Chapter 7

Developing Deeper Understanding of Green Inhibitors for Corrosion of Reinforcing Steel in Concrete

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ABSTRACT

Corrosion of reinforcing steel in concrete is a very serious and significant problem in the construction industry. The primary cause of corrosion of reinforcing steel is chloride attack or carbonation. Among several protection measures for concrete corrosion, the usage of corrosion inhibitors is very attractive from the view of cost and ease of application. Though there are numerous organic and inorganic compounds that have been tested and applied industrially as corrosion inhibitors, restrictive environmental regulations have compelled and motivated researchers towards the development of cheap, non-toxic and environmentally benign natural or green corrosion inhibitors. Recent studies on green inhibitors have shown that they are more effective and highly environmentally benign compared to synthetic inhibitors used in the industries. This chapter contributes to developing awareness, understanding and innovative involvement of materials and engineering students in this area that is vital to reduce expenditure related to corrosion problems when they serve in the industries.

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INTRODUCTION

The development and building of large concrete structures for offshore oil and gas production in the 1970s had led to increased attention on corrosion of steel reinforcement. Worldwide, reinforced concrete is the most durable, versatile, and widely used construction material which has a wide range of applications from making small posts to vast bridges and tall buildings. The corrosion of reinforcing steel has the same basis as any other steel, but in this case, the occurrence of corrosion is associated with concrete. Thus, it is essential to consider the concrete's properties as well.

Concrete is a composite material which mainly consists of Cement, Aggregate (Fine and Coarse) and Water. Additionally, other materials called admixtures may be added to modify the properties of the concrete. Ordinary concrete is good in compressive strength but weak in tensile, flexural or shear forces. In addition, all concrete structures suffer from volume changes resulting from shrinkage, creep and thermal changes, producing cracks that are detrimental to the performance of the structure. To impart ductility to structures, ordinary concrete is reinforced with high tensile material such as steel. Steel in concrete is protected from corrosion by passivation, due to high alkalinity of concrete. However, one of the huge challenges facing the concrete industry is the corrosion of reinforcing bars in concrete. Over time, reinforcing steel bars may undergo various types of degradation or corrosion depending on composition, structure and the environment.

The content of this chapter can be used for developing deeper understanding by Materials Science and Engineering (MSE) students on various aspects of corrosion of reinforcement in concrete. The discussion starts with the mechanism of corrosion, followed by corrosion testing and corrosion protection using inhibitor. The emphasis placed on green corrosion inhibitors for reinforcement protection is in line with the current educational and industry trends towards sustainable development.

BACKGROUND

In general, corrosion does not damage the concrete structures. The reason is that the pores in concrete contain high levels of calcium, sodium, and potassium hydroxide, which maintain a pH between 12 and 13. This high level of alkalinity passivates the steel inside the concrete, forming a dense gamma ferric oxide (γ–$Fe_2O_3.H_2O$) that is self-maintaining which prevents rapid corrosion. But, since concrete is porous, both moisture and oxygen can easily penetrate through the pores and micro cracks in the concrete which subsequently create the basic requirements for corrosion of reinforcing steels.

Corrosion issues on reinforcing steel in concrete have significance in both structural integrity and in economic aspects. Corrosion can cause potholes, spalls, and delamination of reinforced highway structures such as bridge decks. Parking garages and support pillars also face damage because automobiles carry salt-bearing snow and ice through the garages, which melt further and permit aggressive chloride ions to permeate through the concrete. Similarly, coastal structures are subjected to corrosion when exposed to seawater containing high amounts of chloride.

A survey in the United States revealed that the cost of damage due to deicing salts alone is estimated between $325 to $1,000 million / year for reinforced concrete bridges and car parks. In North Africa, near coastal zones, and in the Middle East Arabian Gulf area, a few buildings were completely destroyed due to deterioration of the structures as a result of corrosion of reinforced concrete (El – Reedy, 2008). The cost can be considerably reduced by mitigating the corrosion problems of existing structures. It is estimated that $450–550 million could be saved per year by combating and solving the corrosion problems (Sastri, 2011). Furthermore, corrosion accidents may cause loss of human lives which cannot be estimated in monetary value.

Hence, it is very important to know and understand the concrete parameters, causes of corrosion, and the environmental exposure conditions. Numerous researches are proceeding for these purposes and focusing more towards finding the effective corrosion protection for concrete structures. Some of the protection methods include epoxy–coated reinforcement, improved quality of concrete cover, galvanized steel and corrosion inhibitors.

The schematic illustration of corrosion of steel in concrete is given in Figure. 1. Due to porosity in concrete, oxygen can easily diffuse through concrete, becoming dissolved in pore solution and at the end reaching the surface of the steel. Hazardous species can penetrate through concrete cover without causing significant damage and then promote the corrosion of steel.

The passivity over the steel can be destroyed either by carbonation, or by depassivating anions such as chlorides which are able to reach the steel. Typical electrochemical reactions are induced over the steel surface and resulted in formation of rust which is associated with the following mechanisms:

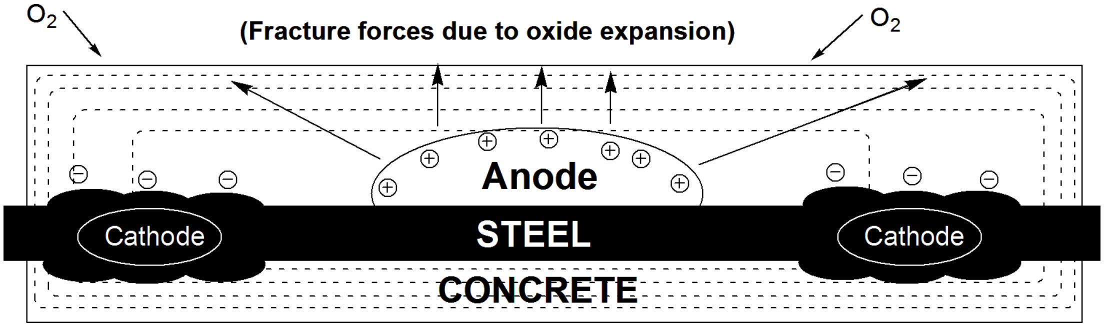
- **Carbonation:** Carbonation is a process in which carbon dioxide in the air diffuse into the concrete. Carbon dioxide dissolves into the available pore water to form carbonic acid which neutralizes the alkalis in the pore water and produces calcium carbonate that lines the pores (El – Reedy, 2008).

$$CO_2+H_2O \rightarrow H_2CO_3$$
$$H_2CO_3+Ca\left(OH\right)_2 \rightarrow CaCO_3+H_2O$$

The carbonates formed from this reaction consume the hydroxides present and thereby lower the pH of the concrete below the value of 9.0. At this level of alkalinity, the passive layer protection cannot protect the steel, correspondingly, the corrosion phenomena starts to proceed.

- **Chloride Attack:** Chloride ions penetration and the associated risk for reinforcement corrosion have been considered as

Figure 1. Corrosion process for steel in concrete



Anode Reaction

$Fe \longrightarrow Fe^{2+}+2e^-$

$Fe^{2+}+2OH^- \longrightarrow Fe(OH)_2$

$Fe(OH)_2+O_2+2H_2O \longrightarrow 4\ Fe(OH)_3 \longrightarrow$

$2Fe_2O_3.H_2O$ (RUST) + $4H_2O$

Cathode Reaction

$1/2\ O_2 + H_2O + 2e^- \longrightarrow 2OH^-$

the most significant degradation mechanism for reinforced concrete infrastructure. Regardless of the high level of alkalinity, the presence of chloride ions can readily destroy the passivity protection of alkalinity over reinforcement. Chloride contamination over concrete is considered the main cause of this phenomenon (Arup, 1983). The prime source of chloride is from inside the concrete during the casting process; in which chlorides exist in concrete as a result of the following:

- ◦ Usage of seawater or water which has high concentrations of chloride ions than specified for the concrete mixture;
- ◦ Usage of Calcium chloride as an additive for accelerating the setting time;
- ◦ Usage of other additives which have higher chloride content than that defined by specification.

Additionally, the external sources of chloride penetration into the concrete include the following:

- Exposure of concrete in sea water /in salt water;
- Usage of deicing salt in order to melt the ice;
- Storage of chemical substances with chloride ions that can attack the concrete structure (salt storage, brine tanks, aquaria etc.).

Unlike carbonation phenomenon, the depassivation mechanism for chloride attack involves no drop in overall pH. But the chloride ions act as catalysts to corrosion when there is sufficient concentration at the rebar surface to break down the passive layer. Chloride ions are not consumed in the process but they help to destroy the passive layer over steel surface and allow the corrosion process to proceed quickly.

The following are the chemical reactions incurred during chloride attack. When chloride ions appear in solution around iron, they react with Fe^{2+} of passive film over steel surface and form an iron – chloride complex.

$$\mathrm{Fe^{2+} + Cl^{-} \rightarrow [FeCl\ complex]^{+}}$$

Subsequent hydrolyzes of iron – chloride complex results in ferrous hydroxide and also liberate the chloride ions for further attack over the iron surface.

$$\mathrm{[FeCl\ complex]^{+} + 2OH^{-} \rightarrow Fe(OH)_2 + Cl^{-}}$$

Thus, chloride ions are not consumed in the process while the consumption of OH^- lowers the pH of the surrounding concrete pore solution which enhances the corrosion process.

Factors Affecting Corrosion of Steel in Reinforced Concrete

Factors affecting corrosion of steel can be classified into external and internal categories (Ahmad, 2003). External factors involve mostly through the following environmental parameters:

- **Oxygen and Moisture Availability at Rebar Level:** Presence of moisture fulfills the electrolytic requirement of corrosion cell and also combines with oxygen and helps in generating OH^- which produce rust namely $Fe\ (OH)_3$.
- **Relative Humidity and Temperature:** Relative humidity mainly affects the carbonation process of concrete and promotes corrosion. A rise in temperature increases the electrode reaction and subsequently corrosion rate also increased. If the situ-

ation is conductive for corrosion to take place, the corrosion rate is increased along with high temperature and high humidity (Uhlig, 1983).

