

b. The Pitting Corrosion

Pitting is typically brought about by the presence or ingress of chloride ions with characterization in the form of galvanic action between large areas of passive steel acting as cathode and small anodic areas, where the local environment has a high chloride concentration and a low pH. The average potential is typically -200 to -500 mV SCE and is between that of the passive steel and that of the local anode.
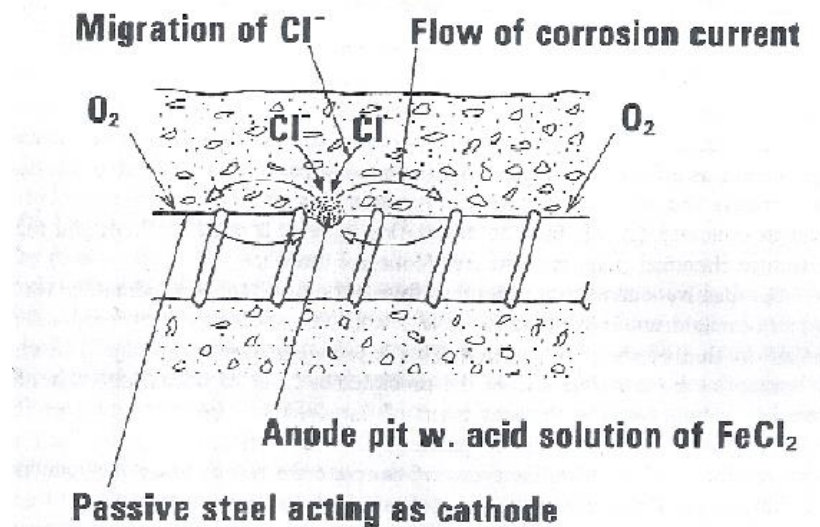

Figure 2-2. Electrochemical Corrosion Processes around a Corrosion Pit on Steel in Concrete.

c. General Corrosion

General corrosion happens due to the loss of passivity on the rebar due to carbonation and excess chloride ions and is similar to that of corroding steel in other environments. The electrochemical potential is typically around -450 to -600 mV SCE, and the potential gradients are not very great.

d. Active, Low-potential Corrosion

Active low-potential corrosion is initiated where the access of oxygen level is so limited and thus the passive film cannot be maintained. The equilibrium potential of iron in a solution of pH 13 is around -1000 mV SCE. Corrosion rate is however very low and re-passivation of the steel is possible when more oxygen is available.
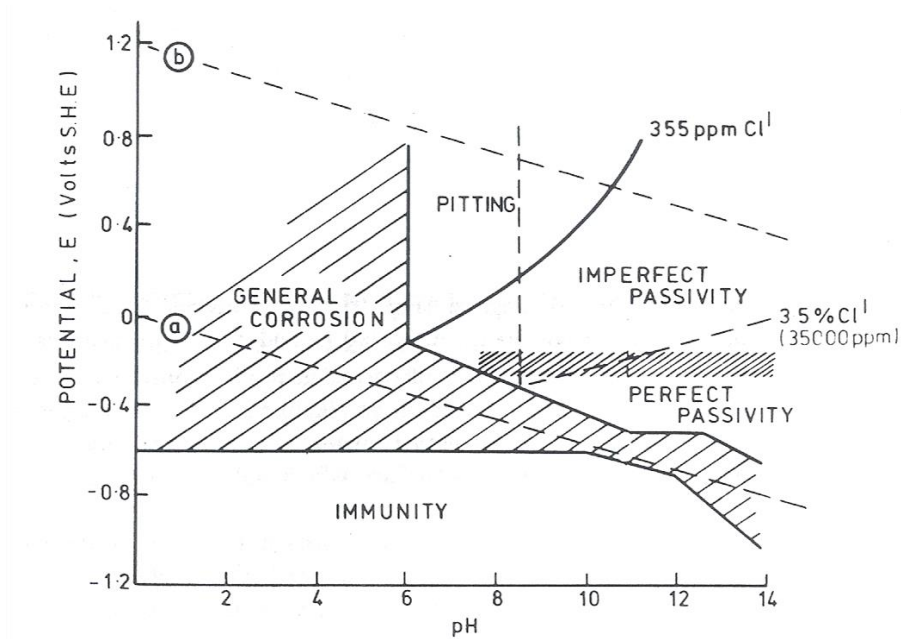
Figure 2-3. Influence of Chloride on Corrosion and Passivation of Iron

2.2   CORROSION INHIBITORS

Inhibitors are chemical compounds that, when added in relatively small amount, can help in slowing down or stopping the corrosion of metals and alloys. Corrosion inhibitors are one of a variety of techniques that can be employed in an effort to suppress and control the rate of steel corrosion in concrete structures, although their effectiveness is still open to debate and the subject of detailed research.

Due to the large number of commercially available concrete corrosion inhibitors, which vary widely in their respective formulations and inhibitive properties, categorisation is difficult. However, it is possible to divide concrete corrosion inhibitors into two generic categories.

- Concrete admixture inhibitors - used as a preventative measure.
- Surface applied and drilled-in inhibitors - used as a curative or preventative measure.

These two generic categories can be further subdivided into anodic, cathodic and mixed inhibitors depending upon the formulation of the inhibitor.

2.2.1 MECHANISMS OF CORROSION INHIBITOR

Corrosion inhibitors will usually react with the metallic surface, or the environment this surface is exposed to, thus giving the metal surface a certain level of protection. Thus, they often work by adsorbing themselves on the metallic surface and protect the metallic surface by forming a film or they are also able to slow corrosion process by reducing the movement or diffusion of ions to the metallic surface (acting as pore blockers).

2.3   TEST METHODS

2.3.1 FOURIER TRANSFORM INFRARED SPECTROMETRY

Fourier transform infrared (FTIR) spectrometry is a useful tool in helping to identify both organic and inorganic chemicals. Inhibitors categorized by their chemistry are split into inorganic, organic and vapour phase.

Inorganic inhibitor	Organic inhibitor	Vapour phase inhibitor
Nitrites, phosphates and other inorganic chemicals.	Amines and other organic chemicals.	A subgroup of the organic inhibitors (generally amino alcohols) that have a high vapour pressure.

Table 2-1. Categories of Corrosion Inhibitors

There are a number of ways to subdivide inhibitors, namely, by their action or by their chemistry and function. In this case, the interest was placed in the chemistry section as the chemical structure of VAPPRO CRI 4030 will be identified. After which, it will be useful in helping to propose its possible mechanisms. It is important to note for organic molecules that absorptions between 4000 and 1300 cm^{-1} are primarily due to the specific functional groups and bond types. Those between 1300 and 909 cm^{-1} is the fingerprint region, primarily due to more complex vibrational motions.

2.3.2 COMPRESSIVE STRENGTH TEST

[4] Concrete compressive strength is the most common test conducted for acceptance of concrete. Most concrete will require a minimum level of strength for structural design purposes regardless of the application. It is important for testing of compressive strength of concretes because:

a. It can investigate the fundamental physical behavior of concrete (permeability and strength characteristics)
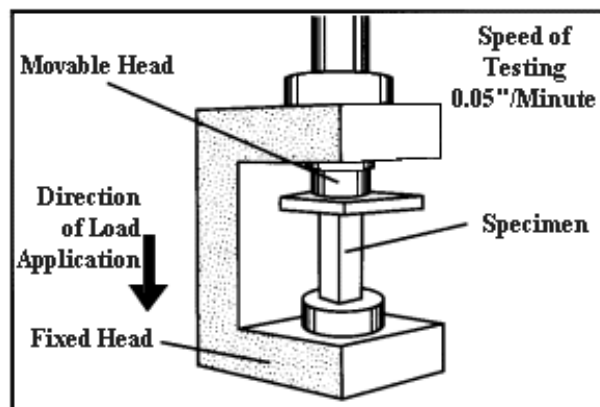b. Physical material constants need to be determined (modulus of elasticity & quality control)

Figure 2-4. Diagram of the Compressive Strength Testing Machine.

2.3.3 HALF – CELL POTENTIAL TESTING

Half-cell potential testing is most likely to be used for assessment of the durability of reinforced concrete where corrosion is suspected. Reported uses include the location of areas of high reinforcement corrosion risk in marine structures, bridge decks. Used in conjunction with other tests, it has been found helpful when investigating concrete contaminated by salts. Electrochemical techniques are useful for evaluating the behaviour of steel in concrete because many of the methods are non-destructive and can be used to monitor corrosion over time. Measuring the corrosion potential is the easiest electrochemical technique for monitoring corrosion in a structure (Bentur et al. 1997).

According to ASTM C876-91, half-cell potential test is able to measure the degree of corrosion by measuring the potential of an embedded reinforcing bar relative to a reference half-cell placed on the concrete surface. The half-cell used is usually a copper/copper sulphate cell but other combinations should also be applicable as well.
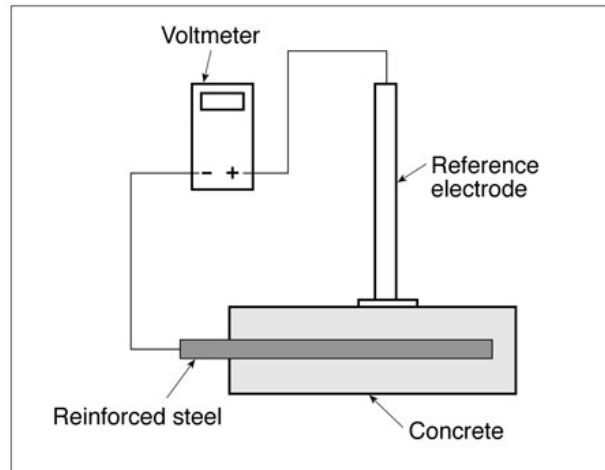

Figure 2-5. A Copper-Copper Sulphate Half-Cell.

The concrete functions as an electrolyte and the porous plug in the end of the cell allow the electrolyte to make contact with the concrete surface. As corrosion occurs, the potential reading differs for each location, thus potential is being measured at various locations to find out the probability of corrosion at each of the region. After measurements were taken, the readings are then compared with the ASTM standard (Table 2-2) to check the probability of corrosion occurring on the rebar.

Table

Potential Difference (mV)	Probability of Corrosion
>-500	visible evidence of corrosion
-350 to -500	95%
-200 to -350	50%
< -200	5%

2-2.

Probability of Corrosion According to Half-Cell Potential Readings (Cu/CuSO$_4$ electrode) [ASTM C876-91(1999)]

In this experiment, saturated calomel electrode (SCE) was used as well. This is because theoretically electrodes can be used interchangeably with adjustment to the calculation of

potential. For example, a potential reading of -200mV (Cu/CuSO$_4$) will be equal to -126mV (SCE) as calculation was done accordingly to the equation as follows:

$E_{\text{Metal vs. Electrode X}} = E_{\text{Metal vs. SHE}} - E_{\text{Electrode X vs. SHE}}$

$-0.2 \text{ V} = E_{\text{Metal vs. SHE}} - 0.318 \text{ V}$

$E_{\text{Metal vs. SHE}} = 0.118 \text{ V}$

$E_{\text{Metal vs. SCE}} = 0.118 \text{ V} - 0.244 \text{ V}$

$\qquad\qquad = -0.126 \text{ V}$

Potential Difference (mV)	Probability of Corrosion
>-426	visible evidence of corrosion
-276 to -426	95%
-126 to -276	50%
< -126	5%

Table 2-3. Probability of Corrosion According to Half-Cell Potential Readings
(Saturated Calomel Electrode)

## 2.3.4 ACID – SOLUBLE CHLORIDE IONS DETERMINATION TESTING

ASTM standard C 1152/1152M is the standard method for acid soluble chloride in concrete and mortar. In this method, powdered concretes were obtained by use of rotary impact drill and several such samples were mixed to obtain homogeneity. At least 20 grams of powder concrete was obtained and to minimise contamination, direct contact with the powder was avoided. The powder was then collected and mixed homogenously before pounding and weighing out 10g for use.

Sample digestion (Chapter 3.4.4 Section A) was carried out in nitric acid and deionised water (in 3:1 ratio) and boiled before filtering using a suction filter. After the solution was collected from the suction filter and by using silver nitrate as the titrant, the end-point volume reading was taken when the potentiometer reading of the solution reads -60.0 mV of the equivalence point determined in the water. Lastly, using the equation given, Cl % = 3.545*[(V$_1$-V$_2$)*N]/W, the amount of chloride in that sample was determined.

Two other methods were used instead in this project and they were Mohr's method of titration and ion selective electrode method.

2.3.4.1 MOHR'S METHOD OF TITRATION

This method determines the chloride ion concentration of a solution by titrating it with silver nitrate. Precipitate of silver chloride forms as the silver nitrate solution is slowly added. When all the chloride ions are precipitated, the titration reaches its end point. Additional silver ions react with the chromate ions of the indicator, potassium chromate, to form a red-brown precipitate of silver chromate.

Ag^+ (aq) + Cl^- (aq) $\rightarrow$ AgCl (s)

2 Ag^+ (aq) + CrO_4^{2-} (aq) $\rightarrow$ Ag_2CrO_4 (s)
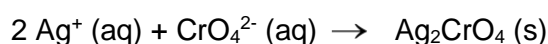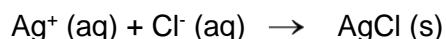
This method can be applied in determining the chloride ion concentration of water samples such as seawater. The Mohr method must also be performed in the pH range of 6.5 to 10. If the pH is too high, brownish silver hydroxide forms and masks the endpoint. If the pH is too low, the chromate is converted to dichromate and the endpoint comes too late or cannot be perceived at all. [5]

2.3.4.2 ION SELECTIVE ELECTRODE

The Ion Selective Electrode (ISE) uses ion selective membrane to allow only Cl^- ions to penetrate to the electrode. A potential drop is developed between the two sides of the sensing membrane. This potential is proportional to the logarithm of the concentration of the chloride ion according to the Nernst equation:

$$E = E_0 + S \ln(C)$$

Where E is the measured voltage, E_0 is the reference potential, S is the gradient and

C is the chloride concentration.

The response curve or calibration curve of an ion-selective electrode can be measured and plotted as the signal (electromotive force) versus the activity of the analyte when using a series of calibrating solutions. Based on the linear range obtained, it can be used to determine the activity

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[5] http://www.outreach.canterbury.ac.nz/chemistry/documents/chloride_mohr.pdf

of the target ion in any unknown solution. However, at constant ionic strength, a linear relationship between the signal measured and the concentration of the analyte is maintained due to the relationship between the ion activity and concentration.