- **Entry of Acidic Gases, Pollutants, and Carbonation to Rebar Level:** Acidic gases namely NO_2 and SO_2 as well as carbonation process have the tendency to reduce the pH of the concrete which cause commencement of reinforcement corrosion. Entry of other aggressive ions mostly chloride ion reaching to the rebar level also promotes the corrosion rate.
- **Stray Currents:** Electrolytic corrosion may be produced because of stray current sources namely building power supply systems, locomotive power supply systems and cathodic protection systems etc. (Uhlig, 1971).
- **Bacterial Action:** Anaerobic bacteria may produce iron sulfides in oxygen deficit conditions while aerobic bacteria may also aid in the formation of differential aeration cells, which can lead to corrosion reaction.

The following concrete quality parameters are classified under internal factors:

- Cement content and composition;
- Impurities and aggregates: Aggregates containing chloride salts can cause serious corrosion problems;
- Impurities in mixing and curing water;
- Aggregate size and grading;
- Chemical composition and structure of the reinforcing steel;
- Cover over reinforcing steel: Cover thickness has a significant in case of corrosion due to ease of penetration of aggressive agents.

Among many corrosion prevention methods, the application of corrosion inhibitors is more acceptable based on cost effectiveness as well as ease of application. Hundreds of chemicals including inorganic and organic – have been studied and recommended as corrosion inhibitors for a range of metals in a variety of environments – aqueous, nonaqueous, molten salts, and dry atmospheres. The negative side of these synthetic inhibitors is their cost, toxicity for living beings and hazardousness to the environment. Nevertheless, inhibitors still play a critical role in corrosion prevention.

The environment is being continuously polluted via automobile smoke into air, industrial wastes into water and nuclear plant wastes; hence the scientist's prime aim is to develop a "green solution" for any existing issues. It is evident from recent literature that many researchers tested different plant extracts for their corrosion inhibition potentials. Inhibition ability of these naturally occurring substances proved that they can serve as green inhibitors for different metal and alloy corrosion in different aggressive media.

Most university programs' prospectuses in engineering disciplines require undergraduate and postgraduate engineering students to take a course in materials engineering, which typically covers the basics of the relationships between structure, properties and processing. The concepts related to materials selection on corrosion topics are usually not treated at in-depth level. As a result, graduating engineers have little understanding of corrosion in metals or how to design against it and even less when it comes to the degradation of non – metals (National Research Council of the National Academics, 2009). Further, bachelors' students including Materials Science and Engineering (MSE) or related fields such as metallurgy, ceramics engineering and so on, receive little or no education in corrosion science and engineering. Hence, there is a significant pressure on MSE departments to include courses on emerging areas such as nanotechnology and biomaterials while corrosion and other longer established areas of materials engineering are edged out. The development of a particular scientific education in the modern higher education requires the correspondence of instructional materials and in-depth knowledge of instructors for teaching and research purposes.

CORROSION MONITORING TECHNIQUES

Corrosion has been studied by engineers and scientists for about more than 150 years and remains relevant in almost every aspect of materials usage. Corrosion monitoring for reinforced steel in concrete corrosion is a widely studied topic and many electrochemical and non – destructive techniques are available for continuous evolving. Inhibitors have to be tested in laboratory, both in solutions (screening tests) as well as in mortar and concrete (Elsener, 2001). Standard methods are listed below. Using these techniques, concrete resistivity, reference electrode potential and corrosion rate can be measured.

- Non-perturbing tests–immersion/exposure test, half-cell potential measurement, macrocell tests and impedance measurements at the open circuit potential.
- Perturbing electrochemical tests – polarization curves, potentiostatic / galvanostatic polarization.

Materials and Methods

This section of the chapter provides a brief description of materials and methods used for corrosion measurement in reinforced concrete; which includes the preparation of concrete mix and steel rods. The readers are encouraged to refer to other sources for more detailed description. The best environment in which to test the rebar corrosion is concrete and several test methods are available. A standard test method namely ASTM G 109, was issued in 1992 for determining the effects of chemical admixtures on the corrosion of embedded steel reinforcement in concrete exposed to chloride environment (Baboian, 2005). This method uses relatively high water to cement (w/c) ratio concrete with low concrete cover.

Preparations of concrete admixtures and steel rods have different standards which were reported by many researchers. The following standard is suggested by Poursaee (2011). A combination of carbon steel bars and portland cement is the common practice for making reinforced concrete. Standard concrete mixture proportions used for making 1 m^3 concrete is given in Table 1.

Steel bars (standard ASTM A 615, diameter 15.9 mm) can be used for embedding inside the concrete cubes (Figure 2). Carbon steel, Mild steel, Thermo mechanically treated (TMT) and stainless steel bars with length 230 mm can be used in concrete prism of known size of 200 x 150 x 80 mm. Initial weight (accurate) of the steel bars has to be noted before it is embedded into a concrete prism.

Non–Perturbing Tests

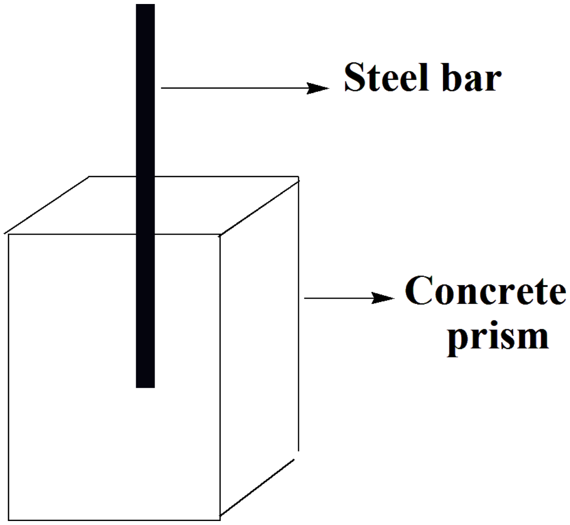
Mass Loss Test

Immersion test is the easiest way to investigate the inhibitor's ability, where the inhibitor is mixed with concrete and exposed to aggressive chloride solutions. The formation of corrosion products can be assessed by visual observation followed

Table 1. Proportion of concrete mixture for making 1 m^3 concrete

Component	Amount
Portland cement (Type 10)	355 kg
Sand	770 kg
Aggregate (20 mm)	1070 kg
Water	160 L
Eucon MRC air entrainment	40 ml / 100 kg
Water / Cementitious ratio	0. 43

Figure 2. Steel rebar embedded in concrete prism



by mass loss test (Elsener, 2001). The inhibitors should be added while mixing water according to the manufacturer's specification. While chloride ions should be introduced and penetrated into the concrete by ponding, repeated ponding and drying cycles.

The loss of metal due to corrosion is measured by exposing the pre-weighed metal specimen embedded in concrete prism to the corrosive environment (for example 3. 5% NaCl) for a known period of time (60–90 days). After the exposure time, the steel bar has to be removed by breaking the concrete prism carefully. The difference in steel bar weight before and after the exposure (weight loss) is calculated and is helpful in corrosion rate measurement. Usually, duplicate/triplicate measurements are carried out while the average weight loss is noted. Weight loss of steel bars before and after electrochemical studies namely polarization and impedance studies are also used for this purpose. According to Shetty, Venkataramana and Gogoi (2012) actual mass of rust per unit surface area may be determined as,

$$Mac = \frac{(Wi - Wf)}{\pi \times D \times L}$$

where, Mac - actual mass of rust per unit area of the bar (g/cm^2), Wi, Wf - Initial and final weight (g) of the bar before and after corrosion respectively, for a given duration of induced corrosion (T), D – Diameter of the rebar (cm) and L – Length of the rebar sample (cm). From the weight loss value, the corrosion rate (CR) can be calculated by using the following formula.

$$CR(\mu m.year^{-1}) = \frac{87600 \times W}{D \times A \times T}$$

where, D is density of iron (gcm^{-3}), A is the area (cm^2), T is the time of immersion, (h) and W is the weight loss in mg. Even though, this method is a time consuming and inaccurate method of measuring the corrosion rate, it still remains as reliable reference because of the following reasons.

- **Simple:** No sophisticated instrumentation is required.
- **Direct:** A direct measurement is obtained, with no theoretical assumptions/approximations.
- **Versatile:** It is applicable to all corrosive environments, and gives information on all the forms of corrosion.

Open Circuit Potential

Since corrosion involves electrochemical reactions, various electrochemical techniques are available to measure the corrosion rate. For example, when electrochemical cells are used in the tests, the *open* circuit potential of the sample immersed in a solution or embedded in mortar or concrete can be measured against the reference electrode namely; saturated calomel electrode (SCE), copper / copper sulphate electrode (CSE) and silver / silver chloride. For mortar or concrete samples, the reference electrode (mostly Ag / AgCl or Mn/MnO_2) can be embedded in the mortar or concrete; these embedded electrodes should be checked periodically against an external reference electrode. Typical electrochemical cell setup is depicted in Figure 3.

Open circuit potential data brings the details of overtime, passivation, depassivation, and eventual repassivation of the steel. The probability of corrosion of rebar with regard to OCP is given in Table 2.

OCP measurement alone is not reliable, since they provide information of corrosion probability and do not give the corrosion rate. Furthermore, OCP values are affected by the following factors (Song & Saraswathi, 2007):

- Concrete porosity,
- Presence of high resistive layer,
- Polarization by limited diffused oxygen.

Figure 3. Schematic diagram of electrochemical analysis

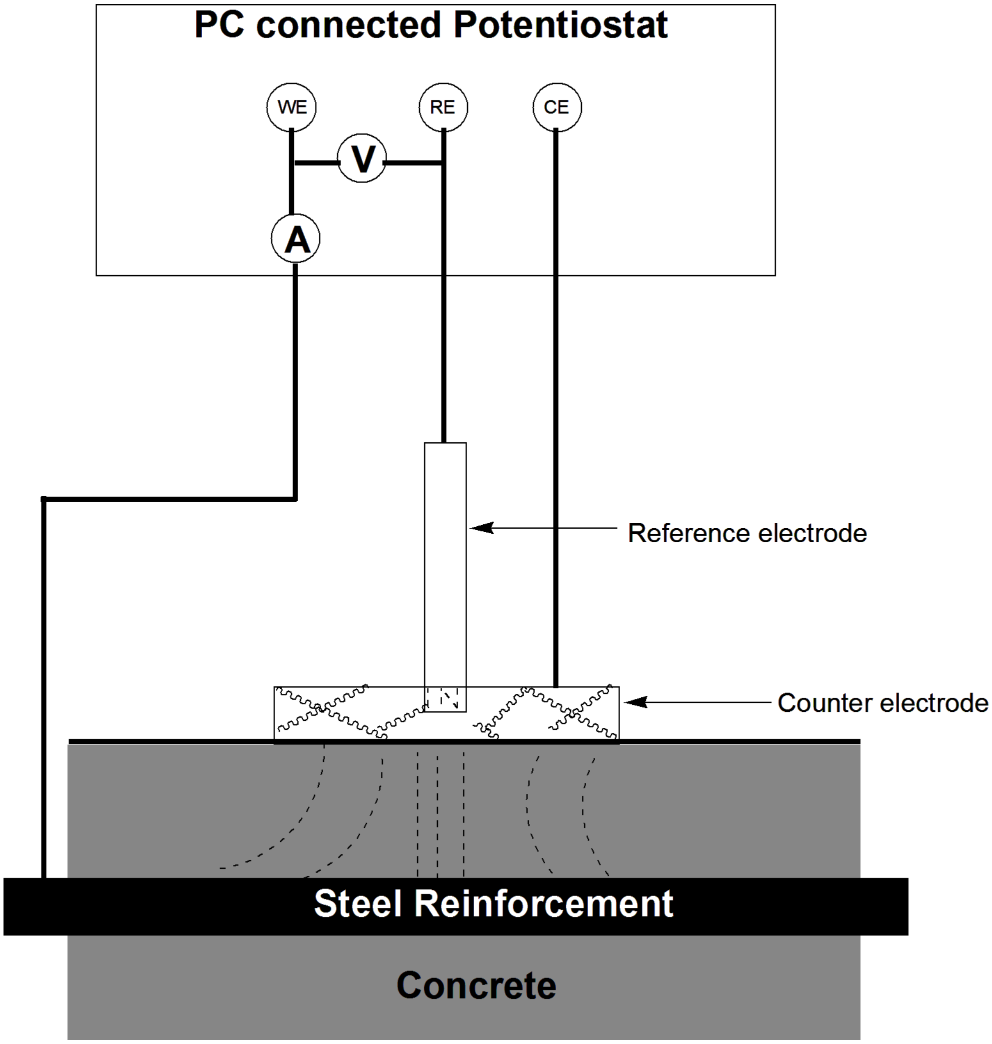


Table 2. Corrosion condition accordingly with OCP values

Open Circuit Potential (OCP) Values		Corrosion Condition
mV (vs) SCE	mV (vs) CSE	
< -426	< -500	Severe corrosion
< -276	< -350	High (90% risk of corrosion)
-125 to -275	- 200 to -350	Intermediate risk of corrosion
> -125	> -200	Low (10% risk of corrosion)

(ASTM C 876 standard. 1999; Song & Saraswathi, 2007).

However, OCP is still used by many researchers because OCP is helpful in finding out the anodic and cathodic sites in reinforced concrete structures provided the reinforcing bars are exposed to the environments.

Linear Polarization Resistance (LPR) Measurement

Due to the widespread corrosion of reinforcing steel in concrete structures, there has been a serious demand for the development of non-destructive techniques. While Linear polarization / polarization resistance (LPR) measurements fulfills this need, it requires polarizing the steel with an electric current and screening its effect on the reference electrode potential (Broomfield, 2007).

The LPR technique is considered as a non–destructive method since it is performed ± 10 mV around the open circuit potential. The principle of LPR is based upon polarizing the corrosion equilibrium on the surface of steel reinforcing bars by the introduction of a small perturbative DC signal using a counter electrode. The response of the equilibrium to this perturbation is measured with respect to a reference half-cell on the surface of the concrete. If the current applied (ΔI) is considered as a perturbative signal and the resulting potential (ΔE) is measured; the polarization resistance (Rp) can be given as,

$$Rp = \frac{\Delta E}{\Delta I}$$

From Rp, corrosion current density (i_{corr}) can be calculated as follows.

$$i_{corr} = \frac{B}{R_{ct}.A}$$

where, B is Stearn – Geary constant, A is surface area of the metal and R_{ct} is charge transfer resistance which can be calculated by subtracting the concrete cover resistance (Rs) and polarization resistance (Rp).

$$R_{ct} = Rp - Rs$$

Table 3 represents the corrosion rate accordingly with LPR measurements.

Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) involves the same electrochemical set up as with LPR technique, the difference is that the current use in LPR is DC while EIS uses AC. Impedance (Z) is the ratio of AC voltage to AC current. Normally, an AC voltage signal with frequency range from 1 MHz to 100 kHz approximately is applied and the resulting AC current (Bohni, 2005) and phase angle are measured for various frequencies. The response for AC input is complex impedance which has both real (resistance - Z) and imaginary (conductance and inductance – Z”).

Table 3. Typical corrosion rates from LPR measurements

Corrosion Classification	i_{corr} (Corrosion Current Density)	Corrosion Penetration Rate
Passive/very low	Up to 0.2 µA / cm^2	Up to 2 µm / year
Low/moderate	0.2 – 0.5 µA / cm^2	2 – 6 µm / year
Moderate/high	0.5 – 1.0 µA / cm^2	6 – 12 µm / year
Very high	> 1.0 µA / cm^2	> 12 µm / year

(Andrade & Alonso, 1996).

From impedance spectrum, the ohmic resistance of the concrete or the polarization resistance can be determined.

The plot of imaginary impedance vs real impedance gives a semicircle, with a diameter equal to charge transfer resistance (Rct). A simple equivalent circuit diagram and impedance is depicted in Figure 4 and 5 respectively. In EIS spectra, concrete cover zone produces Ohmic resistance (Rs) between the reference half–cell and reinforced bar being measured which has to be subtracted from the calculated resistance. At the highest point on the semicircle the frequency (f_{max}) can be found and the double layer capacitance value can be calculated from the following equation.

$$C_{dl} = \frac{1}{2\pi f_{\max} R_{ct}}$$

EIS analysis has following advantages,

- It involves measurement of both capacitance and charge transfer resistance.
- This technique uses amplitudes which are in the range 5 – 10 mV peak to peak. Hence the perturbation is at minimum and reduces the errors caused by the measurement.
- This method does not involve potential scan and therefore can be applied to low conductivity media also.

The main drawback of this method is the time exposure for measurements, which depend on the lowest frequency and hence EIS is barely applied on real structures. However, this method has successful application for inhibitor performance, coating performance and passive layer characteristics

Galvanostatic Pulse Measurement

Polarization resistance (Rp) can be effectively (length of time per measurement approximately 10 seconds) determined by using Galvanostatic pulse measurement (GPM). A galvanostatic current is applied to the reinforcement in the concrete and the polarization is monitored subsequently. The applied current is usually in the range of 10 to

Figure 4. Simple equivalent circuit for impedance analysis (Rs –Ohmic resistance of concrete cover zone, Rct – charge transfer resistance, Cdl – capacitance double layer)

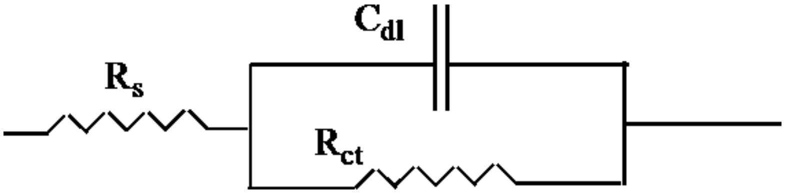
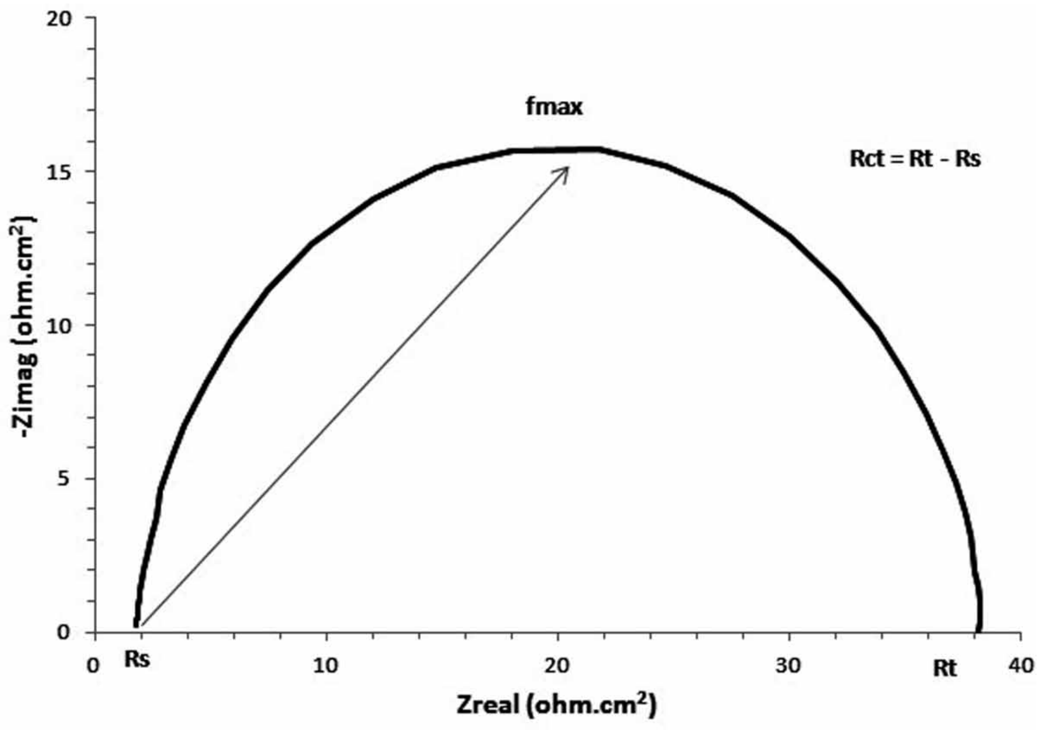


Figure 5. Impedance spectra (Nyquist plot)



200 μA and the typical pulse duration is up to 10 seconds. The reinforcement steel is polarized in anodic direction from its free corrosion potential while the resulting change of the electrochemical potential is recorded by a reference electrode as a function of polarization time. Polarization resistance (Rp) can be calculated by curve fitting and extrapolation of ohmic resistance of the concrete.