2.3.5 SCANNING ELECTRON MICROSCOPY ANALYSIS

Scanning Electron Microscopy (SEM) is a type of electron microscope capable of producing high-resolution images of a sample surface. Due to the manner in which the image is created, SEM images have a characteristic three-dimensional appearance and are useful for judging the surface structure of the sample.

The SEM has compensating advantages, though, including the ability to image a comparatively large area of the specimen; the ability to image bulk materials (not just thin films or foils); and the variety of analytical modes available for measuring the composition and nature of the specimen. Depending on the instrument, the resolution can fall somewhere between less than 1 nm and 20 nm. In general, SEM images are much easier to interpret than TEM (Transmission Electron Microscopy) images. [6]

Four rebars taken from the concretes dosed with different amount of VAPPRO CRI 4030 were used for this SEM experiment. With the help of SEM, the elements present on the surface of these rebars were determined.

2.3.6 VISUAL INSPECTION

Visual testing is probably the most important of all non-destructive tests and it often provides the first indication for a comprehensive survey. It often provides valuable information about structural serviceability, and material deterioration etc. It is particularly important that the engineer is able to differentiate between the various signs of distress which may be encountered. These include for instance, cracks, pop-outs, disintegration, colour change, weathering, staining, surface blemishes and lack of uniformity. Once the cover has been removed and the concrete has been cut back to expose the bar then the type of corrosion, the degree of pitting and nature of the corrosion products may all be important indicators of the cause of corrosion. Extensive information

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[6] P.R. Thornton. *Scanning electron microscopy: applications to materials and device science.*

can be gathered from visual inspection to give a preliminary indication of the condition of the structure and allow formulation of a subsequent testing. [7]

2.3.6.1 PHENOLPHTHALEIN INDICATOR TEST

All concretes are highly alkaline when they are cast. The alkaline condition of the concrete causes a film to form around the rebar, thereby protecting it from corrosion. The alkalinity protects the rebar by a process called "passivation". A relatively high alkalinity is to be maintained in order to protect the rebar. If the pH of the concrete falls below about 10, the potential for rebar corrosion increases. When the pH is in the 8 to 9 range, it is a good indication that some carbonation is taking place from the surface of the concrete toward the inside.

Concrete is cracked open and sprayed with a solution of 1% phenolphthalein indicator in 95% alcohol. The indicator will turn bright pink if pH of concrete is > 10 and colourless if less than 8. This will thus show whether the concrete is still alkaline or has lose its alkalinity. If it loses its alkalinity, there is a probability that the rebar will be affected by carbonation and loses its passivity. This will result in corrosion of the rebar as the passive film breaks down.

2.3.6.2 FERROXYL INDICATOR TEST

All the mild steel carries a thin, air-formed oxide film on their surfaces. In initial anodic areas develop at points where the film is cracked or otherwise weak (and so produce a blue colour) and the associated cathodic reactions take place at nearby areas (giving the pink colour) where the oxide is probably thicker.

$$Fe \rightarrow Fe^{2+} + 2e^- \text{ (Blue)}$$
$$2H_2O + O_2 + 4 e^- \rightarrow 4OH^- \text{ (Pink)}$$
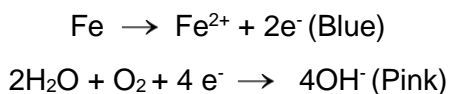
Generally, the initial distribution of anodic and cathodic areas is random although the anodic areas may be distributed along the directions of abrasion of the metal. However, after a time, the oxygen present in the centre of the drop becomes exhausted and the cathodic reaction in this region stops. The cathodic process is now favoured at the edge of the drop where access of oxygen is

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[7] J.L. Dawson, UMIST, Manchester, UK. *Chapter 12: Corrosion Monitoring of Steel in Concrete.*

easier. Any ferrous ions produced in the peripheral region exist in an alkaline environment and a compound will be formed in physical contact with the metal, so stifling any anodic reaction. In the centre of the drop, the anodic reaction will continue since the solution is not alkaline and no precipitate forms.

2.3.7 WEIGH LOSS TEST

As corrosion occurs in the presence of water, rust is formed on the surface of the rebar.

$$Fe \rightarrow Fe^{2+} + 2e^-$$
$$Fe^{2+} + H_2O \rightarrow Fe(OH)_2 + 2H^+$$
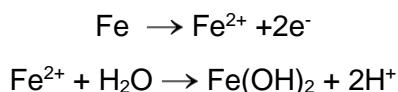
As the oxide layer on the rebar was washed away by acid, the weight of the rebar is reduced. The difference in the initial weight and the final weight of the rebar indicates how much the rebar has corroded. However, in this study, the quantity of weight loss could not be used as a direct measurement of corrosion. This is because the exposed part of rebar has corroded despite the protection of the VCI film and this would play a part in the total weight loss. Interests were place on the parts of the rebar that were covered by the concrete. Nevertheless, it was possible to do relative comparison with regard to the steel rebar's weight loss retrieved from concretes of control, 5 gm, 10 gm and 15 gm dosage level by taking the weight loss due to those areas uncovered by the concrete as a constant since they were protected in the same way by the VCI film and exposed to the same environment.

MATERIALS AND METHODS

3.1   METHODOLOGY

The Vappro CRI 4030 concrete admixture inhibitor was directly added into the concrete mixture according to different dosage levels as an additive during the casting process at the construction site in Tampines Singapore. A total of 16 concretes were cast but only eight of them were implanted with the polished steel rebars. These eight concretes were also labelled A to H to avoid confusion as the concretes were then left to cure overnight. These concretes were then partially submerged in tanks of seawater for 90 days as of 18th December 2017.

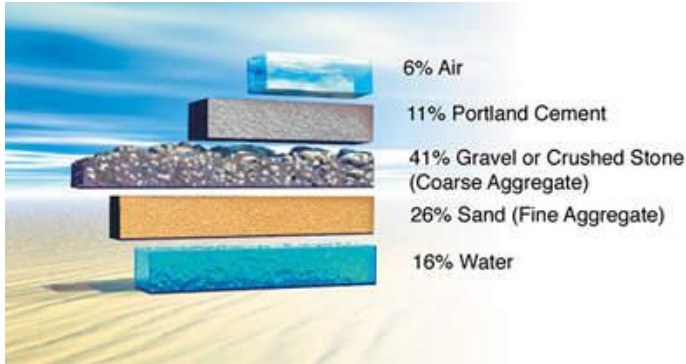Figure 3-1. Partial Submersion of Concretes in Seawater.

At the end of the 90 days period, the reinforced concretes were subjected to tests like half-cell potential (ASTM 876-80) using copper/copper sulphate electrode and saturated calomel electrode; determination of acid-soluble chloride ions with titration and ion selective electrode; and phenolphthalein indicator test. On the other hand, the rebars underwent SEM analysis of their surface; ferroxyl indicator testing and lastly determination of total weight loss.

The remaining eight concretes were labelled I to VIII at the point of casting. They were then fully submerged in pails of tap water for 28 days before undergoing compressive strength test. Last but not least, the chemical functional groups of VAPPRO CRI 4030 were determined by FTIR that it contains amine.

3.2   PREPARATORY WORK

Materials used	Composition

Grade 30 Concrete	Portland cement, aggregate (generally gravel, sand and crushed stone), water and chemical admixtures (retarders; which slow the setting rate of concrete, are used to counteract the accelerating effect of hot weather on concrete setting) Figure 3-2. Composition of Cement; adapted from http://www.cement.org.	Table 3-1. List of
Rebar	Common steel rebar made of carbon and steel with low carbon content (<0.3%) or called mild steel.	
VAPPRO CRI 4030 powder	Developed by Magna International Pte Ltd.	

Materials Used.

3.2.1 PREPARATION OF MILD STEEL REBARS

All the eights mild steel rebars were soaked in 3 M of sulphuric acid for approximately 20-30 minutes to remove as much rusting as possible. Sponges were used to 'scrub' for a more rust-free rebar. Subsequently, they were washed with deionised water and wiped dry singly. Instantaneously, tissue papers were used to wrap the rebars and kept in the chamber until the day for casting of concrete.

3.2.2 CONCRETES CASTING

The casting of all the 16 concretes was done at a construction site in Tampines Singapore and was assisted by the labour workers present. The concrete used was of Grade 30 as indicated by Magna International, Moulds were used for the casting process. Magna's team was there to apply the VAPPRO CRI 4030 powder and making sure that the right amount was introduced and concretes were correctly labelled.

Concrete Sample		Dosage Level of VAPPRO CRI 4030
A	I	5 gram
B	II	
C	III	10 gram
D	IV	
E	V	15 gram
F	VI	
G	VII	0 gram (Control)
H	VIII	

Table 3-2. Labelled Concretes and Corresponding Dosage Levels of VAPPRO CRI 4030.

3.3   REAGENTS AND EQUIPMENT

a. Fourier Transform Infrared Spectrometry
- PerkinElmer Spectrum 100 FT-IR spectrometer
- Mortar and Pestle
- Accessories of KBr Pellet Equipment (Graseby Specac Press, Die Grinder and etc.)
- Absolute Cleaning Ethanol

b. Compressive Strength Test
- Top-Loading Weighing Balance
- Toni Technik Compressive Strength Machine & "Testxpert" Software

c. Half – Cell Potential Test
- Colebrand Saturated Calomel Electrode

- Copper/Copper Sulphate Electrode
- Colebrand High Impedance Voltmeter and Connecting Wire Probes

d. Acid-Soluble Chloride Ions Determination Test
- 0.05 N Silver Nitrate Solution (8.4938 g $AgNO_2$ / 1 L of Deionised Water)
- Methyl Orange Indicator
- Merck Chloride Ion Standard Solution (1000 ppm)
- Potassium Dichromate Solution
- Diluted Nitric Acid (1 M)
- Suction Filter Pump
- Thermo Ionplus Sure-Flow Chloride Ion Selective Electrode
- Orion 3 Star Ion Meter (Thermo)
- Drill suitable for drilling concrete purposes.

e. Scanning Electron Microscopy Analysis
- JOEL JSM – 5300 LV Scanning Microscope
- High Speed Hack Saw

f. Phenolphthalein Test
- Phenolphthalein indicator (1 % Phenolphthalein indicator in 95 % alcohol)

g. Ferroxyl Test
- BDH ProLab Sodium Chloride
- BDH ProLab Potassium Hexacyanoferrate
- Phenolphthalein Indicator

h. Weigh Loss
- 3 M Sulphuric Acid
- Weighing Balance

3.4   PROCEDURES

3.4.1 FOURIER TRANSFORM INFRARED SPECTROMETRY

A clean work space was established before the start of the experiment.

i. 10 mg of VAPPRO CRI 4030 powder and 50 mg of KBr powder were mixed in a mortar and grinded finely with a pestle. The KBr powder was to be of spectroscopic grade purity, and spectroscopically dry.

ii. The mixture was to be homogeneous and had the consistency of fine flour.

iii. The die was assembled, with the lower pellet polished face up.

iv. Thereafter, the grounded mixture was transferred into the cylinder bore so that it was evenly distributed across the polished face of the lower pellet. The plunger was inserted gently and swivelled slightly to achieve a flat, even surface.

v. The second pellet could be then inserted as well with the polished surface towards the mixture, into the bore followed by the plunger.

vi. The die assembly was placed into a hydraulic press and a pressure of 8 – 9 tonnes was applied on it

vii. The mixture would then form a transparent film pellet.

viii. This pellet was then placed onto the sample compartment of the Specac IR sample card holder for FTIR analysis.

ix. The sample card holder was then scanned from 4400 to 450 cm^{-1} and the IR spectrum was obtained and printed.

Figure 3-3. PerkinElmer FTIR Spectrometer

3.4.2   COMPRESSIVE STRENGTH TEST

i.   All the concretes were being weighed out by the top-loading weighing balance initially.

ii. The concretes were being inserted into the Toni Technik Compressive Strength Machine individually for testing.

Figure 3-4 & 3-5. Compressive Strength Test Equipment.

iii. The machine started to compress the concrete and by using "Testxpert" software and the results were being recorded subsequently.

iv. Steps c & d were repeated for the rest of the concretes.

3.4.3   HALF – CELL POTENTIAL TEST [9]

i.   The concretes were pre-wetted for at least 24 hours using soaked cloths to cover the all the 4 sides of the concretes except for the top and base.

ii. The protruding rebars of the all concretes were filed using abrasive and sandpaper to remove as much rust as possible.

iii. The Copper/Copper Sulphate Electrode solution was prepared by dissolving the Copper Sulphate crystals in deionised water.

iv. The Saturated Calomel Electrode (SCE) was prepared by filling the inner electrode with saturated KCl.

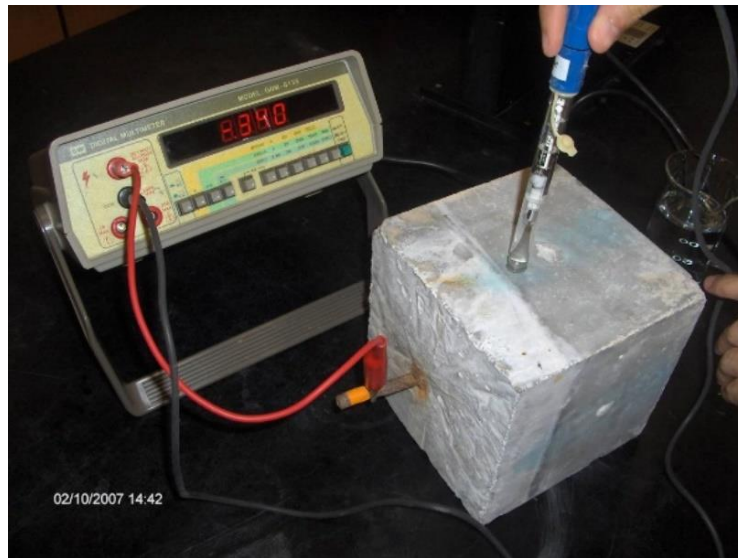v. The half-cell apparatus was set up according to figure 3-6.

Figure 3-6. Half-Cell Potential Connection

vi. The potential readings were taken from 3 positions naming top, middle and bottom of the concrete's sides where they were being partially submerged in seawater.

Figure 3-7. Measurement Positions of Half-cell Potential Testing

vii. Measurements were taken on all four sides of the concretes and this means one concrete will have twelve readings. The average of these readings was calculated.