Macrocell Test

Macrocell test is standardized by the American Society for testing materials as "Standard test method for determining the effects of chemical admixtures on the corrosion of embedded steel reinforcement in Concrete Exposed to Chloride Environments" by ASTM G109-02. The macrocell technique involves the measurement of the current passing between discrete embedded metal members. This technique measures only a fraction of the total corrosion activity, however most corrosion engineers often use it because of simplicity of the measuring process.

For this purpose, reinforcing steel bars placed in two separate containers which are filled with simulated concrete pore solution, are intended to represent the top and bottom reinforcement mats of a bridge deck. Reinforcing bars were either bare or covered with mortar. Sodium chloride is added to one of the containers to initiate corrosion of reinforcing bars in this container (anode). The other container is supplied with scrubbed air to ensure adequate supply of oxygen necessary for reduction reactions (cathode). Reinforcing bars in separate containers were electrically connected over a resistor, and the solutions were connected over a salt bridge. The corrosion potential of reinforcing bars and the macrocell current flowing between the containers through the resistor are monitored.

It can be determined by simply measuring the voltage across the resistor connecting the top bar to the two bottom cathodic bars. The equation is,

$$I = \frac{V}{R}$$

where I is the macrocell current (microamperes), V is the voltage across the resistor (mV) and R is the resistance of the resistor (Ω). In other methods, a zero – impedance ammeter is connected between the cathodic and anodic bars to measure the current density. This method is non – destructive, so macrocell currents can be determined as a function of time for the same specimen.

Perturbing Tests

Potentiostatic/Galavanostatic Polarization Measurements

These techniques are implemented by polarizing the metal to a constant potential and measuring the current necessary to maintain the potential, or applying a constant current and monitoring the potential (Bentur, Diamond, & Berke, 1997). In potentiostatic test, a sharp increase in current indicates corrosion activity while in galvanostatic test a sharp decrease in potential (towards negative values) indicates corrosion activity. These techniques are destructive because they polarize the metal specimen more than 100 mV above corrosion potential. Potentiostatic measurements are preferred by many researchers because this technique is useful for investigations of passivity and its breakdown leading to pitting. This method is clear in showing that even small amounts of chloride in simulated concrete environment are capable of destroying the passivation of steel and permitting corrosion (Chaker, 1986). Their main applications are to determine if concrete admixtures are corrosive to embedded steel or to determine if inhibitors are effective against admixed chlorides.

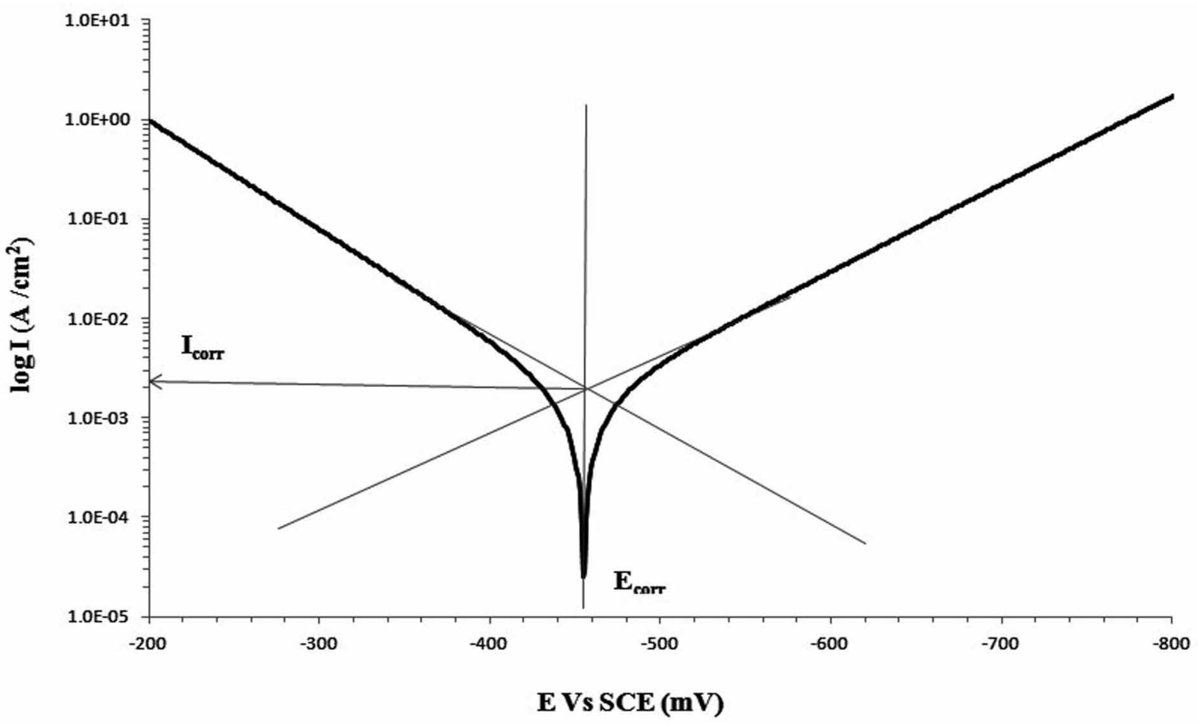
Polarization Curves

The first electrochemical method used for measuring i_{corr} was the “intersection method” of polarization curves. It is based on the extrapolation of corrosion potential (E_{corr}) of the cathodic and anodic branches of the polarization curve (Figure 6). The experimental set up and principle are similar to LPR technique while the difference is the polarizing range (± 10 mV for LPR and ± 250 mV for polarization curves). The usage of polarization curve method is limited due to its destructive nature and a new metal bar is needed for each measurement. This method has the advantage over OCP and Rp measurements as it can provide mechanistic information of inhibitors action. The following advantages make polarization curves technique a popular one for measuring corrosion in reinforced concrete:

- Rapid determination of corrosion rate and accuracy is equal or greater than conventional weight loss methods.
- Possibility to measure extremely low corrosion rates and also continuous monitoring of the corrosion rate of a system.
- It provides a direct measure of the corrosion current, which can be related to corrosion rate.

This method is also identified as a powerful tool for characterization of stress corrosion cracking sensitivity and identification of chloride breakdown potentials (Andrade & Alonso, 1996). However, for commercial inhibitor blends with unknown composition it might be difficult in any case to deduce information on the inhibition

Figure 6. Corrosion current density interpretation using polarization curves



mechanism. Because of the wide potential scan applied in obtaining polarisation curves - especially in the anodic direction - the sample can be greatly altered (e.g. by passivation or pitting corrosion can be induced).

Corrosion Protection

The knowledge of the causes of corrosion in reinforcing steel is very important for any engineer or corrosion scientist in order to design an ideal corrosion protection method. It has been estimated that remedial actions based on a better and more widespread understanding of the corrosion phenomenon could reduce significantly the financial burden of corrosion to nations. Successful applications of corrosion protection method could save billions of dollars annually.

In general, the methods used to protect a metal from corrosion are mainly based on preventing corrosion reactions. The method used depends largely on the environment to which the metal is exposed. Several methods (Winston & Uhlig, 2008) are in practice to control corrosion of steel reinforcements in concrete:

- Concrete of adequate thickness, high quality, and low permeability (specified to protect the reinforcements from the environment).
- Corrosion resistant steel (dual phase steel, epoxy coated steel, galvanised steel, stainless steel).
- Electrochemical method (Cathodic protection).
- The design of the structure (provide for drainage of salt - containing waters away from the reinforced concrete).
- Chloride content of the concrete mix should be kept to a minimum.
- Epoxy – coatings over concrete.
- Application of corrosion inhibitors.

Corrosion Inhibitors

In general, inhibitors are chemical substances which could reduce the corrosion rate at small amounts to an acceptable level and not adversely affect the properties of concrete (Sastri, 2011). Corrosion inhibitors can be introduced into the reinforced concrete by

- Adding it to the mixing water during the concrete preparation – it can extend the initiation period and/or reduce the corrosion rate after depassivation has occurred.
- Applying it to the external surface of rebar – addition during the initiation period (before depassivation occurs), the mode of action is in principle identical as for admixed inhibitors, provided the necessary concentration at the rebar is reached. If corrosion has already started, the only possible mode of action is to lower the corrosion rate.

Corrosion inhibitor for concrete is added only once to the system and no further replenishment of the inhibitor is needed. The following are the performance criteria for an effective inhibitor for concrete:

- The inhibitor should have long term stability and be efficient even at lower concentrations.
- The inhibitor should be soluble to permit homogeneous distribution and not readily leachable from concrete.
- The inhibitor must be compatible with the aqueous cement phase and should not affect the properties of concrete.
- There should be no detrimental effects of the inhibitors such as setting time, strength, and durability of the concrete.

Inhibitors can reduce the corrosion rate and protect the metal surface in either or combination of following routes (Soylev & Richardson, 2008):

- Forming a passive film on the metal surface of reinforcement prior to the ingress of chlorides.
- Buffering the pH on corrosion spot.
- Competitive surface adsorption processes between inhibitor and chloride ions.
- Competitive migration of inhibitor and chloride ions to the corrosion site.
- Scavenging oxygen dissolved in the concrete pore solution and blocking the ingress of oxygen.

Inhibitor Classification

There is a wide range of inhibitors that are used in concrete and they are classified based on their physical-chemical nature, inhibition mechanism, and or application method. In general, they can be classified according to their reaction on metal surface as follows:

Anodic Inhibitors

One of the most recognized categories are anodic inhibitors/passivators usually inorganic oxidizing substances namely; chromates, nitrites and molybdates. These inhibitors are used as admixtures in new structures or patch repairs. In general, inorganic substances passivate the metal surface and shift the corrosion potential towards noble direction. Calcium nitrite is found to be efficient corrosion inhibitors (Ann, Jung, Kim, Kim, & Moon, 2006) and used in large scale for rebar corrosion. It has been preferred over the other passivators namely; sodium benzoate and sodium nitrite, because of its compatibility with concrete properties. The addition of sodium nitrite and sodium benzoate lowers the concrete strength, and also the inhibition effect of stannous chloride was insignificant.