3.4.4   ACID – SOLUBE CHLORIDE IONS DETERMINATION TEST [9]

A. Sample Preparation

ASTM C-1152/1152M was the method used to determine the amount of chloride ions in the concrete. However, due to the limitations such as lack of equipment available that were required in the ASTM and etc., only the initial step adopted was the digestion of the concrete samples obtained. Determination of chloride ions by using other methods was done after digestion of the concrete samples. Drilling was needed to obtain sample from the concrete. Therefore, during the sampling process, it was standardized to drill up to a depth of 30mm for each concrete. Several similar areas drilled were concentrated at the central submerged area as this helps to ensure homogeneity. The following picture would give a rough idea of the drilling process for the concretes.

Figure 3-8. The Concrete after Drilling.

The initial steps to extract out the acid-soluble chloride ions from the concrete were as followed:

i.   Approximately 10 g of sample was extracted from the concrete and transferred into a 250ml beaker.

ii. Sample was diluted in 37.5 ml of de-ionized water and 12.5 ml of dilute nitric acid.

iii. 3 drops of methyl orange indicator was added into the beaker and stirred.

iv. Nitric acid was then added dropwise until the solution turned pink.

v.   10 additional drops of nitric acid were added and the solution was stirred.

vi. Beaker was covered with watch glass and allowed to stand for around 2 minutes.

vii. Covered beaker was heated to boil rapidly and removed from hotplate.

viii. Solution was filtered through the Buchner funnel and filtrate was collected in a 250ml volumetric flask.

From the above preparation, the solutions were then used for analysis through two types of methods, namely Mohr Method of Titration and Chloride Ion Selective Electrode to determine the amount of chloride ions in each sample.

B. Mohr's Method of Titration

(i)   Preparation of Standard Chloride Solutions

Range: 10 ppm, 50 ppm, 100 ppm and 500 ppm

This range was selected to test out the workable concentration range that the Mohr's method of titration would be in our application. After which, back-calculation was done by using chemical equation to check whether the amount of chloride ions present tally with the standard solutions prepared.

Dilution was carried out from using the Merck 1000 ppm Cl⁻ standard solution.

1000 ppm

2x Dilution   10x Dilution   20x Dilution   100x Dilution

500 ppm   100 ppm   50 ppm   10 ppm
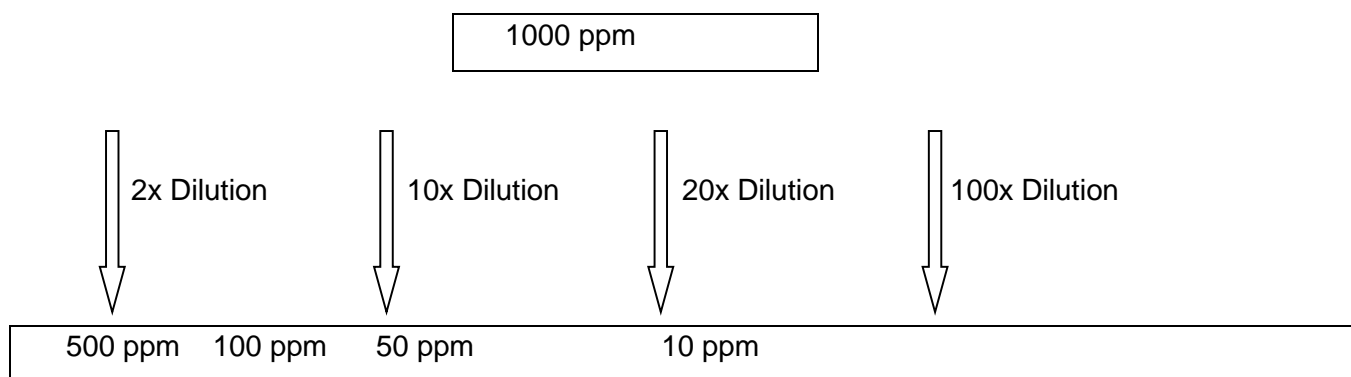
Using the simple equation of $M_1V_1 = M_2V_2$, dilution was carried out as the volume of 1000pm Cl⁻ solution needed was determined as followed:

- For 10 ppm solution, 1 ml of the 1000 ppm standard solution was added into the 100ml volumetric flask and topped up with deionised water.
- For 50 ppm solution, 5 ml of the 1000 ppm standard solution was added into the 100ml volumetric flask and topped up with deionised water.
- For 100 ppm solution, 10 ml of the 1000 ppm standard solution was added into the 100ml volumetric flask and topped up with deionised water.
- For 500 ppm solution, 50 ml of the 1000 ppm standard solution was added into the 100ml volumetric flask and topped up with deionised water.

(ii)   Mohr's Titration using the Standard Solutions prepared

- Potassium chromate indicator was added to the 100 mL standard solutions prepared. (colour will change from colourless to pale yellow colouration)
- Silver nitrate was then titrated against those standard solutions.

- The end point of the titration was reached when solution turned from yellow to reddish brown and the volume used was recorded for calculation later.
- Triplicates of results were achieved with each standard solution of different concentrations.

(iii)   Mohr's Titration using the Concrete Sample Solution Prepared

- Potassium chromate indicator was added to the 50 mL of concrete sample solutions prepared. (colour will remain yellow as the initial solution is pale yellow)
- Silver nitrate was then titrated against concrete samples.
- The end point of the titration was reached when solution turned from yellow to pale brown or reddish brown and the volume used was recorded for calculation later.
- Duplicate of results were achieved with each concrete sample.

C. Chloride Ion Selective Electrode Method

   i. Preparation of Standard Chloride Solutions

Range: 1 ppm, 10 ppm, 100 ppm and 1000 ppm
This range was selected as a calibration graph was to be worked out to determine the amount of chloride in our sample. By using these standards, a linear log graph was plot and the concentration of each sample could be determined by using the calibration graph and calculation.

Dilution was also carried out from using the Merck 1000 ppm Cl$^-$ standard solution.

   ii. Calibration using Standard Solutions Prepared

- Standards of 1 ppm, 10 ppm, 100 ppm and 1000 ppm solutions were prepared in 50mL volumetric flasks.
- Measurements were made from lowest concentration to highest.
- A magnetic rod was put into the solution to maintain homogeneity.
- Readings were taken after they stabilized and the same potential reading was achieved twice consecutively.

- After each concentration, the electrode was washed to ensure as little contaminant as possible.
- A calibration graph was plotted using the set of results.

iii. Measurements for Concrete Sample Solutions

- The Chloride Ion Selective Electrode was washed at least twice with deionized water to ensure no contaminants are on it.
- A magnetic rod was put into the 50 mL of concrete sample solutions prepared and stirred to maintain homogeneity.

- The electrode was then lowered into the concrete sample solutions and readings were taken after they stabilized and the same potential reading was achieved twice consecutively.
- At the end of each reading, the electrode was washed again before taking the next reading.
- Duplicate of results were achieved with each concrete sample.
- Average reading of each concrete sample was then calculated and the results (amount of chloride ions present) were interpreted from the calibration graph. Appropriate calculation was done to re-calculate the original amount of chloride ions present in the 10 gm of concrete sample.

3.4.5 SCANNING ELECTRON MICROSCOPY ANALYSIS

a. Four rebars (A, D, E and G), each taken from the concretes dosed with different amount of VAPPRO CRI 4030 were used for this SEM experiment. About 6 – 7 cm of the embedded area of the rebars was saw for the purpose of this experiment.

b. One specimen sample was placed in the specimen chamber at a time.

c. The air in the chamber was fully withdrawn, leaving it in the vacuum state.

d.   A 500X magnification was used in our case and appropriate optimisation by the TSO Mr. Sunny. The Auto-Beam programme will be able to gather the image of the analysed surface.

e.   For elemental analysis, Link ISIS's X-Ray Analysis programme was required.

3.4.6   PHENOLPHTHALEIN INDICATOR TEST

a.   All the concretes were cracked open using a breaker.
b.   A few drops of phenolphthalein indicator were applied on the surface and the inner part of the concrete which has the closest proximity to the rebar.
c.   The area of the concrete applied with the phenolphthalein will turn pink if the concrete has high alkalinity or otherwise colourless if the concrete had lost its alkalinity.

3.4.7   FERROXYL INDICATOR TEST

a.   250 ml of Ferroxyl indicating solution was prepared using 7.5 g of sodium chloride (NaCl), 0.5 g of potassium hexacyanoferrate [$K_3Fe(CN)_6$] and 1.25 ml of phenolphthalein solution.
b.   Mild steel rebars were dipped into the solutions containing the ferroxyl indicator were left for 5 to 10 minutes of observation.

3.4.8   WEIGH LOSS TEST

a.   The steel rebars were all soaked inside beakers of 3M sulphuric acid for at least three to five minutes to remove as much rust as possible.
b.   After which, the steel rebars were rinsed with deionised water to wash away any rush on it.
c.   The rebars were wiped dry with the hand towels and necessary filing was done to remove any remaining rust.
d.   Their respectively weights were taken using the weighing balance.

RESULTS AND DISCUSSION

4.1   FTIR

The IR spectrum for Vappro CRI 4030 was obtained and identification of its possible chemical functional groups was based on the intense bands shown at various frequencies.

The following table is the showcase of the main bonds that are identified with the intense bands in the IR spectrum.

Possible bonds	Specific context	Predicted frequency range (cm^{-1})	Observed frequency (cm^{-1})
N – H	R$_2$NH	3350 – 3500	
O – H	O – H	3200 – 3600	**3424**
C – C	C = C	1620 – 1680	**1650**
C – O	C – O	1020 – 1275	**1272**
C – N	C – N	1030 – 1230	**1092**
Alkenes	R$_2$C=CH$_2$	890	**881**

Table 4-1. Summary of Peaks from Vappro CRI 4030's IR Spectrum.

Bands observed at 3424 and 1272 cm^{-1} indicate the main functional group of Vappro CRI 4030 and it can be deduced that this inhibitor might have amine and alcohol functional groups. Other bonds identified include C-N and alkenes (C = C). This further reinforced the possible identity of Vappro CRI 4030 contains amine and alcohol functional group.

4.2   COMPRESSIVE STRENGTH TEST

As stated in the theory, concrete compressive strength is one of the most common tests conducted for the acceptance of concrete. Therefore, most concrete will require a minimum level of strength for structural design purposes regardless of the application.

The table below shows the results gathered after conducting the compressive strength test on the samples of concrete with different dosage levels of Vappro CRI 4030 and two control samples (G & H) with no Vappro CRI 4030. The test was conducted using the Toni Technik compressive strength machine.

Concrete No.	Amount of Vappro CRI 4030 in concrete (grams)	Weight (Kg)	Compressive Strength (kN)	Average Compressive Strength (kN)	Standard Deviation (kN)
A	5	7.9541	1317.09		
B	5	8.0232	1294.45	*1305.77*	16.0089
C	10	7.9996	1300.87		
D	10	8.0516	1243.32	*1272.10*	40.6940
E	15	8.0547	1045.21		
F	15	7.9212	1123.33	*1084.27*	55.2392
G	0	7.9711	1206.22		
H	0	8.1105	1387.67	*1296.95*	128.3045

Note: The compressive strength values are generated by the "Testxpert" software thus no calculations are included.

Table 4-2. Summary of Compressive Strength Test Results.

The bar chart below depicts a clear picture of the relationship of the compressive strength with the dosage levels of Vappro CRI 4030.
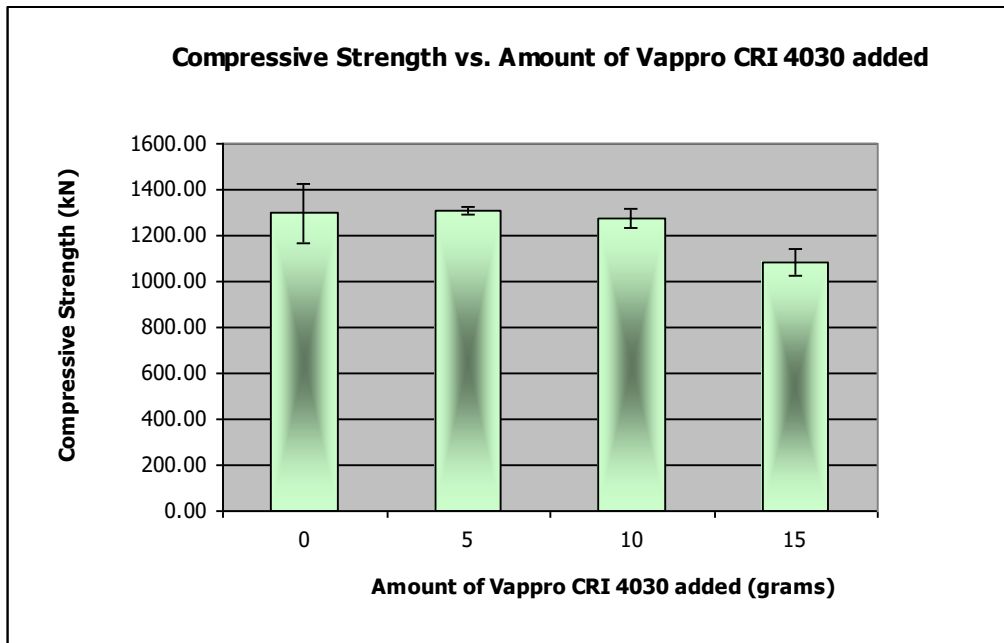

Figure 4-1. The Bar Graph of Compressive Strength vs. Amount of Vappro CRI 4030 added.

The duplicate results were combined and shown on the graph above together with the standard deviation involved. It could be seen that the compressive strength of control and that of those concretes with dosage levels of 5 gm and 10 gm Vappro CRI 4030 seem to be more or less the same. While on the other hand, the concretes dosed with 15 gm of Vappro CRI 4030 seems to have a lower compressive strength compared to the rest.
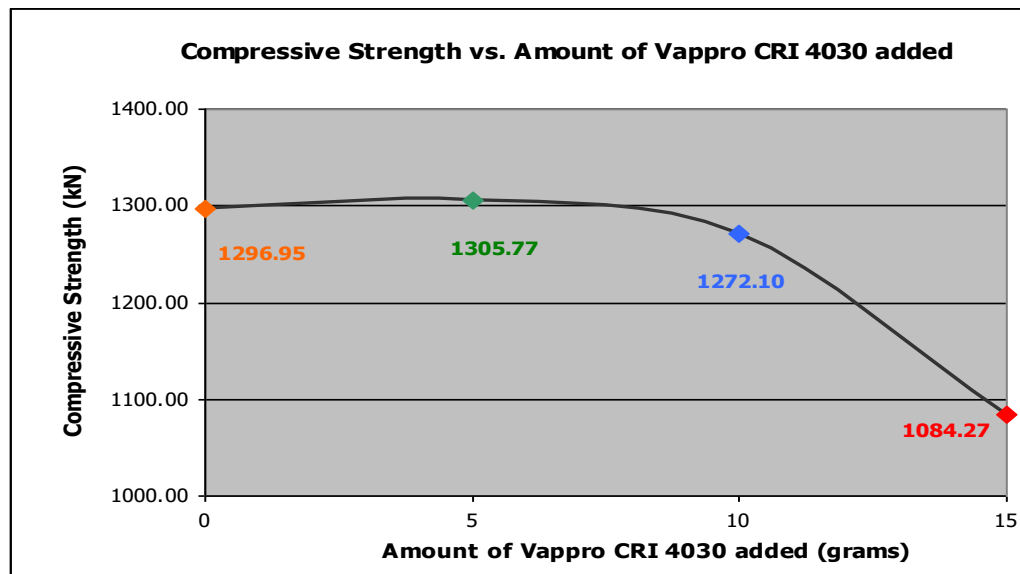

Figure 4-2. Trend line Graph of Compressive Strength vs. Amount of VAPPRO CRI 4030 added.

From the trend line graph, it could be seen once again that adding 5 or 10 gm of Vappro CRI 4030 in the concrete did not really cause a significant effect on the compressive strength. On the other hand, the change was rather obvious when 15 gm of VAPPRO CRI 4030 was added instead. The difference accounted is about 200 kN.

Hypothesis testing on the difference of means to determine whether those concretes added with 5 gm, 10 gm and 15 gm of Vappro CRI 4030 had any significant effect on the value of compressive strength was ruled out. The reasons were due to the small sample size and preciseness of the Toni Technik Compressive Strength machine.

However, it could be inferred that adding 15 gm of Vappro CRI 4030 powder into the concretes had caused their compressive strength to be lower with reference to the control, 5 gm and 10 gm after 28-day immersion in tap water. A lower compressive strength value means that the concrete in turn has higher permeability. This suggested that ionic species from the surrounding

environment have a greater chance of advancing into the matrix of the concrete as more pores are present.

One reason that can be suggested for this decrease of compressive strength was the complexes that the Vappro CRI 4030 might have formed with the calcium/aluminum/silicone present in the concrete. These complexes supposedly help filling up the pores in the concrete during the curing process. It was likely that 15 gm of Vappro CRI 4030 might form too much of such complexes and these complexes might instead create minute cracks among the whole matrix of the concrete and thus resulting in higher permeability and a lower compressive strength.

4.3   HALF – CELL POTENTIAL TEST

In this half-cell potential testing, 12 readings were taken on every individual concrete and the average was determined. Thereafter, the duplicate of the three different dosage levels and the control sample were averaged and compared. In addition, two different reference electrodes: copper/copper sulphate electrode and saturated calomel electrode were used in this testing

4.3.1   Copper/Copper Sulphate Electrode (CSE)

Concrete	Amount of Vappro CRI 4030 added	Average of 12 readings (V)	Average of Duplicate (V)
A	5 grams	-0.335	-0.370
B	5 grams	-0.405	
C	10 grams	-0.316	-0.315
D	10 grams	-0.314	
E	15 grams	-0.314	-0.313
F	15 grams	-0.312	
G (control)	0 gram	-0.387	-0.377
H (control)	0 gram	-0.366	

Table 4-3. Summary of Half-Cell Potential Results using CSE.

This was done in accordance with ASTM C876-91. With reference to Table 2-2. which states the probability of corrosion with regards to the potential differences, the probability of corrosion for the rebar in concrete could be summarised in the following table:

Dosage levels of Vappro CRI 4030.	Experimental reading (V)	Probability of Corrosion
Control (0 gm)	-0.377	95%
5 gm	-0.370	95%
10 gm	-0.315	50%
15 gm	-0.313	50%

Table 4-4. Summary of Corrosion Probability and the Experimental Readings.
(Electrode used: CSE)

From the table above, it could be seen that the steel rebars embedded in the concretes of 10 gm Vappro CRI 4030 had a 50% probability of corrosion and that was similar to the 15 gm of Vappro CRI 4030. This was in contrast to the other two dosage levels of 5 gm and control as the steel rebars embedded in concretes had probability of corrosion stated at 95%.

4.3.2 Saturated Calomel Electrode (SCE)

Concrete	Amount of Vappro CRI 4030 added	Average of 12 readings (V)	Average of Duplicate (V)
A	5 grams	-0.321	
B	5 grams	-0.354	-0.338
C	10 grams	-0.264	
D	10 grams	-0.258	-0.261
E	15 grams	-0.258	
F	15 grams	-0.254	-0.256
G (control)	0 gram	-0.340	
H (control)	0 gram	-0.234	-0.287

Table 4-5. Summary of Half-Cell Potential Results using SCE.

With reference to Table 2-3, the probability of corrosion for the steel rebars in the concretes using the potential readings gathered could be summarised as follows:

Dosage levels of VAPPRO CRI 4030.	Experimental reading (V)	Probability of Corrosion
Control (0 gm)	-0.287	95%
5 gm	-0.338	95%
10 gm	-0.261	50%
15 gm	-0.256	50%

Table 4-6. Summary of Corrosion Probability and the Experimental Readings.
(Electrode used: SCE)

From the table above, it could be seen that only the steel rebar embedded in the concretes containing 10 gm of VAPPRO CRI 4030 indicated a 50% probability of corrosion. Control showed a potential of -0.287 V which was more negative than the passing mark of -0.276 V for 95% probability of corrosion. Other two dosage levels of 10 gm and 15 gm showed similar results in the two tests with different electrodes.

It is important to note that the probability of corrosion stated cannot be taken as the corrosion rate of the rebars; neither do they give the exact condition of the rebar being corroded. It is only used as a prediction of the probability of corrosion on the rebar.
Based on the two tables of potential voltages results, it could be concluded that the steel rebar embedded in concrete with 10 grams and 15 grams of Vappro CRI 4030 showed one of the lowest voltages and possibly only 50% of corrosion chances which is also known as the 'uncertain' range. Bentur et al. 1997 states that in the 'uncertain' range, potential differences and other corrosion detection methods must be used. Although potential measurements are not uniquely related to corrosion, they can provide a good indication as to whether corrosion is active in a particular area.

However, the control showed both high and 95% chances of corrosion when using CSE and SCE respectively.

Research through references had also stated that in the field, half-cell measurements are usually taken using a **copper-copper sulphate (CSE) electrode**, and are fairly accurate when proper pre-wetting of the concrete is used (ACI 222 1996). Other common reference electrodes for use

on steel in concrete are the **saturated calomel electrode (SCE)** and the silver/silver chloride electrode (Ag/AgCl) (Bentur et al. 1997).

In the ASTM table 2.2, the 95%, 50% and 5% probability of corrosion contained huge intervals in between; it was thus impossible to have corrosion probabilities of 20%, 40% or 80%. This meant that a minute 0.001 V change from 0.349 V and 0.350V CSE could mean a difference of 50% and 95 % probabilities of corrosion. This huge jump from 50% to 95% could lead to a mindset of definite corrosion on the embedded rebar.

Another usage of potential readings of reinforced concretes was that it could indicate the state of corrosion that might be occurring at the point of measurement. In the theory, it was mentioned that the average potential for pitting corrosion occurred between -200 and -500 mV SCE in extreme environments like low pH and high concentration of chloride ions. Thus, based on the results gathered, it might indicate that the rebar is undergoing pitting corrosion.

A more negative potential reading was known to indicate higher probability of corrosion and could be explained according to the following research.

According to Bentur et al. (1997), "Variations in chemical activity from place to place are associated with corresponding differences in electrical potential; it is these electrical potential differences which are the actual driving forces for the corrosion reactions." The steel reinforcement in the concrete acts as a cathode when it is in the passive state. When the passive layer was lost, either uniformly by a reduction in the pH of the concrete due to carbonation, or by local breakdown due to chloride ions, parts of the steel would act as an anode and started corroding. Ferrous ions, Fe^{2+}, would be lost into the solution, which freed up electrons in the steel and made the potential more negative. Potential differences between cathodic and anodic sites within a structure cause current to flow in the pore solution of the concrete, and through the metal reinforcement (Polder 1998).
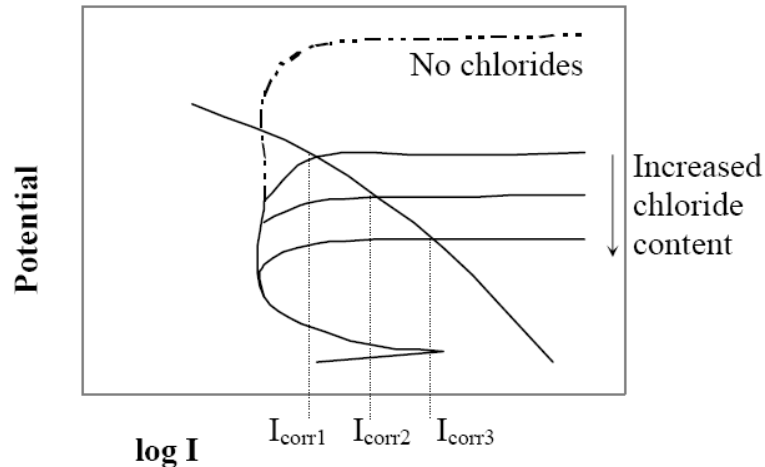
Figure 4-3. Polarisation Curves for Iron in the Presence of Chlorides.

Figure 4-3 showed that the higher the chloride content present on the rebar surface, the lower the potential reading would be. Therefore, it could be suggested that surfaces of the rebars taken from those concretes dosed with 5 and 15 gm of VAPPRO CRI 4030 would have a higher chloride content compared to the rebars taken from the control and concretes dosed with 10 gm of VAPPRO CRI 4030.

4.4   ACID – SOLUBE CHLORIDE IONS DETERMINATION TEST

Two methods, titration and ion selective electrode, were used for determining the chloride content in the concrete samples.

4.4.1   MOHR'S METHOD OF TITRATION

Mohr's Method of Titration was used to determine the amount of chloride ions in the concrete initially. Different concentrations of standards were prepared to determine the workable concentration range of this method.

With 5, 10, 15 grams and control concrete samples, a total of six samples instead of eight were used for titration. This was due to the difficulty encountered during the determination of end-point. The end-point colour change was somehow interfered by the turbidity of the concrete samples' solutions despite attempt to increase its purification through filtration. Figure 4-4 below showed the difficulty in determining the end-point as the expected colour change of reddish brown was hindered. They remained at brownish and dusty and any addition of silver nitrate made no difference.

Figure 4-4. Examples of Difficulty in Determining the End-Point Colour Change

The testing range of 10ppm to 500ppm was initiated and used. They were obtained through dilution from a 1000ppm chlorine standard from Merck. Three titrations were done for each concentration and the mean volume was used for the calculation as mention above to determine the amount of chloride. The results are as follows:

a) Results for Standard Cl⁻ Solutions

Concentration	1st Titration	2nd Titration	3rd Titration	Mean	Calculated (ppm)
10ppm	2.1ml	1.8ml	1.8ml	1.90ml	28.87
50ppm	3.6ml	3.2ml	3.3ml	3.37ml	51.20
100ppm	6.6ml	6.6ml	6.4ml	6.53ml	99.21
500ppm	32.0ml	31.3ml	31.3.ml	29.60ml	479.12

Table 4-7. Summary of Titration Results for Standard Chloride Solutions

4.4.2   CHLORIDE IONS DETERMINATION TEST CALCULATIONS

A.   Mohr's Method of Titration (Sample calculation (for 100ppm standard solution):

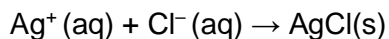**1.   Determine the average volume of silver nitrate used.**

<u>6.53 ml</u>

2. Calculate the moles of silver nitrate reacting.

$(6.53/1000)$ x $0.0428M$ = 2.7948 x 10^{-4} moles

The $AgNO_3$ solution prepared was found to be 0.0428 N and is equivalent 0.0428 M.

3. Use the following reaction equation to calculate the moles of chloride ion reacted.

$$Ag^+ (aq) + Cl^- (aq) \rightarrow AgCl(s)$$

1 mole of Ag^+ will react with 1 mole of Cl^-

Therefore, mass of chloride ions reacted (mg) = 2.7948 x 10^{-4} x 35.5 x 1000

= 9.9217mg

This means that there are 9.9217 mg of chloride ions present in that 100ml of standard solution prepared.

4. Present concentration in terms of ppm.

9.9217mg x 10 = 99.217mg / 1000ml
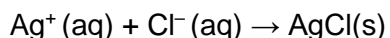
= 99.217ppm

Sample calculation (e.g. for concrete A):

1. Determine the average volume of silver nitrate used.

11.1 ml

2. Calculate the moles of silver nitrate reacting.

$(11.1/1000)$ x 0.0428 M = 4.7508 x 10^{-4} moles

3. Use the following reaction equation to determine the moles of chloride ions reacted.

$$Ag^+ (aq) + Cl^- (aq) \rightarrow AgCl(s)$$
1 mole of Ag^+ will react with 1 mole of Cl^-

Therefore, mass of chloride ions reacted (mg) = 4.7508 x 10^{-4} x 35.5 x 1000

= 16.8653

This means that there are 16.87 mg of chloride ions present in the 10 g of concrete sample.

4. Present concentration in terms of ppm for each individual concrete samples.

16.8653 x 100 = 1686.53mg / 1Kg

= 1686.53ppm

(For seawater 50X dilution)
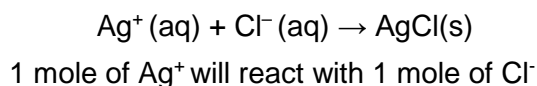
1. **Determine the average volume of silver nitrate used.**

10.4 ml

2. **Calculate the moles of silver nitrate reacting.**

(10.4/1000) x 0.0428 M = 4.4512×10^{-4} moles

3. **Use the following reaction equation to determine the moles of chloride ions reacted.**

$$Ag^+ (aq) + Cl^- (aq) \rightarrow AgCl(s)$$
1 mole of Ag^+ will react with 1 mole of Cl^-

Therefore, mass of chloride ions reacted (mg) = 4.4512×10^{-4} x 35.5 x 1000
= 15.8018mg

This means that there are 15.8018 mg of chloride ions present in 1 ml of seawater.