Corrosion inhibition potential of calcium nitrite was well documented by many researchers (Gaidis, Rosenberg, & Saleh, 1980, Nmai & Krauss, 1994). Among many hypotheses the following is the mechanism proposed for corrosion inhibition of calcium nitrite in concrete.

$$2Fe^{2+} + 2OH^{-} + 2NO_2^{-} \rightarrow \gamma - Fe_2O_3 + 2NO\uparrow + H_2O$$

During inhibition, nitrite ions compete with both chloride and hydroxyl ions to react with ferrous ions (Fe_2^+). Eventually, nitrite and / or an alkaline environment free of chlorides will reduce the number of flaws in the protective film, thus decreasing the number of available sites from which to form chloride complexes. With higher chloride content, more nitrite is required for protection or more probable that chloride will form complexes with free iron. Only monolayers are involved, virtually no nitrite or hydroxide is consumed in forming the initial protective oxides or hydroxides.

Cathodic Inhibitors

Cathodic inhibitors/precipitators slow down the corrosion by reducing the rate of hydrogen evolution/oxygen reduction on the steel surface. Mostly, they form precipitates over the cathodic locations to minimize the access of cathodic reaction species and thus reduce the rate of corrosion progress (Cicek & Al - Numan, 2011). Precipitators are not effective as compared to passivators but they are not likely to cause pitting corrosion (Davis, 2000). Salts of Zn (Heiyantuduwa, Alexander, & Mackechnie, 2006) and Mg (Baiqing, Xiaowei, Qin, & Yisheng, 2003) are considered as cathodic inhibitors since they form precipitates (corresponding hydroxides) over the cathodic site. Sodium hydroxide and sodium carbonate are the most commonly used cathodic inhibitors which act by increase the pH near metal and reduce the oxygen movement by shielding steel surface (Soeda & Ichimura, 2003). Phosphates (Gallant & Simard, 2005), ethanolamine (Martin & Miksic, 1989), silicates and polyphosphates are also considered and used as cathodic corrosion inhibitors (Soeda & Ichimura, 2003).

Mixed Inhibitors

Mixed inhibitors act on both anodic and cathodic sites which correspondingly retard their corrosion reaction by adsorption over metal surface. Organic substances with hetero atoms (N, O and S) and π – electronic clouds in their molecular skeleton namely; thiols, amines, esters, polyphenolics, are classified under mixed corrosion inhibitors. They usually donate their lone pair electrons to iron, form a protective film over the steel surface of reinforcing bars and reduce the attack of aggressive ions. Organic polymer compounds as amines and amino alcohols are identified and used as mixed type inhibitors (Qian & Cusson, 2004, Maeder, 1996, Wombacher, Maeder, & Marazzabum 2004).

Inhibitors can be further classified based on their applications as follows (Soylev & Richardson, 2008):

- Addition of inhibitor on fresh concrete as an admixture;
- Applied over the hardened concrete surface (penetrating / migrating / surface - applied corrosion inhibitor).

Need for Green Inhibitors

Currently, a number of corrosion inhibitors including organic and inorganic corrosion substances have been successfully identified, developed, patented, employed and commercialized in industries. Organic inhibitors namely; thiourea, salicylic acid as well as inorganic inhibitors namely; vanadium, antimony, copper, cobalt, tin and sulfur compounds have been patented (Veawab & Tontiwachwuthikul, 2001). However, these inhibitors are expensive, non - biodegradable and toxic (chromate, arsenic, hydrazine).

Toxicity of chemicals is defined as the ability of a substance to damage an organ system such as the liver or kidneys, to disrupt a biochemical process, such as blood-forming mechanism, or to disturb an enzyme system at some sites in the body (Sharma, 2012, Martin, Alink, Braga, McMahon, & Weare, 1995). In general, toxicity is a property of a chemical that causes damage to the body of a living organism. The toxicity may arise either during the synthesis of the compound or during its applications.

Most of the toxic effects are reversible and do not cause permanent damage, while complete recovery takes longer time. Some poisons can cause irreversible / permanent damage also. Poisons can have serious effect on just one particular organ system or they may produce generalized toxicity by affecting a number of systems. The respiratory system includes body parts such as nose, trachea, and lungs. When toxins are present in this system, the organism is likely to experience irritation, coughing, chest pain, and choking. In the case of gastrointestinal organs such as the stomach and intestines, the common syndromes are nausea, vomiting, and diarrhea.

Renal organs are kidneys, and the victim will suffer from back pain, difficulty in urinating, and abnormalities when urinating. The amount of urine can be dramatically less or more than usual. When the brain and spinal cord are affected by toxins, the victim feels dizzy and is likely to suffer from headaches. Victims may have depression and confusion and with the possibility to progress to coma. Chromate which is an inorganic substance may induce critical damage to the reproductive system. Women often experience miscarriage and abnormal fetus development. Based on their toxicity nature, inorganic / organic corrosion inhibitors can be classified as, irritants, asphyxiants, anesthetics and narcotics, systemic poisons, sensitizers, carcinogens, mutagens and teratogens (Sharma, 2012).

Impacts of these inhibitors' toxicity on human health and environment have recently been decreased, since their usage has been limited by environmental regulations. However, there is a need for further regulations, since worldwide guidelines on application and disposal of corrosion inhibitors have not yet been provided (Sastri, 2011). Since safety is a prime concern, all industries have a stake in developing non-toxic corrosion inhibitors. According to Uhlig (2004) inhibitors toxicity is measured as lethal dose (LD) and lethal concentration (LC). LD_{50} is the lethal dose of a chemical at which 50% of a group of animals are killed for 24 h exposure time, whilst LC_{50} is lethal concentration in air or water which kills 50% of test population. The BOD is a measure of how long the inhibitor will persist in the environment. Less-toxic corrosion inhibitors can be designed, if one has a reliable method of estimation of toxicity of these compounds before they are actually synthesized. Toxicity index for a few reported inhibitors is given in Table 4.

Throughout the world, a series of controlling regulations have been introduced to provide strategy on the use and discharge of the synthetic / toxic corrosion inhibitors. The U.S. Environmental Protection Agency (EPA) classified those corrosion inhibitors containing vanadium, antimony,

Table 4. Toxicity index of a few corrosion inhibitors

Chemical	LC_{50} (mg/kg)
Propargyl alcohol	55
Hexynol	34
Cinnamaldehyde	2200
Formaldehyde	800
Dodecyl pyridinium bromide	320
Napthyl methyl quinolinium chloride	644
Nonyl phenol – ethylene oxide surfactants	1310

(Sastri, Ghali, & Elboujdaini, 2007).

copper, and thiocyanate compounds as hazardous substances which are also considered as toxic pollutants under the clean water act (CWA). In Canada, the use of toxic substances including several inorganic heavy metals is restricted under the Canadian Environmental Protection Act (CEPA). The adopted rules and regulations restrict the usage of synthetic toxic corrosion inhibitors as well as make it difficult and costly to dispose of the industrial waste (Singh & Bockris, 1996). Green inhibitor should be ISO 14001 compliant which is a key element of Environment Management Systems (EMSs). All these factors encourage researchers to focus on "green corrosion inhibitors" or "eco-friendly inhibitors" which show good inhibition efficiency with low risk of environmental pollution.

Green Corrosion Inhibitors

The term "green inhibitor" can be defined as non–toxic substance that is biocompatible such as plant extract since they are of biological origin (Kesavan, Gopiraman, & Sulochana, 2012). Discovery and development of green corrosion inhibitor will be an innovative proposal for corrosion issues which also opens the gate for new education and research subjects for engineer and scientists. Recently, many alternative eco-friendly corrosion inhibitors have been studied and developed; they range from rare earth elements to natural products and/or organic compounds. The following factors are to be considered when choosing an inhibitor (Raja & Sethuraman, 2008a):

- **Cost:** May be expensive when the amount needed is huge.
- **Toxicity:** Can cause jeopardizing effects on human beings, and other living species.
- Availability of the inhibitor.
- Environmental friendliness.

Nature is one of the very rich sources of substances with wide varieties of chemical structures. It is needless to synthesize injurious chemicals while the nature around us is full of the safest ones. Plants are great chemical factories which can supply us with the chemicals required to inhibit the corrosion process. For example, phyto-constituents namely alkaloids, flavanoids and polyphenols that are very rich in N, O and π – electronic clouds; have been identified as electron donor centers of organic corrosion inhibitors. Most of the naturally occurring substances are safe and can be extracted, synthesized and characterized by simple and standard procedures. Numerous examples were reported such as henna (Ostovari, Hoseinineh, Peikari, Shadizadeh, & Hashemi, 2009), honey (El-Etre & Abdallah, 2000), onion (Sulaiman, Nor – Anuar, Abd-Razzak, & Chelliapan, 2012), *Aloe vera* (Abiola & James, 2010), lawsonia (El-Etre, Abdallah & Tantawy, 2005), mangrove tannin (Rahim, Rocca, Steinmetz, & Kassim, 2008), *Neolamarckia cadamba* (Raja, Qureshi, Rahim, Awang, & Osman, 2013), and black pepper (Raja & Sethuraman, 2008b), etc.

Recent reviews on natural corrosion inhibitors for metals (Raja & Sethuraman, 2008a) showed that the naturally occurring substances have incredible potential to reduce the corrosion rate which could also be used as a remedy to replace the synthetic corrosion inhibitors. Reviews on concrete corrosion inhibitors (Abdulrahman, Ismail, & Hussain, 2011, Hansson, Mammoliti, & Hope, 1998, Berke & Rosenberg, 1989) also revealed the significance of using green and eco-friendly corrosion inhibitors.

Table 5 depicts the literature of green corrosion inhibitors reported for reinforced concrete corrosion. These reported inhibitors exhibit competitive inhibition performance with commercial concrete corrosion inhibitors namely; calcium nitrate, magnesium salt and ethanolamine. In particular, *Bambusa arundinacea* extract (Asipita, Ismail, Majid, Abdullah, & Mirza, 2014) showed excellent concrete strength, pore blocking effect which prevents the formation of differential aeration of cells and also reduced the chloride ion diffusivity.