4. Present concentration in terms of ppm.

15.8018 x 1000 = 15801.8mg / 1 L

= 15801.8ppm

B. **Chloride Ion Selective Electrode** (Sample Calculation)

For concrete A; 1st reading is 34.7 mV and the first calibration curve's equation is

y = -25.033*ln(x) + 172.36

To calculate the concentration using the equation stated:

x = EXP ((34.7-172.36)/-25.033)

= 244.48

This means that in the 50ml of sample we have, the concentration of chloride ions present is 244.48 ppm.

$$244 \text{ ppm} = 244 \text{ mg/L}$$

$$\text{In 50 ml, the amount of chloride ions} = 244/1000*50 = 12.2 \text{ mg}$$

Therefore, during sample preparation, we extracted 10 g of concrete sample and this means that there is 12.2 mg of chloride ions present in that 10g of sample. And if we are to recalculate back to ppm concentration, it will be:

$$12.2 \text{ mg/10 g} = 12.2*100$$
$$= 1222 \text{ppm}$$

From the above table, it could be seen that there were discrepancies between the calculated amount and the expected concentration. The deviation in concentration for 50ppm and 100ppm was around 1ppm but the deviation for 10ppm and 500ppm was in the range of 10 to 20ppm. This gave an indication that Mohr's method of titration might be applicable within range from approximately 50 to 400 ppm. For a lower concentration of 10ppm or higher range of 500ppm, the titration might not be able to work well. Therefore, the method of titration might not be applicable for concrete samples after dilution as the concentration might be lower than 10ppm or higher than 400ppm.

b) Results for Concrete Sample Solutions & Seawater

Concrete	Amount of silver nitrate used (ml)	Mass of chloride ions present in diluted sample (mg)	Concentration of chloride ions present in concrete (ppm)
A	11.1	16.8653	1686.53
B	7.5	11.3955	1139.55
C	11.3	17.1692	1716.92
D	11.4	17.3212	1732.12
E	13.6	20.6638	2066.38
H	11.7	17.7770	1777.70
seawater (50x dilution)	10.4	15.8018	15801.76
seawater (100x dilution)	5.2	7.9009	15801.76

Table 4-8. Summary of Titration Results for Concrete Samples Solutions & Seawater

From the amount of silver nitrate used, the amount of chloride ions was determined by the calculation stated in the 4.4.2.

From Table 4-8, it could be seen that the amount of chloride ions was increasing from sample A to sample E, from 1686 ppm to 2066 ppm. The concentrations for all the duplicates were close to each other except for sample B where the concentration differed from its duplicate sample A. This could be due to a few factors, for examples, human bias during titration and the workable pH range of the solution. Titration required the end point to be reddish brown for the standard solution. However, the end point of chloride ions in concrete sample differed from dark orange to dusty brownish.

Therefore, the determination of end point might not be accurate compared to the end point of the chlorine standard solution (pinkish) due to human bias. This would cause a difference in the concentration of duplicates. According to calculations, an increment of about 0.5ml of silver nitrate would cause an increase of 100 ppm of chloride ions present. The second factor could be the pH of the solution which had to be in the range of 6.5 to 10 in order for the titration to work well. For our concrete samples, the pH level was around 11, therefore Mohr's method of titration did not give satisfactory results as the accuracy of the end-point was affected with the precipitation of silver hydroxide.

4.4.3 CHLORIDE ION SELECTIVE ELECTRODE METHOD

By using the ISE method, the error occurred when determining the end-point's colour change would be removed. In ISE, a calibration using at least four different concentration levels (10 times difference) was required. It was also a requirement to do calibration if the electrode was to be used on different days.

a) Calibration Graphs

Concentration (ppm)	Potential reading (mV)	
	First calibration	Second calibration
1	170.3	153.4

10	117.7	100.4
100	57.3	50.9
100	-1.7	-8.5

Table 4-9. First and Second Calibration – Corresponding Potential Readings for Each Concentration Levels.

A counter-check was done at the end of the experiment (i.e. after the samples had been tested). This counter-check was done by using concentration of 5, 50 and 500 ppm chloride solutions. This counter-check will reaffirm the accuracy of the ISE to produce the expected potential for the corresponding concentrations.

Note: The counter-check was only done in the first calibration graph.

Counter-Check

Concentration (ppm)	Potential (mV)
5	137.40
50	80.3
500	24.1

Table 4-10. Corresponding Potential Readings for Each Concentration Levels (Counter-Check)
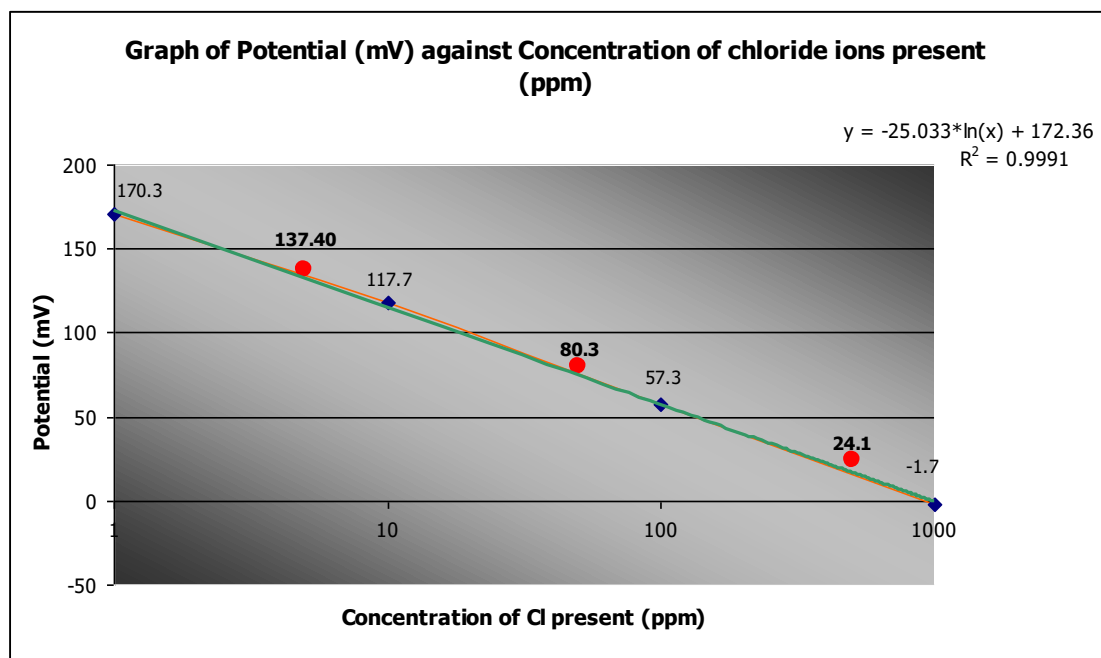

Figure 4-5. The 1st Calibration Graph for the Chloride ISE with Counter-Check.
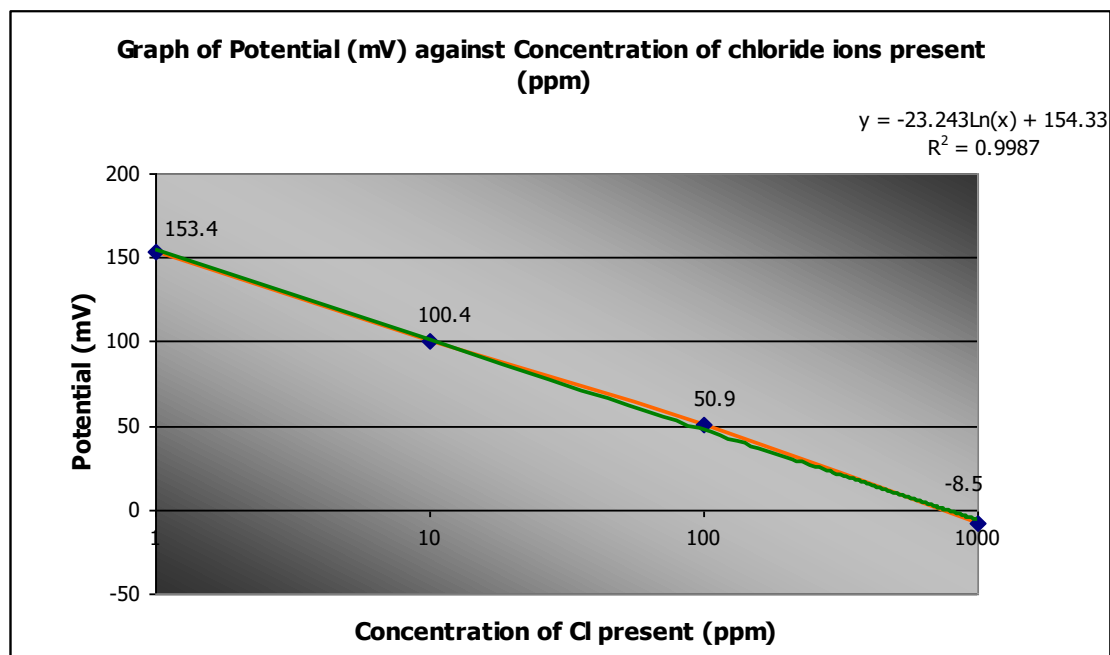
Figure 4-6. The 2nd Calibration Graph for the Chloride ISE

It could be seen that the potential reading changed for the same concentration if the test was conducted on another day. This proved that calibration before every use was important. However, this would not cause any difference in determining the concentration of chloride ions in the solutions as long as the correlation efficient R^2 is relatively near 1.

b) Results for Concrete Sample Solutions

Concrete	Amount of VAPPRO CRI 4030 added (g)	Potential reading* (mV)		Corresponding Concentration (ppm)		Average Concentration (ppm)	Standard Deviation (ppm)
		1st reading	2nd reading	1st reading[#]	2nd reading[^]		
A	5	34.70	28.50	1222.41	1122.27	1117.07	130.53
B	5	41.50	27.10	931.63	1191.95		
C	10	35.00	24.30	1207.85	1344.54	1285.19	76.04
D	10	34.50	24.10	1232.21	1356.16		
E	15	26.40	19.50	1702.99	1652.96	1706.13	49.42
F	15	25.40	18.90	1772.40	1696.19		

G	0	39.00	33.50	1029.48	905.05	938.92	70.15
H	0	40.90	34.50	954.23	866.94		
seawater 50 X dilution	N.A.	18.2	N.A.	472.61	N.A.	23630.51$^{\alpha}$	2266.15
seawater 100 X dilution	N.A.	39.2	N.A.	204.26	N.A.	20425.69 $^{\alpha}$	

Table 4-11. Summary of Results for Chloride Ions Selective Electrode Method

$^{\alpha}$ The actual concentration of seawater.

* Each reading was taken after the same potential was achieved twice consecutively.

Concentration was computed by using the reading and the equation achieved from the first calibration graph [$y = -25.033*\ln(x) + 172.36$] where x is the concentration and y is the potential reading and back-calculated to achieve the final concentration value.

^ Concentration was computed by using the reading and equation achieved from the second calibration graph [$y = -23.243*\ln(x) + 154.33$] where x is the concentration and y is the potential reading.

Refer to 4.4.2 for calculation

c) Comparison of ISE & Mohr's Method of Titration

Concrete	+Calculated Concentration by using ISE (ppm)	Calculated Concentration by using Titration (ppm)	Deviation (ppm)
A	1172.34	1686.53	514.19
B	1061.79	1139.55	77.76
C	1307.70	1716.92	409.22

D	1294.19	1732.12	437.93
E	1677.98	2066.38	388.40
H (control)	910.59	1777.70	867.15
seawater	22028.10	15801.76	6226.34

Table 4-12. A Comparison of Results achieved by Mohr's Titration and Chloride ISE Method.

[+] The results stated are based on the first and second readings for each individual concrete. From the Table 4-12, it could be clearly seen that the difference in the concentration between the same samples. Although there was an increasing trend in both of the methods, the concentration of each sample in Mohr's method of titration differed significantly from the concentration of each sample obtained from chlorine ISE Method.

This could be due to the error in detecting the end point of the chloride ions. As the color differed for each of the sample, there were possibilities that the end point was detected late.

Seawater composition (by mass)			
Element	**%**	**Element**	**%**
Oxygen	85.84	Sulphur	0.091
Hydrogen	10.82	Calcium	0.04
Chlorine	1.94	Potassium	0.04
Sodium	1.08	Bromine	0.0067
Magnesium	0.1292	Carbon	0.0028

Table 4-13. Composition of Global Seawater.

It could be seen from Table 4-13 that the chlorine composition is 1.94% by mass which is 19.4g/kg or 19400 ppm. From the titration done, the amount was 15801 ppm. Compared to the percent composition from the table, the difference was about 3600 ppm. The test for concentration of seawater was also done using Chlorine Ion Selective Method. As shown from the seawater composition table, the amount of chlorine was higher than the amount calculated from the table by 2600 ppm approximately.

In the case of seawater, either method to determine the concentration of chloride was applicable. As the amount of chloride ions in seawater is known to be abundant, dilution of at least 50 to 100 times was needed to be done before any measurements. Such dilution would result in errors and coupled with the uncertainty already present in each method, the measurements would thus deviate from the actual composition stated.

Magnitude of the seawater could also be a factor. Due to the high concentration of chloride ions in seawater, the amount present could be in a range but not a fixed amount. Therefore, the result should be acceptable if the range was of ten thousand ppm and not in the range of only hundreds ppm.

By comparing the two methods, results obtained for the concrete samples by chloride ISE seemed to be more reliable.

d) Hypothesis Testing for the Results obtained by Chloride ISE Method (Difference on Means)

The t-distribution for testing of hypothesis was used since the samples are small, only two which is less than 30. TWO-TAILED TEST was used here as the alternative hypothesis is stated as an inequality.

Null Hypothesis, H_0: There is no significant difference in the chloride concentration of the concretes with or without adding 5 gm of VAPPRO CRI 4030 against the control.

Alternative Hypothesis, H_1: There is a significant difference in the chloride concentration of the concretes with or without adding 5 gm of VAPPRO CRI 4030 against the control.

Degree of freedom, $v = n_1 + n_2 - 2$

$$= 2 + 2 - 2$$
$$= 2$$

where n = sample size

$\sigma = [\sqrt{(n_1 \times s_1^2) + (n_2 \times s_2^2)}] / v$

$= [\sqrt{(2 \times 130.53^2) + (2 \times 70.15^2)}] / 2$

$= 104.783$

Where s = sample standard deviation

$$t_{cal} = (X'_1 - X'_2) / [\sigma \times \sqrt{(1/n_1 + 1/n_2)}]$$
$$= (1117.07 - 938.92) / [104.783 \times \sqrt{(1/2 + 1/2)}]$$
$$= 1.70018$$

For now, an alternative way was done by using the absolute values of t_{cal}.