Table 5. Green corrosion inhibitors for reinforced concrete

Corrosion Inhibitors	Authors
Bambusa arundinacea	Abdulrahman & Ismail, 2011 Abdulrahman & Ismail, 2012 Asipita, Ismail, Majid, Abdullah, & Mirza, 2014
Rhizophora mangle L	Okeniyi, Loto, & Popoola, 2013
Vernonia amygdalina	Loto, Joseph, Loto, & Popoola, 2014 Eyu, Esah, Chukwuekezic, Idris, & Mohammad, 2013
Arghel extract	Abdel-Gaber, Khamis, & Hefnawy, 2010
Opuntia ficus indica	Acosta, 2007
Magrabe banana stem	Tantawi & Selim, 1996
Tannin – sugar fractions	Wieckzorec & Gust, 1995

Table 6 depicts the electrochemical results of *Bambusa arundinacea* extract in chloride contaminated concrete. For ideal corrosion inhibitor,

- **R_c:** Concrete resistivity should be high.
- **R_p:** Polarization resistance value should be high.
- **I_{corr}:** Corrosion current density value should be less.
- **C_{dl}:** Capacitance double layer value should be less.

Corrosion rate values should be less.

The data clearly evident that *Bambusa* inhibitor's concrete resistivity (R_c), polarization resistance (R_p), corrosion current density (I_{corr}) and corrosion rate values are well comparable with calcium nitrate inhibitor. Further, *Bambusa arundinacea* extract classified as mixed type inhibitor as like organic inhibitors has proven as an effective replacer for calcium nitrate inhibitor.

However, the literature (Table 5) revealed that only a few green inhibitors were reported for rebar corrosion. This is because the studies on green inhibitor have the following drawbacks.

For laboratory level research,

- Need sophisticated instruments and expertise;
- Longer time duration for corrosion monitoring;

Table 6. Electrochemical results of Bambusa Arundinacea extract on reinforced steel in chloride contaminated concrete

System Studied	Time (Days)	LPR				EIS				
		R_c (KΩ)	R_p (KΩ)	I_{corr} $\mu A/cm^2$	Corrosion Rate (10^{-3}) mmpy	C_{dl} mF	R_c (KΩ)	R_p (KΩ)	I_{corr} $\mu A/cm^2$	Corrosion Rate (10^{-3}) mmpy
Control	180	4.10	170	0.1525	1.80	0.112	3.97	142	0.1883	2.19
Control with $MgCl_2$	180	3.42	130	0.2008	2.30	0.133	3.44	120	0.2179	2.50
$CaNO_2$ Inhibitor	180	3.46	226	0.1153	1.30	0.115	3.64	138	0.1883	2.19
Bambusa Inhibitor	180	5.71	202	0.1285	1.50	0.080	5.73	198	0.1312	1.53

(Abdulrahman & Ismail, 2011).

*LPR – Linear Polarization Resistance, EIS – Electrochemical Impedance Spectroscopy, Rc - Concrete resistivity, Rp – Polarization resistance, Icorr – Corrosion current density, Cdl – capacitance double layer.

- Same plant species may show variable results with age, season and soil;
- Uncertain life time of inhibitors in electrolytes/concrete;
- Difficulty in finding out active ingredient responsible for corrosion inhibition potential;
- Difficulty in understanding the corrosion inhibition mechanism;
- Usage of carcinogenic solvents (Benzene, Acetone, Petroleum ether etc.,) for plant extraction;
- Difficulty in testing corrosion inhibitors blends with uncertain concrete composition.

For commercialization,

- Risk of microbiological corrosion;
- Less efficiency as compare with synthetic inhibitors;
- Stability of green inhibitors in atmospheric conditions is a question;
- Uncertain life time of green inhibitors inside the concrete;
- No "green" standards yet found as like inorganic inhibitor (Calcium nitrite) for comparison;
- Need for large scale of raw materials (plant sources) for manufacturing;
- Disposal of raw materials after extraction;
- Usage of herbs and rare species may adversely affect the plant kingdom.

However, these problems can be overcome by applying the following methods:

- Standardization of corrosion monitoring techniques;
- Standardization of green corrosion inhibitors (stability in concrete/electrolytes/atmospheric conditions/different temperatures and pressure);
- Usage of green solvents/recovery of solvents after extraction;
- Usage of agricultural wastes as corrosion inhibitors (example: paddy fibers after harvesting, mango seeds, sugar cane waste from field and industry);
- Usage of biocides to increase the stability of inhibitors;
- Ideal selection of plant extract according to the nature of electrolytes (example: alkaloid extracts are more effective in acid medium, polyphenol extracts are more effective in alkaline medium);
- Corrosion monitoring over prototype setup before used in industry/field;
- Assign an ideal solid waste disposal method for raw materials.

DISCUSSION AND RECOMMENDATIONS

Engineering students can gain more knowledge of corrosion if they are given exposure through the following activities:

- Conduct a one day workshop for the students in order to create an awareness of corrosion and it causes.
- Involve students in short or long term research on corrosion according to their level of studies.
- Assign short projects to document the corrosion causes and damages inside and outside the campus (including concrete as well as in metal).
- Motivate the students to find out eco–friendly materials to be developed as corrosion protection agents.
- Provide hands–on training for simple corrosion measurement techniques such as weight loss test.

- Teach the students to understand the corrosion causes in household materials and its protection methods.
- Conduct an industrial visit to illustrate the depth of corrosion impact on buildings and reaction vessels.
- Conduct a coastal zone trip to enable students to better understand the marine corrosion in bridges and ships.
- Motivate students towards industrial collaboration project work in corrosion.
- Offer a corrosion course for all engineering students with at least for six credits hours.

PROPOSED CORROSION COURSE

Corrosion is not a mandatory course in curriculum of most bachelor's degree programmes in Materials science and engineering (MSE). As a result, most bachelor's-level graduates of materials - and design - related programmes have an inadequate background in corrosion engineering principles and practices. It is highly recommended that all MSE departments in various universities should introduce such required learning outcomes on corrosion / green corrosion protection strategies into their curricula. All MSE undergraduate students should be required to take a course in corrosion control so as to improve the corrosion knowledge of graduate materials engineers.

A comprehensive course on green corrosion inhibitors, typically involves about 5 - 10 hours of classroom instruction for graduate students. A typical modern class would cover the following chapters:

- Corrosion basics (including kinetics and thermodynamics);
- Economic importance of corrosion;
- Corrosion of reinforced steel in concrete;
- Mechanism of concrete corrosion;
- Corrosion protection methods;
- Corrosion inhibitors;
- Classification of corrosion inhibitors;
- Corrosion monitoring techniques;
- Green corrosion inhibitors;
- Applications and limitations of green inhibitors.

The coverage is primarily theoretical, grounded in the theory of corrosion and the principles of electrochemistry. The following books can be used as references by the engineering students:

- Broomfield, J. P. (2007). *Corrosion of steel in concrete – Understanding, Investigation and Repair* (2nd Edition).
- Bentur, A., Diamond, S., & Berke, N. S. (1997). *Steel corrosion in concrete – Fundamentals and civil engineering practice*.
- Sastri, V. S. (2011). *Green corrosion inhibitors – Theory and Practice*.
- Sharma, S. K. (2012). *Green corrosion chemistry and engineering – Opportunities and challenges.*

Objectives of the Course for Undergraduate/Post-Graduate MSE Programme

This course aims to develop in Materials science and engineering (MSE) students:

- Knowledge on relation between the processing of materials and the material's structure, and the material's properties,
- Knowledge on the relationships between material's composition, processing and corrosion resistance, and
- Awareness of the potential susceptibility of materials to corrosion, eco-friendly and economically viable methods for reducing corrosion.

Assessment of Student Progress toward Course Objectives

- Two mid-term exams.
- Four homework assignments.
- Final exam.

Outcomes of the Course

On successful completion of the course, the student will:

- Understand the fundamentals of corrosion over reinforced steel in concrete and its socio -economic impacts.
- Discuss the mechanism involved in concrete corrosion and influence of various factors.
- Analyse and select the various corrosion protection methods.
- Describe the basics of corrosion inhibitor including its measurement techniques.
- Understand the importance of greener approach for corrosion protection.
- Find and propose eco-friendly and economically viable remedial actions that will eliminate or reduce corrosion to a tolerable level.

Practical Corrosion Exercise (Laboratory Level Experiments)

This section describes how to perform corrosion testing on several metals to demonstrate methods of effective corrosion protection and to make qualitative comparisons between protected and unprotected metals that are suitable instructional activities for inclusion in undergraduate corrosion courses. Conventional corrosion testing often takes long periods, uses extremely hazardous corrodents, (such as boiling hydrochloric acid) and requires careful weighing of samples to determine corrosion rates.

The loss of metal due to corrosion is measured by exposing the metal specimen of known area to the corrosive environment for a known period of time and the difference in the weight before and after the exposure (weight loss) is calculated. This laboratory experiment is intended to be performed quickly, perhaps over a period of two or three weeks, and uses relatively innocuous corrodents. The primary objective to help engineering students understand how corrosion occurs based on these experiments was achieved. The students are given a data sheet to use for observations.

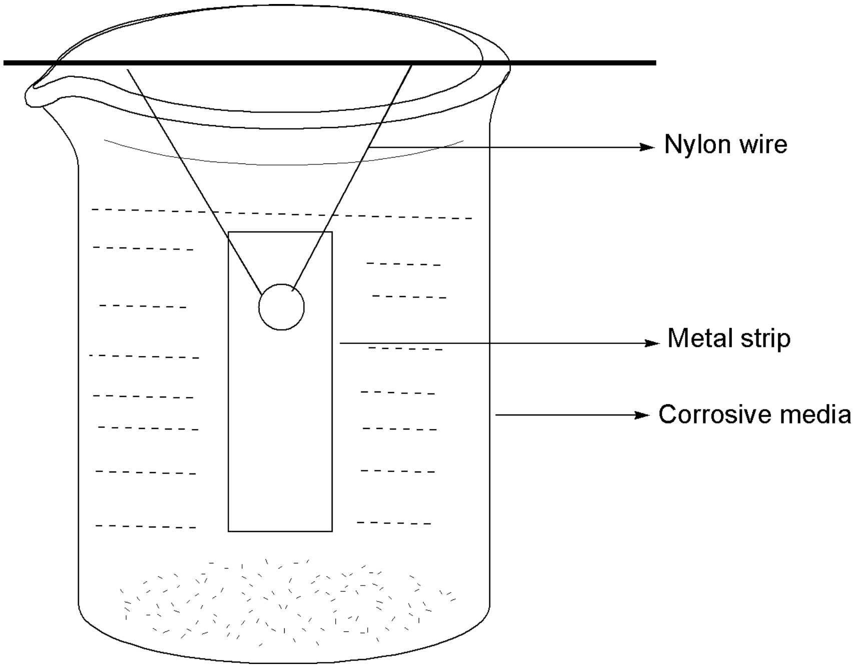
The following materials with known size (example: 3 cm length * 1 cm width and 0.5 cm thickness) and weights (example: 5 – 10 gm) are required for corrosion testing:

- Mild steel strip;
- Low carbon hot rolled steel strip;
- Straight and bent common steel nails;
- Aluminum strip;
- Copper strip;
- Cadmium coated bolts or screws.