- If the absolute value of the test statistic is less than or equal to the table value at the specified confidence level, then the null hypothesis is accepted as being true.
- If the absolute value of the test statistic is greater than the table value at the specified confidence level, then the alternative hypothesis is accepted as being true.

Therefore, in our case, t_{cal} which is $1.7 < t_{tab} = 4.303$, the null hypothesis will be accepted instead and a conclusion was arrived that there is no significant difference in the chloride concentration of the concretes with or without adding 5 gm of Vappro CRI 4030 against the control.

Using the same calculation method of finding v, σ and finally t_{cal}.

10 gm of VAPPRO CRI 4030	15 gm of VAPPRO CRI 4030
$v = 2$	$v = 2$
$\sigma = 73.154$	$\sigma = 60.677$
$t_{cal} = 4.733$	$t_{cal} = 12.644$

Absolute value of test statistic is $4.733 > 4.303$. Therefore, the alternative hypothesis was accepted and concluded that there is significant difference in the chloride concentration of the concretes with the adding of 10 gm of VAPPRO CRI 4030 against the control.

Absolute value of test statistic is $12.644 > 4.303$. Therefore, the alternative hypothesis was accepted once again and concluded that there is significant difference in the chloride concentration of the concretes with the adding of 15 gm of VAPPRO CRI 4030 against the control.

Therefore, at 95% confidence level, the dosage level at 5 gm of Vappro CRI 4030 does not have a significant effect on the resultant chloride concentration compared to control while the dosages

at 10 gm and 15 gm have a significant effect on the resultant chloride concentration when compared to the control itself.

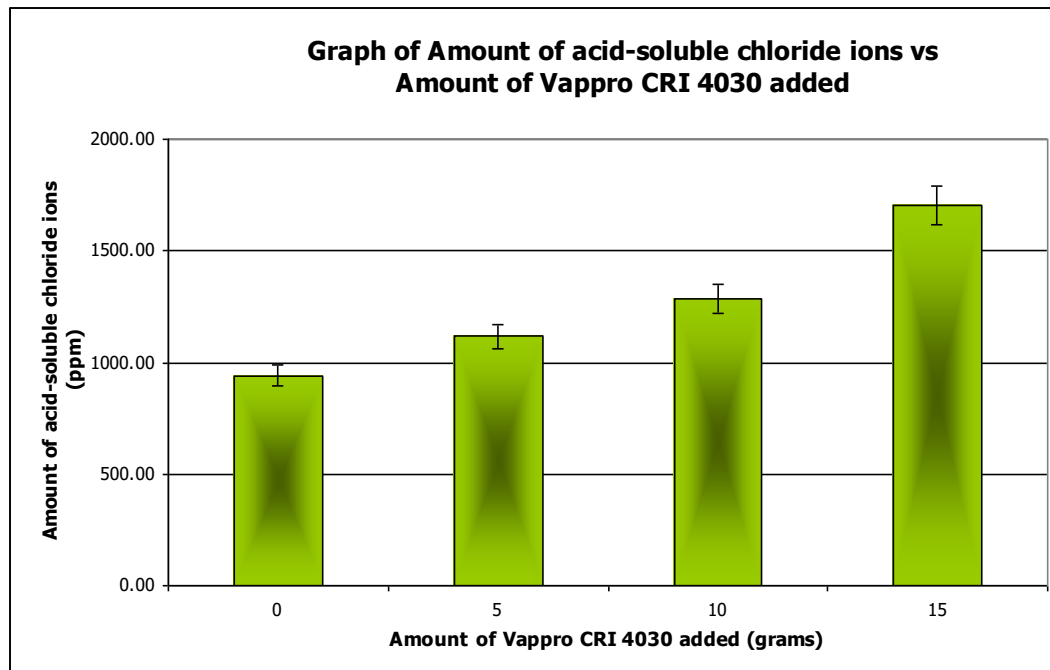e) Conclusion for Chloride Determination by ISE Method

Graph of Amount of acid-soluble chloride ions vs Amount of Vappro CRI 4030 added

Figure 4-7. The Bar Graph of Amount of Chloride Ions Present in Concrete vs. Amount of Vappro CRI 4030 added.

By summarising the results achieved in Table 4-11 into a bar graph, it was relatively clear that the additional of more VAPPRO CRI 4030 powder into the cast concrete had resulted in higher amount of chloride ions to invade into the concrete instead.
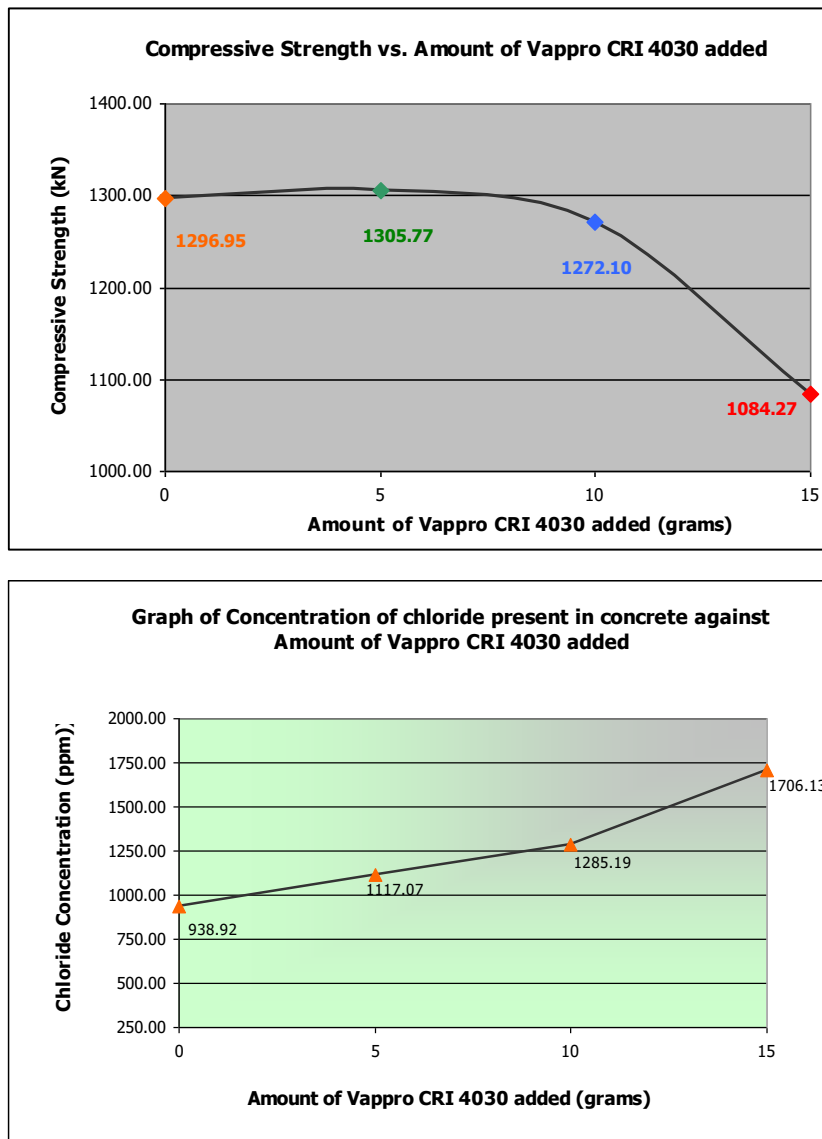
Figure 4-8. Comparison of Trend Line Graphs of Compressive Strength (Top)
against Amount of Chloride Ions Present in the Concretes.

From Figure 4-8 above, both the trend line graphs are going in the opposite direction. It could be suggested that the decrease in compressive strength actually resulted in the increase of the amount of chloride ions present in the concretes.

This could be explained that the Vappro CRI 4030 actually did form complexes in the concretes. However, by dosing the concrete with 15 gm of VAPPRO CRI 4030, the complexes formed were

too much and this caused the compressive strength to decrease instead of increase as explained under the discussion section of compressive strength test. As such, the chloride ions had a greater chance to ingress into the concrete which has lower permeability.

4.5   SCANNING ELECTRON MICROSCOPY ANALYSIS

In this SEM analysis, one sample each of 0 gm, 5 gm, 10 gm and 15 gm of VAPPRO CRI 4030 (Rebar G, A, D and E) were analysed. Each steel rebar was analysed twice at different locations and the results obtained are as follows:
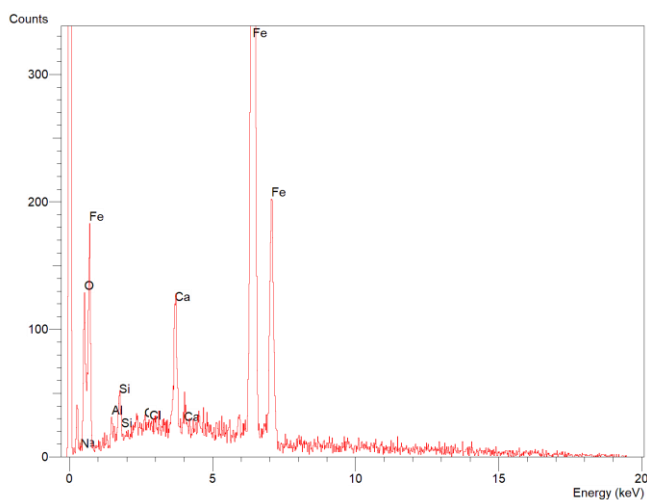
Rebar A
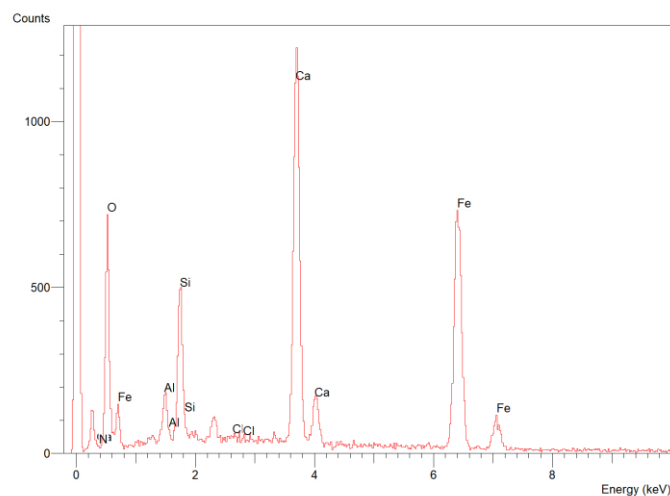Dosage of Vappro CRI 4030 in concrete where rebar was taken: 5 grams

Element	Location (1)	Location (2)
	Percentage Present (%)	
Al K	0.81	2.65
Ca K	2.69	18.68
Cl K	0.1*	0.21*
Fe K	88.70	29.15
N K	-2.92*	-16.82*
O K	9.29	58.63
Si K	1.33	7.49

* denotes equal or less than 2 sigma.

Table 4-14. Percentage of Element Present in Rebar A at Different Locations.

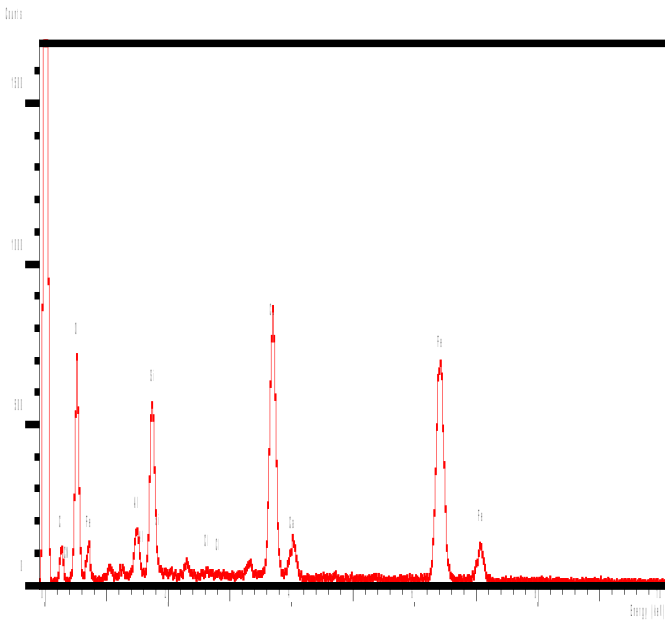Location 1   Location 2

Rebar D
Dosage of Vappro CRI 4030 in concrete where rebar was taken: 10 grams

Element	Location (1)	Location (2)
	Percentage Present (%)	
Al K	2.24	1.12
Ca K	10.42	5.68
Cl K	0.09*	0.1*
Fe K	50.23	12.52
N K	-9.81*	16.71*
O K	39.64	48.50
Si K	7.19	3.44
C K	-	11.93

* denotes equal or less than 2 sigma.

Table 4-15. Percentage of Element Present in Rebar D at Different Locations.

Location 1

Location 2

Rebar E
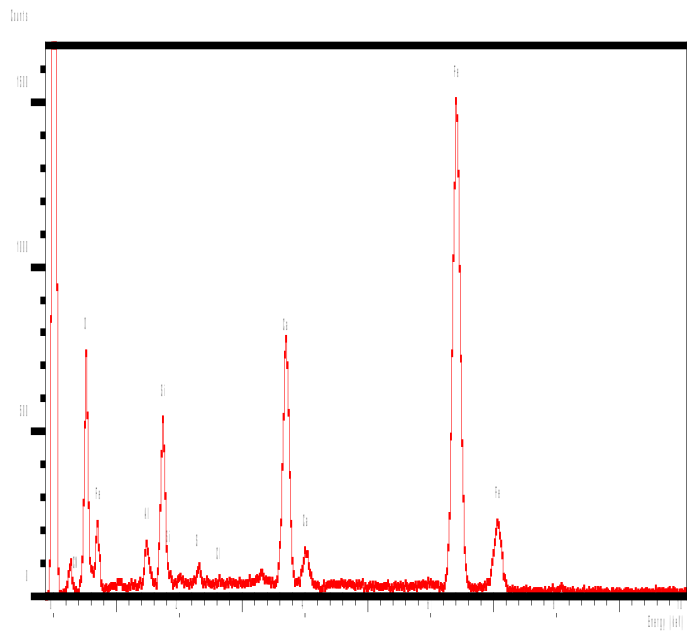Dosage of VAPPRO CRI 4030 in concrete where rebar was taken: 15 grams

Element	Location (1)	Location (2)
	Percentage Present %	
Al K	3.60	3.35
Ca K	24.63	11.16
Cl K	0.08*	0.18*
Fe K	2.98	35.29
N K	-8.65*	16.8*
O K	66.6	30.26
Si K	10.76	2.96

* denotes equal or less than 2 sigma.