The metal strips are drilled for hole for a support string. A piece of nylon fish line / polyethylene film is inserted into the hole and used to suspend the specimen in the glass beaker filled with corrosive media (HCl, H_2SO_4, NaCl, NaOH etc.). Metal strips have to be abraded into uniform surfaces with the help of grinding machine by using different grades of emery papers. These are finally polished by various polishing papers to a mirror like surface. Furthermore, the specimens are thoroughly washed with running water and finally degreasing is done with acetone. A typical set up is given in Figure 7.

The initial weight of the specimens should be noted and the specimens should be completely immersed in the corrosive environment (with and without corrosion inhibitor) for known period of 2 hours to 2 weeks. The inhibitor chosen may be any soluble natural substance (plant extract,

Figure 7. Weight loss experimental setup



fruit syrup, and natural juice) in corrosive media. Students can visualize the hydrogen evolution during the corrosion process. After immersion, the specimens have to be taken out then washed thoroughly with distilled water, dried completely and their weights noted using digital balance. Using the initial and final weights the loss in weights can be calculated as follows:

$$\text{Inhibition efficiency} = \frac{\begin{pmatrix}\text{Weight loss without inhibitor} - \\ \text{Weight loss with inhibitor}\end{pmatrix}}{\text{Weight loss without inhibitor}} \times 100$$

BRIDGE OF INDUSTRY AND CORROSION EDUCATION

A possible collaboration between of industry and university engineering departments can be done in following ways:

- Industry may strengthen the provision of corrosion courses and support corrosion related learning outcomes by disseminating skills sets for corrosion technologists and engineers.
- Industry may partner with engineering departments to create industry – guided capstone design courses.
- Industry may support the engineering faculties to develop research in the field of corrosion science and engineering.
- Industry should give universities incentives, such as endowed chairs in corrosion control, to promote their hiring of corrosion experts.
- Industry may partner with MSE and other engineering departments to offer corrosion-related internships and sabbatical opportunities for students and faculty, respectively.
- Industry may support their engineers to participate in short courses on corrosion

studies which will improve the knowledge and awareness of corrosion control.

- Any engineering syllabus including MSE should include industry-based cases studies or examples in their curricula which enlighten the real problems faced in industries.
- University engineering departments may test their prototype corrosion inhibitors in industries as field studies and can later develop them as commercial products.
- Wastes/by-products from industries can be tested as corrosion inhibitors in universities.

FUTURE RESEARCH DIRECTIONS

There is a tremendous room for innovation in various stages of development and applications of green corrosion inhibitors for the protection of reinforcement steel in concrete. Greener technology can be introduced in the development of green corrosion sensors, green nano coatings and self-healing coatings (smart corrosion inhibitors). Further, application of agricultural wastes, expired drugs, marine species as green inhibitors for constructions in coastal zones may enlighten an innovative route in corrosion inhibitor research. There are also avenues for novel interdisciplinary research which involves concrete technology, natural products chemistry, metallurgy, physical chemistry, electrochemistry, biological factors, environmental science and economy calculations. The major contributions of such research direction include selection of plant materials (eco-friendly/cost effective), corrosion protection methods, corrosion monitoring techniques and standardization.

CONCLUSION

Reinforced concrete is the major element used in construction industries worldwide, since it has superior physical properties and low cost. Corrosion of reinforced concrete is a common phenomenon; it impacts not only the national economy but also causes accidents which can involve loss of lives. Remedies (synthetic corrosion inhibitors) found, are dangerous to human beings and form a serious threat to the environment. Thus, it is important to understand the corrosion phenomena and develop a “green solution” for everlasting corrosion problem especially among engineering students.

Natural resources provide enormous choices to isolate corrosion inhibitors which can be well serve as a “green remedy” for corrosion prevention. Many natural corrosion inhibitors have been developed and successfully reported for metal protection of boilers, pipelines and cooling towers. Thus, a similar trend of research has to be extended to concrete corrosion as well. Usage of green corrosion inhibitors has some drawbacks, which can be easily overcome by adopting ideal inhibitors regarding the corrosive environment. Current scenario of worldwide research is to avail “eco-friendly” / “green” cure for all the existing problems and to provide “Greener Earth” to next generation. This trend covers the zone of concrete corrosion as well, while the investigations have clearly shown that “green corrosion inhibitors” have bright prospects in the future and can replace the synthetic, toxic, commercial products used in industries globally. Consequently, the addition of corrosion education on “green inhibitors” for MSE student’s curricula will serve as an effective strategy for building awareness regarding “eco-friendly / greener solution” for reinforcement steel corrosion in concrete.

REFERENCES

Abdel-Gaber, A. M., Khamis, E., & Hefnawy, A. (2011). Utilizing *Arghel* extract as corrosion inhibitor for reinforced steel in concrete. *Materials and Corrosion*, *62*(12), 1159–1162. doi:10.1002/maco.201005653

Abdulrahman, A. S., & Ismail, M. (2011). Green plant extract as a passivation: Promoting inhibitor for reinforced concrete. *International Journal of Engineering Science and Technology*, *3*, 6484–6490.

Abdulrahman, A. S., & Ismail, M.Abdulrahman A. S. (2012). Evaluation of corrosion inhibiting admixtures for steel reinforcement in concrete. *International Journal of Physical Sciences*, *7*(1), 139–143. doi:10.5897/IJPS11.966

Abdulrahman, A. S., Ismail, M., & Hussain, M. S. (2011). Corrosion inhibitors for steel in reinforcement concrete: A review. *Scientific Research and Essays*, *6*, 4152–4162.

Abiola, O. K., & James, A. O. (2010). The effects of *Aloe vera* extract on corrosion and kinetics of corrosion process of zinc in HCl solution. *Corrosion Science*, *47*(2), 661–664. doi:10.1016/j.corsci.2009.10.026

Acosta, A. A. T. (2007). Opuntia – Ficus – Indica (Nopal) mucilage as a steel corrosion inhibitor in alkaline media. *Journal of Applied Electrochemistry*, *37*(7), 835–841. doi:10.1007/s10800-007-9319-z

Ahmad, S. (2003). Reinforcement corrosion in concrete structures, its monitoring and service life prediction – a review. *Cement and Concrete Composites*, *25*(4-5), 459–471. doi:10.1016/S0958-9465(02)00086-0

Andrade, C., & Alonso, C. (1996). Corrosion rate monitoring in the laboratory and on site. *Construction & Building Materials*, *10*(5), 315–328. doi:10.1016/0950-0618(95)00044-5

Ann, K. Y., Jung, H. S., Kim, H. S., Kim, S. S., & Moon, H. Y. (2006). Effect of calcium nitrite based corrosion inhibitor in preventing corrosion of embedded steel in concrete. *Cement and Concrete Research*, *36*(3), 530–535. doi:10.1016/j.cemconres.2005.09.003

Arup, H. (1983). The mechanisms of the protection of steel by concrete. In A. P. Crane (Ed.), *Corrosion of reinforcement in concrete construction* (pp. 151–157). Chichester: Ellis Horwood Limited.

Asipita, S. A., Ismail, M., Majid, M. Z. A., Abdullah, C., & Mirza, J. (2014). Green *Bambusa arundinacea* leaves extract as sustainable corrosion inhibitor in steel reinforced concrete. *Journal of Cleaner Production*, *67*, 139–146. doi:10.1016/j.jclepro.2013.12.033

ASTM C876-91. (1999). *Standard test method for half-cell potentials of uncoated reinforcing steel in concrete.* West Conshohocken: American Society for Testing and Materials.

Baboian, R. (2005). *Corrosion tests and standards: Application and interpretation* (2nd ed.). USA: ASTM International. doi:10.1520/MNL20_2ND-EB

Baiqing, Z., Xiaowei, W., Qin, L., & Yisheng, P. (2003). Performance and mechanism of a water stabilizer for low hardness cooling water. *Anti-Corrosion Methods and Materials*, *505*(5), 347–351. doi:10.1108/00035590310492261

Bentur, A., Diamond, S., & Berke, N. S. (1997). *Steel corrosion in concrete: Fundamentals and civil engineering practice*. USA: Chapman & Hall.

Berke, N. S., & Rosenberg, A. (1989). Technical review of calcium nitrite corrosion inhibitor in concrete. *Transportation Research Record*, *1211*, 18–27.

Bohni, H. (2005). *Corrosion in concrete structures*. USA: CRC Press. doi:10.1201/9781439823439

Broomfield, J. P. (2007). *Corrosion of steel in concrete: Understanding, Investigation and Repair* (2nd ed.). New York: Taylor and Francis Publications.

Chaker, V. (Ed.). (1986). Corrosion effect of stray currents and the techniques for evaluating corrosion of rebars in concrete, Baltimore, MD: American society for testing and materials. doi:10.1520/STP906-EB

Cicek, V., & Al-Numan, B. (2011). *Corrosion chemistry*, USA: Scrivener Publications.

Davis, J. R. (2000). *Corrosion: Understanding the basics*. USA: ASM International.

El-Etre, A. Y., & Abdallah, M. (2000). Natural honey as corrosion inhibitors for metals and alloys. II. C-steel in high saline water. *Corrosion Science*, *42*(4), 731–738. doi:10.1016/S0010-938X(99)00106-7

El-Etre, A. Y., Abdallah, M., & El-Tantawy, Z. E.(2005). Corrosion inhibition of some metals using lawsonia extract. *Corrosion Science*, *47*(2), 385–395. doi:10.1016/j.corsci.2004.06.006

El-Reedy. M. A. (2008). Steel reinforced concrete structures: Assessment and repair of corrosion, USA: CRC Press.