Table 4-16. Percentage of Element Present in Rebar E at Different Locations.

Location 1

Location 2
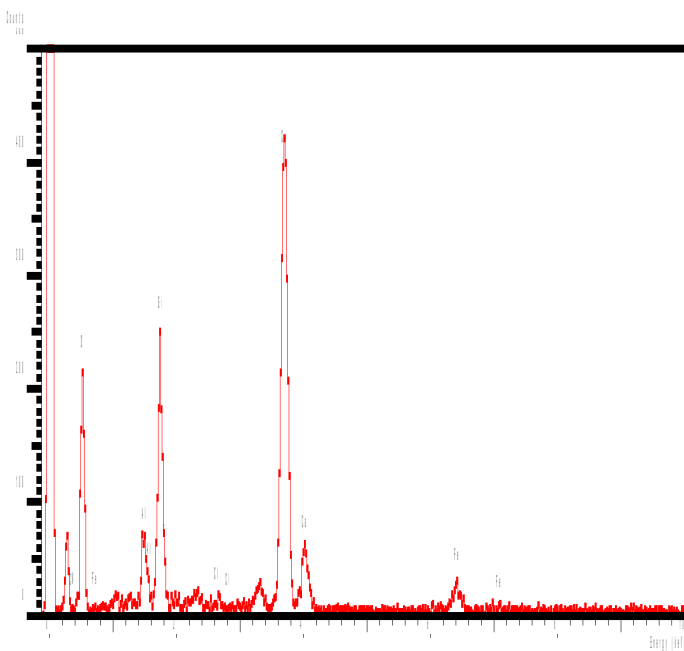
Rebar G
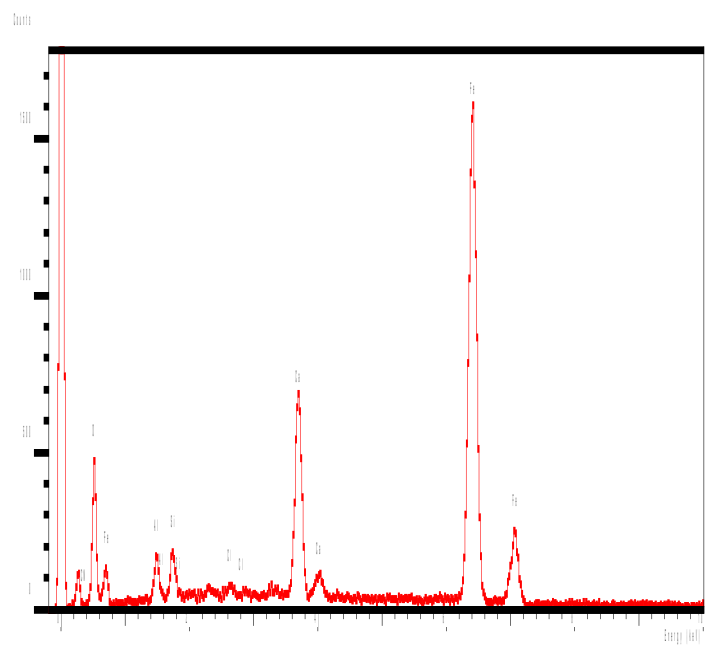Dosage of Vappro CRI 4030 in concrete where rebar was taken: 0 grams

Element	Location (1)	Location (2)
	Percentage Present %	
Al K	3.73	2.64
Ca K	18.50	19.60
Cl K	0.15*	0.29
Fe K	23.50	44.01
N K	-12.02*	-23.88*
O K	59.17	52.04
Si K	6.97	5.30

* denotes equal or less than 2 sigma

Table 4-17. Percentage of Element Present in Rebar G at Different Locations.

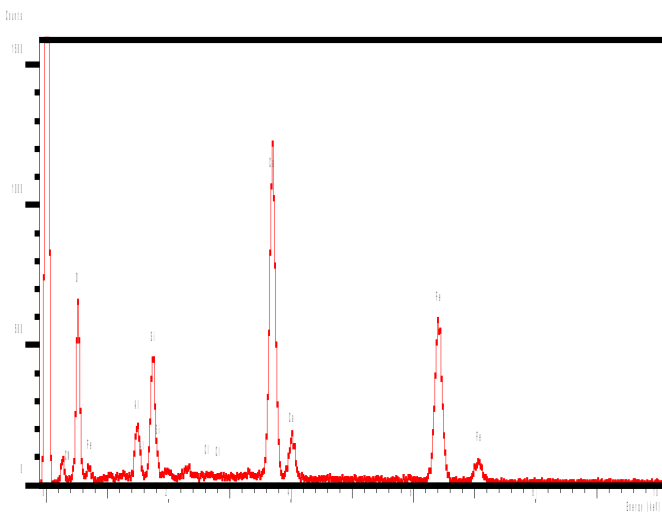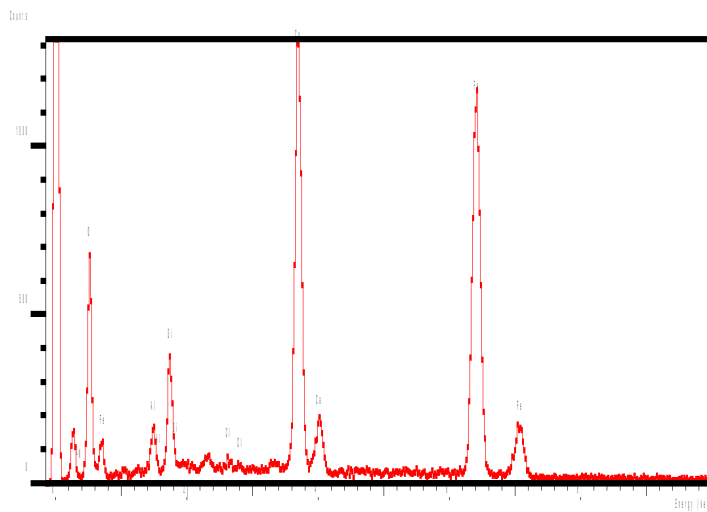Location 1   Location 2

From the rebar surface analysis for elements present, it was noted that nitrogen element was present on rebar D and E but not on rebars A, and G. Therefore, the theory of VAPPRO CRI 4030 to act as a migrating corrosion inhibitor could not be put off. This however might be concentration-dependent.

Secondly, it would be useful to determine the amount of chloride ions present on the steel bars as well. The amount of chloride ions present on both steel rebars D and E were comparably similar but was lesser compared to rebars A and G. This verified the creditability of the half-cell potential

test results where it was said that rebars A with 5% Vappro CRI dosage and rebar G without Vappro CRI 4030 could have a higher amount of chloride ions content on their surfaces.

The presence of aluminium, silicone and calcium present on the steel could be due to the Portland cement mixture which was stated earlier known to contain these three elements.

4.6   PHENOLPHTHALEIN INDICATOR TEST

The following photographs were taken from the fresh concretes B, D, F and H after cracking them using a breaker.

Figure 4-9. Concrete B

Figure 4-10. Concrete D

Figure 4-11. Concrete F

Figure 4-12. Concrete H

All concretes are highly alkaline when they were cast. The alkaline condition of the concrete caused a passive oxide layer to be formed around the rebar, thereby protecting it from corrosion. The alkalinity will protect the rebar by a process called "passivation".

The pictures above showed that the concretes were still in alkaline condition after 90 days of submersion in seawater and the pH could be higher than 10. If the pH of the concrete falls below about 10, the potential for rebar corrosion increases. When the pH is in the 8 to 9 range, it is a good indication that some carbonation is taking place from the surface of the concrete toward inside.

Therefore, it could be concluded that the four concretes were still in their alkaline condition. Any corrosion of the steel rebars was thus probably not due to carbonation.

4.7 FERROXYL INDICATOR TEST

Ferroxyl Indicator Test was to detect corrosion areas by dying the cathodic and anodic ends in the different colours. The anodic area, which is also the corroding area, can be identified by the bluish green colour. On the other hand, the cathodic area can be recognised by the pinkish colouration. This test is applicable only for ferrous metal like the steel rebar.
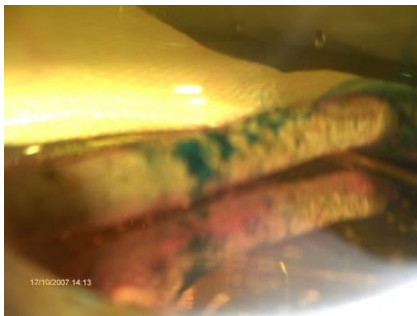

Figure 4-13. Rebar A

Figure 4-14. Rebar D

Figure 4-15. Rebar E

Figure 4-16. Rebar G

As observed from the pictures, which were taken after immersion in the ferroxyl indicator solution, it showed that rebar A and rebar G showed a larger amount of green dye, indicating corrosion compared to rebars D and E.

For rebars D and E, the visible form of corrosion as well as the amount of blue/green dye observed was much lesser.

It could now be said that more corrosion occurred at rebars A and G whereas rebar D and E showed limited corrosion. This could be explained by the SEM elemental analysis on rebar D and E which showed the presence of nitrogen element and this could be due to the presence of VAPPRO CRI 4030 vapour molecules. As a result, rebar D and E was protected from more severe corrosion.

4.8   WEIGT LOSS TEST

	B (5 gm)	C (10 gm)	F (15 gm)	H (control)
Initial Weight (grams)	97.9636	86.1790	85.3324	93.3154
Final Weight* (grams)	96.8552	85.3196	84.5090	92.1855
Weight Loss (grams)	1.1084	0.8594	0.8234	1.1299

Note: * denotes the weight taken after the rebar was embedded in the casted concrete for 90 days.

Table 4-18. Weight Loss Results.

From the measured weights of the steel rebars, the results showed that at 15 gm dosage level of Vappro CRI 4030, the amount of weight loss was considered the least (0. 8234 gm). Coming in very closely in terms of results was the 10 gram dosage where the weight loss amount is just 0.036 gm higher than the former.

On the other hand, over the period of 90 days, the steel rebars that were embedded into the concretes that have dosage levels of 5 gm and control have lost approximately 1.1 gm whereas the weight loss of the control was 1.13 gram of weight. Therefore, it could be said that there was

more corrosion occurred compared to those rebars embedded in control and 5 gm of Vappro CRI 4030.

This method can be treated as a relatively simple way to determine the rate corrosion; however, a longer analysis time and large sample size would be more appropriate if the accuracy of the results was to be improved.

4.9 Ascertaining the functional group of Vappro CRI 4030

The purpose of this section was to ascertain the chemical functional group of Vappro 4030. As mentioned in Section 4.1, Vappro CRI 4030 might contain amine or alcohol functional groups. FTIR spectrum graph below deduced that Vappro 4030 contains amine and alcohol functional group.

FTIR SPECTRUM OF VAPPRO CRI 4030
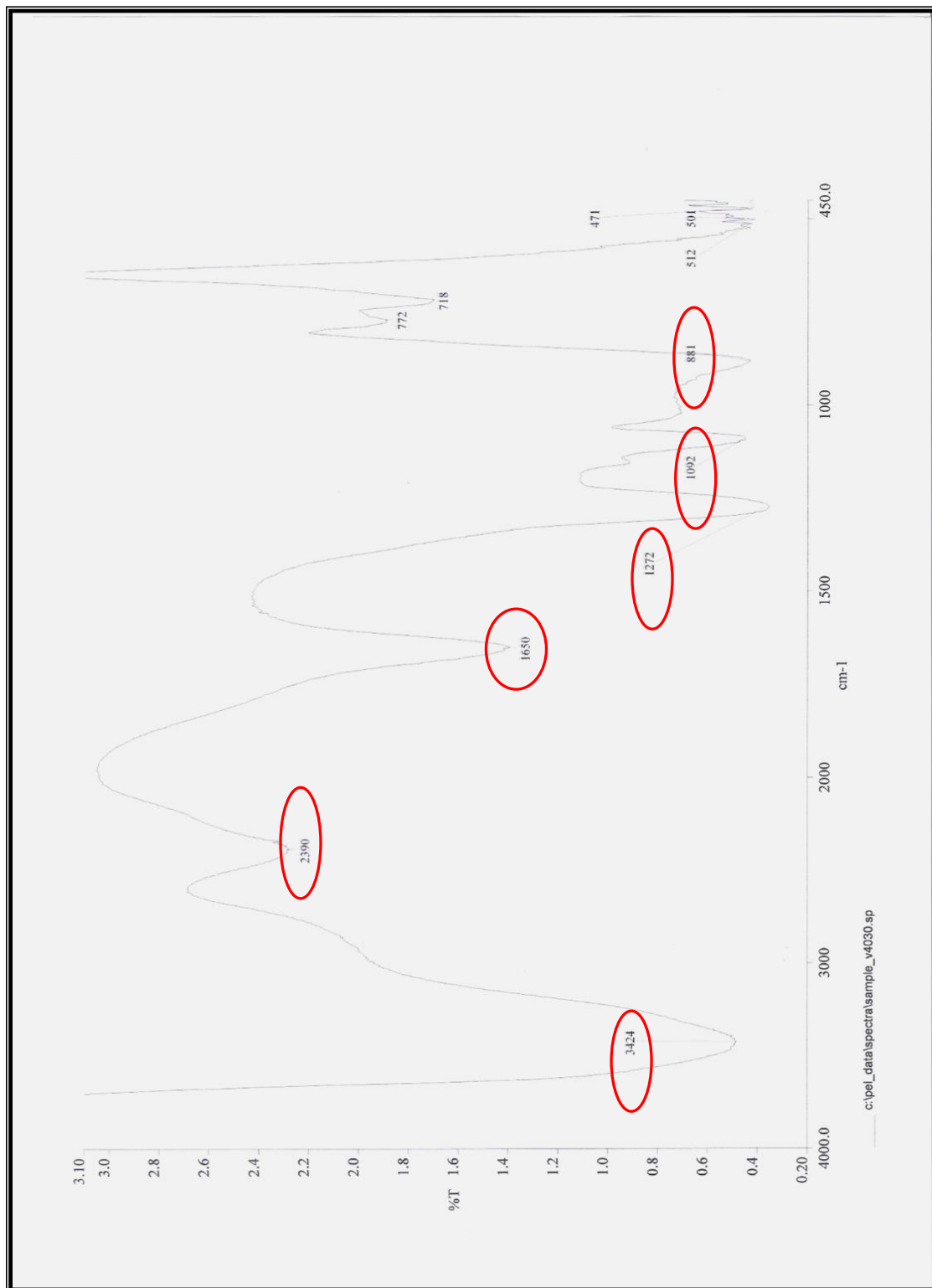
IR SPECTRA INTERPRETATION REFERENCE TABLES

Vibrational Frequencies for Organic Molecules

Bond Type	Specific Context	n, cm^{-1}
Stretching Frequencies		
C-H	$C_{sp}3$-H	2800-3000
	$C_{sp}2$-H	3000-3100
	C_{sp}-H	3300
C-C	C-C	1150-1250
	C=C	1600-1670
	C⁰C	2100-2260
C-N	C-N	1030-1230
	C=N	1640-1690
	C⁰N	2210-2260
C-O	C-O	1020-1275
	C=O	1650-1800
C-X	C-F	1000-1350
	C-Cl	800-850
	C-Br	500-680
	C-I	200-500
N-H	RNH_2, R_2NH	3400-3500 (two)
	RNH_3^+, $R_2NH_2^+$, R_3NH^+	2250-3000
	$RCONH_2$, RCONHR'	3400-3500
O-H	ROH	3610-3640 (free)

		3200-3400 (H-bonded)
	RCO_2H	2500-3000
N-O	RNO_2	1350,1560
	$RONO_2$	1620-1640, 1270-1285
	$RN=O$	1500-1600
	$RO-N=O$	1610-1680 (two), 750-815
	$C=N-OH$	930-960
	R_3N-O^+	950-970
S-O	R_2SO	1040-1060
	$R_2S(=O)O$	1310-1350 1120-1160
	$R-S(=O)_2-OR'$	1330-1420, 1145-1200
Cumulated systems	$C=C=C$	1950
	$C=C=O$	2150
	$R_2C=N=N$	2090-3100
	$RN=C=O$	2250-2275
	$RN=N=N$	2120-2160
Out-of-plane bending vibrations		
Alkynes	C^oC-H	600-700
Alkenes	$RCH=CH_2$	910, 990
	$R_2C=CH_2$	890

	trans-RCH=CHR	970
	cis-RCH=CHR	725, 675
	$R_2C=CHR$	790-840
Aromatic	mono-	730-770, 690-710 (two)
	o-	735-770
	m-	750-810, 690-710 (two)
	p-	810-840
	1,2,3-	760-780, 705-745 (two)
	1,3,5-	810-865, 675-730 (two)
	1,2,4-	805-825, 870, 885 (two)
	1,2,3,4-	800-810
	1,2,4,5-	855-870
	1,2,3,5	840-850
	penta-	870
Carbonyl Stretching Frequencies		
Aldehydes	RCHO	1725
	C=CCHO	1685
	ArCHO	1700
Ketones	$R_2C=O$	1715
	C=C-C=O	1675

	Ar-C=O	1690
	four-membered cyclic	1780
	five-membered cyclic	1745
	six-membered cyclic	1715
Carboxylic Acids	RCOOH	1760 (monomer) 1710 (dimmer)
	C=C-COOH	1720 (monomer) 1690 (dimmer)
	RCO_2^-	1550-1610, 1400 (two)
Esters	RCOOR	1735
	C=C-COOR	1720
	ArCOOR	1720
	g-lactone	1770
	d-lactone	1735
Amides	$RCONH_2$	1690 (free) 1650 (associated)
	RCONHR'	1680 (free) 1655 (associated)
	$RCONR_2'$	1650
	b-lactam	1745
	g-lactam	1700
	d-lactam	1640
Acid anhydrides		1820, 1760 (two)

Acyl halides		1800

4.9.1   MECHANISM OF VAPOUR CRI 4030

Experimental findings ascertained that Vappro CRI 4030 was able to be transmitted as vapours, and the vapour phase is controlled by the structure of the crystal lattice and the character of chemical bond in the molecule. The protective vapours would expand within the enclosed space until the equilibrium determined by their partial pressure of the vapour is reached. These vapours form an extremely thin film over certain metal surfaces, especially those of iron and steel, thereby rendering them passive.

In general, Vappro CRI 4030 vapour molecule would reach the metal surface and formed a thin film of crystals. This proposed mechanism of action could be supported by an article retrieved from NACE International 2000, Corrosion Science Section, titled "***An Overview:*** *Vapour Phase Corrosion Inhibitors"* [10]

This article stated that amines, especially on iron, were able to form coordination bonds between the unshared electron pair of the nitrogen in the non-hydrated amine and metal. They adsorbed on metals for which there were unoccupied electronic orbitals and through the defects present in the oxides on metals with fully occupied orbitals. Therefore, Vappro CRI 4030 must thus be able to migrate through the concrete mixture and reach the rebar. This migration, however, may be concentration-dependent. Thus, the dosage level became important. Figure 4-17 below depicts the proposed mechanism mentioned.
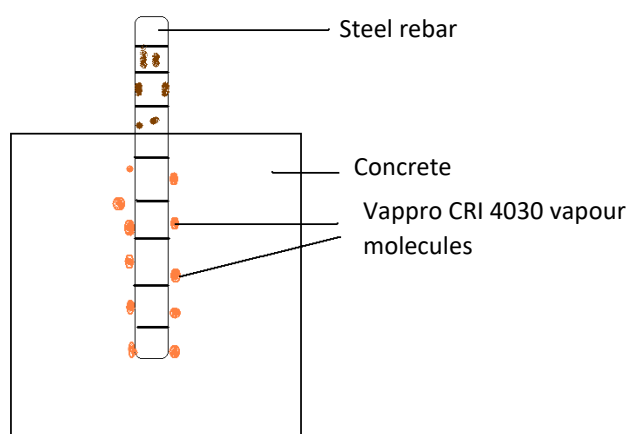
Figure 4-17. Schematic Diagram of the First Proposed Mechanism of Vappro CRI 4030.

4.9.2 FORMATION OF Vappro CRI 4030 – Ca/Al/Si COMPLEXES

Concrete is a construction admixture that consists of cement (commonly Portland cement), aggregates and water. Concrete solidifies and hardens after mixing and placement due to a chemical process known as hydration. The raw materials for Portland cement production are a mixture of minerals containing calcium oxide (61 – 67 %), silicon oxide, and aluminium oxide. Therefore, it became likely that the calcium or aluminium or silicone ions from the Portland cement accepted the lone pair of electrons from amine functional group of VAPPRO CRI 4030 to form a cationic complex within the concrete matrix. These complexes formed were then able to reduce the movement of the chloride ions diffused into the concrete from the seawater by decreasing the permeability of the concrete. Figure 4-18 below depicts the proposed mechanism mentioned. Possible chemical equation:

$$Ca/Al/Si + VAPPRO\ CRI\ 40\overset{\cdot\cdot}{3}0 \sim NH_2 \rightarrow Ca/Al/Si - {}^+NH_2 \sim VAPPRO\ CRI\ 4030\ complex$$
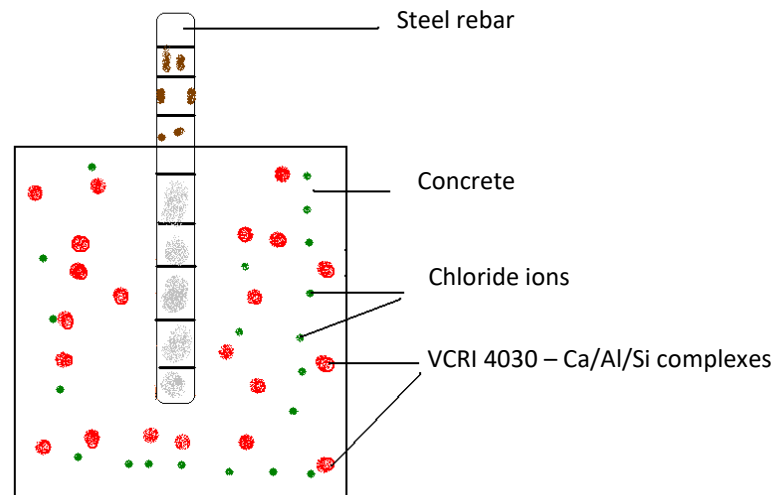

Figure 4-18. Schematic diagram of the second proposed mechanism of VAPPRO CRI 4030

However, it is still important to take note that both mechanisms may apply in this experiment. For Vappro CRI 4030 to migrate to the rebar surface, the dosage level is critical. Therefore, the second mechanism (forming complexes) may come into action when the dosage level deviates from the "optimum dosage". This means that the Vappro CRI 4030 may form complexes instead if it failed to migrate to the surface of the rebar.

CONCLUSION

All the results that were obtained in this whole experimental findings would be summarised as follows:

(A)   For concretes dosed with 5 gm of VAPPRO CRI 4030

- Compressive Strength Test and Chloride Ions Determination Test

✓ Both tests have shown that adding 5 gm of VAPPRO CRI 4030 did not cause a significant change to both the concrete's compressive strength and the amount of chloride ions that invaded compared to the control samples. Therefore, it could be suggested the complexes it formed were insufficient to cause any changes to the compressive strength. This in turn meant that the complexes formed would not be able to block the ingress of chloride ions.

- Half – Cell Potential Test, SEM Analysis, Ferroxyl Indicator Test & Weight Loss Test

✓ Half – cell potential tests showed an average reading of -0.370 V CSE for the rebars which indicates a 95 % probability of corrosion. The SEM analysis indicates no sign of nitrogen element. Thus, the absence of any amine vapour molecules on the rebar was possible. A larger amount of chloride ions content was also detected on the rebar's surface. Evidence of corrosion was visible when the rebar showed several patches of green cathodic areas. Weight loss test shows that the rebar had the highest weight loss attributed at 1.1 gm.

Based on the results obtained, the effectiveness of protecting the rebar from corrosion by adding 5 gm of VAPPRO CRI 4030 was not promising. The amount might be insufficient for the VAPPRO CRI 4030 to migrate. Thus the second mechanism might come into action as VAPPRO CRI 4030 form complexes in the concrete.

(B)   For concretes dosed with 10 gm of Vappro CRI 4030

- Compressive Strength Test and Chloride Ions Determination Test

- ✓ In the compressive strength test, it was noted that adding 10 gm of VAPPRO CRI 4030 to the concrete did not have any difference on its compressive strength compared to the control. Therefore, the possible amount of complexes formed were however insufficient. There was a significant increase when it comes to the amount of chloride ions invaded compared to the control at 95 % confidence level statistically. It could be possible that the amount of complexes formed was lesser than that of those formed by adding 5 gm of VAPPRO CRI 4030.

- ▪ Half – Cell Potential Test, SEM Analysis, Ferroxyl Indicator Test & Weight Loss Test

- ✓ Half – cell potential test showed an average reading of -0.315 V CSE for the rebars which indicates a 50 % probability of corrosion. SEM analysis indicates signs of nitrogen element hence the presence of amine vapour molecules on the rebar was possible. Evidence of corrosion was not very visible as the rebar did not indicate several patches of green cathodic areas.

Based on the results obtained, the effectiveness of adding 10 gm of Vappro CRI 4030 to protect the rebar was encouraging but more tests or analyses should be carried out. It could thus be suggested that at 10 gm of VAPPRO CRI 4030 dosage level, it has reached the so called "critical or threshold concentration" where the amine inhibitor was able to migrate in the concrete and leave lesser or none to form the complexes. The equilibrium actually favours the migration of the VAPPRO CRI 4030 molecules instead of forming complexes. With almost lesser or no patches of green cathodic areas when undergoing the ferroxyl indicator test; least weight loss; a 50% probability of corrosion, concrete with 10 gm of VAPPRO CRI 4030 has showed the most favourable results in terms of corrosion protection and compressive strength of the concrete.

(C)   For concretes dosed with 15 gm of VAPPRO CRI 4030

- ▪ Compressive Strength Test and Chloride Ions Determination Test

- ✓ In the compressive strength test, it showed that adding 15 gm of VAPPRO CRI 4030 to the concrete did have a significant decrease on its compressive strength compared to the control. As it was discussed earlier, this decrease was probably due to the excessive

amount of complexes formed. From these two tests, adding 15 gm of VAPPRO CRI 4030 to prevent corrosion to the rebar looked very promising.

- Half – Cell Potential Test, SEM Analysis, Ferroxyl Indicator Test & Weight Loss Test

✓ Half – cell potential test showed an average reading of -0.313 V CSE for the rebars which indicates once again 50 % probability of corrosion. SEM analysis indicates signs of nitrogen element hence the presence of amine vapour molecules on the rebar was possible. The amount of chloride ions content present on the rebar's surface was the lowest among the three different dosages in the concretes. Evidence of corrosion was not very visible as the rebar did not indicate several patches of green cathodic areas. Weight loss test shows that the rebar had the lowest weight loss.

Based on the results obtained, the effectiveness of adding 15 gm of VAPPRO CRI 4030 was satisfactory.

RECOMMENDATIONS

7.1 IMPROVEMENT ON EXPERIMENTS

a) Mohr's method of titration is not a suitable method to determine the amount of acid-soluble chloride ions present in concrete. The colour change at the end-point was hindered by the turbidity (precipitation of silver hydroxide) of the solution.

It was thus recommended to employ the method of ion selective electrode as an alternative to measure the amount of chloride ions present. This method is relatively time and cost-effective. But the requirement of the results were to be very accurate, the suggestion was to use ion chromatography instead which is considered a high end instrument.

b) It was also suggested to have more samples for each dosage levels of VAPPRO CRI 4030. This was because with a larger sample size, the hypothesis testing would be more accurate.

c) With regards to the half-cell potential testing, it would be better to keep to the ASTM method C876-91 of using copper sulphate electrode to do the testing. Although theoretically it would be alright to use another reference electrode like SCE, it would require the criteria table (Table 2-2) to be reconverted like Table 2-3. This conversion might contain errors where probability of corrosion was different, like the case encountered in this project.

d) More agitation could be set-up for the concretes in tanks as the durability of concrete may be adversely affected by water movements such as waves, currents and tides. This represents a more realistic environment.

e) Soaking the concretes in seawater alone was not very effective to initiate corrosion or for the corrosion to reach a certain extent. It was recommended that the temperature and the humidity level in the tanks to be controlled as well.

f) For monitoring the actual corrosion behaviour of steel rebar, the ideal way was to conduct AC electrochemical impedance spectroscopy (EIS) as the conductivity of concrete was low. In EIS, the changes in the resistance polarization and the corrosion potential of the rebar are monitored. This is important as now this project had indicated that VAPPRO CRI 4030 had the possibility to migrate to the rebar. EIS will be able to ascertain the degree of effectiveness for a migrating corrosion inhibitor.

g) Since the optimum amount of VAPPRO CRI 4030 to be used was found out to be 10 gm in these experimental findings, we strongly recommend dosage for the Vappro CRI 4030 to be 10 gram for field application.

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