Elsener (2001). *Corrosion inhibitors for steel in concrete: State of the art report*. London: Maney Publishing.

Eyu, D. G., Esah, H., Chukwuekezie, C., Idris, J., & Mohammad, I. (2013). Effect of green inhibitor on the corrosion behaviour of reinforced carbon steel in concrete. *APN Journal of Engineering and Applied Sciences*, *8*, 326–332.

Gaidis, J. M., Rosenberg, J. M., & Saleh, I. (1980). Improved test methods for determining corrosion inhibition by calcium nitrite in concrete. In D. E. Tonini & J. M. Gaidis (Eds.), *Corrosion of reinforcing steel in concrete* (Vol. 713, pp. 64–75). Baltimore: ASTM STP. doi:10.1520/STP27469S

Gallant, D., & Simard, S. (2005). A study on the localized corrosion of cobalt in bicarbonate solutions containing halide ions. *Corrosion Science*, *47*(7), 1810–1838. doi:10.1016/j.corsci.2004.08.008

Hansson, C. M., Mammoliti, L., & Hope, B. B. (1998). Corrosion inhibitors in concrete – Part I: The principles. *Cement and Concrete Research*, *28*(12), 1775–1781. doi:10.1016/S0008-8846(98)00142-2

Heiyantuduwa, R., Alexander, M. G., & Mackechnie, J. R. (2006). Performance of a penetrating corrosion inhibitor in concrete affected by carbonation-induced corrosion. *Journal of Materials in Civil Engineering*, *186*(6), 842–850. doi:10.1061/(ASCE)0899-1561(2006)18:6(842)

Kesavan, D., Gopiraman, M., & Sulochana, N. (2012). Green inhibitors for corrosion of metals: A review. *Chemical Science Review and Letters*, *1*, 1–8.

Loto, C. A., Joseph, O. O., Loto, R. T., & Popoola, A. P. I. (2013). Inhibitive effect of *Vernonia amygdalina* extract on the corrosion of mild steel reinforcement in concrete in 3. 5 M NaCl environment. *International Journal of Electrochemical Science*, *8*, 11087–11100.

Maeder, U. A. (1996). A new class of corrosion inhibitors for reinforced concrete. In *Proceedings of the CANMET / ACI international conference on concrete in marine environment*, St. Andrews by the Sea, Canada.

Martin, P., & Miksic, B. A. (1989). *Corrosion inhibition in reinforced cement* (Canadian Patent No. 1, 258, 473).

Martin, R. L., Alink, B. A., Braga, T. G., McMahon, A. J., & Weare, R. (1995). Environmentally acceptable water soluble corrosion inhibitors [NACE]. *Corrosion*, *36*, 121–125.

National Research Council of the National Academics. (2009). *Assessment of corrosion education*. USA: The National Academic Press.

Nmai, C. K., & Krauss, P. D. (1994). Comparative evaluation of corrosion-inhibiting chemical admixtures for reinforced concrete. In V. M. Malhotra (Ed.), *Durability of Concrete* (Vol. 145, pp. 245–262). USA: ACI SP.

Okeniyi, J. O., Loto, C. A., & Popoola, A. P. I. (2014). Corrosion inhibition performance of *Rhizophora mangle L* bark extract on concrete steel reinforcement in industrial / microbial simulating environment. *International Journal of Electrochemical Science*, *9*, 4205–4216.

Ostovari, A., Hoseinineh, S. M., Peikari, M., Shadizadeh, S. R., & Hashemi, S. J. (2009). Corrosion inhibition of mild steel in 1M HCl solution by henna extract: A comparative study of the inhibition by henna and its constituents (Lawson, Gallic acid, α-D-Glucose and Tannic acid). *Corrosion Science*, *51*(9), 1935–1949. doi:10.1016/j.corsci.2009.05.024

Poursaee, A. (2011). Corrosion measurement techniques in steel reinforced concrete. *Journal of ASTM International*, *8*(5), 1–15.

Qian, S., & Cusson, D. (2004). Electrochemical evaluation of the performance of corrosion-inhibiting systems in concrete bridges. *Cement and Concrete Composites*, *26*(3), 217–233. doi:10.1016/S0958-9465(03)00041-6

Rahim, A. A., Rocca, E., Steinmetz, J., & Kassim, M. J. (2008). Inhibitive action of mangrove tannins and phosphoric acid on pre-rusted steel via electrochemical methods. *Corrosion Science*, *50*(6), 1546–1550. doi:10.1016/j.corsci.2008.02.013

Raja, P. B., Qureshi, A. K., Rahim, A. A., Awang, K., & Osman, H. (2013). *Neolamarckia cadamba* alkaloids as eco-friendly corrosion inhibitors for mild steel in 1M HCl media. *Corrosion Science*, *69*, 292–301. doi:10.1016/j.corsci.2012.11.042

Raja, P. B., & Sethuraman, M. G. (2008a). Natural products as corrosion inhibitor for metals in corrosive media – a review. *Materials Letters*, *62*(1), 113–116. doi:10.1016/j.matlet.2007.04.079

Raja, P. B., & Sethuraman, M. G. (2008b). Inhibitive effect of black pepper extract on the sulphuric acid corrosion of mild steel. *Materials Letters*, *62*(17-18), 2977–2979. doi:10.1016/j.matlet.2008.01.087

Sastri, V. S. (2011). *Green corrosion inhibitors: Theory and practice*. New Jersey, USA: John Wiley Publications. doi:10.1002/9781118015438

Sastri, V. S., Ghali, E., & Elboujdaini, M. (2007). *Corrosion prevention and protection: Practical solutions*. UK: John – Wiley Publications. doi:10.1002/9780470024546

Sharma, S. K. (2012). *Green corrosion chemistry and engineering: Opportunities and challenges*. Germany: John Wiley Publications.

Shetty, A., Venkataramana, K., & Gogoi, I. (2012). Performance evaluation of rebar in accelerated corrosion by gravimetric loss method. *International Journal of Earth Sciences and Engineering*, *5*, 154–159.

Singh, W. P., & Bockris, J. O'M. (1996). Toxicity issues of organic corrosion inhibitors: applications of QSAR Model. In Proceedings of Corrosion 96 (Paper 225). NACE International, Houston.

Soeda, K., & Ichimura, T. (2003). Present state of corrosion inhibitors in Japan. *Cement and Concrete Composites*, *25*(1), 117–122. doi:10.1016/S0958-9465(01)00058-0

Song, H. W., & Saraswathi, V. (2007). Corrosion monitoring of reinforced concrete structures – A review. *International Journal of Electrochemical Science*, *2*, 1–28.

Soylev, T. A., & Richardson, M. G. (2008). Corrosion inhibitors for steel in concrete: State-of-the - art report. *Construction & Building Materials*, *22*(4), 609–622. doi:10.1016/j.conbuildmat.2006.10.013

Sulaiman, S., Nor-Anuar, A., Abd-Razak, A. S., & Chelliapan, S. (2012). A study of using Allium cepa as natural corrosion inhibitor in industrial chill wastewater system. *Research Journal of Chemical Sciences*, *2*, 10–16.

Tantawi, S. H., & Selim, I. Z. (1996). Improvement of concrete properties and reinforcing steel inhibition using a natural product admixture. *Journal of Materials Science and Technology*, *12*, 95–99.

Uhlig, H. H. (1971). *Corrosion and corrosion control - An introduction to corrosion science and engineering*. New York: John Wiley & Sons.

Uhlig, H. H. (1983). *Corrosion and corrosion control*. New York: John Wiley & Sons.

Uhlig, H. H. (2004). *Corrosion and control*. London: George Harrap and Co. Ltd.

Veawab, A., Tontiwachwuthikul, P., & Chakma, A. (2001). Investigation of low toxic organic corrosion inhibitors for CO_2 separation process using aqoues MEA solvent. *Industrial & Engineering Chemistry Research*, *40*(22), 4771–4777. doi:10.1021/ie010248c

Wieczorek, G., & Gust, J. (1995). Tannin - sugar fractions of vegetable extracts as corrosion inhibitors of reinforcing steel. In *Proc. 8th Europ. Symp. Corrosion Inhibitors*, Vol. 1 (pp. 599 – 608). Italy: Universith de Ferrara.

Winston, R. R., & Uhlig, H. H. (2008). *Corrosion and corrosion control – An introduction to corrosion science and engineering* (4th ed.). New Jersey, USA: John Wiley Publications.

Wombacher, F., Maeder, U., & Marazzani, B. (2004). Aminoalcohol based mixed corrosion inhibitors. *Cement and Concrete Composites*, *26*(3), 209–216. doi:10.1016/S0958-9465(03)00040-4

ADDITIONAL READING

Ahmad, Z. (2006). *Principles of corrosion engineering and corrosion control*. USA: Elsevier Publicaitons.

Ash, M., & Ash, I. (2004). Handbook of green chemicals. NY: Synapse information resources Inc.

Baloun, C. H. (Ed.). (1990). *Corrosion in natural waters*. Ann Arbor, Mich: ASTM Publications. doi:10.1520/STP1086-EB

Bertolini, L., Elsener, B., Pedeferri, P., & Polder, R. B. (2004). *Corrosion of steel in concrete: Prevention, diagnosis, repair* (2nd ed.). Weinheim: Wiley – VCH Publications.

Buchheit, R. G., Kelly, R. G., Missert, N. A., & Shaw, B. A. (2004). *Corrosion and protection of light metal alloys*. USA: The Electrochemical Society Inc.

Chaker, V. (Ed.). (1992). *Corrosion forms and control for infrastructure*. Ann Arbor, Mich: ASTM Publications. doi:10.1520/STP1137-EB

Chawla, S. L., & Gupta, R. K. (1993). *Materials selection for corrosion control*. USA: ASM International Publications.

Clark, J. H. (Ed.). (2002). Handbook of green chemistry and technology. USA: Blackwell science Publications. doi:10.1002/9780470988305

Dhir, R., & Green, J. (Eds.). (2003). Protection of concrete. In *Proceedings of the International Conference*, *University of Dundee, September 1990*. CRC Press.

Dhir, R. K., & Newlands, M. D. (Eds.). (1999). *Controlling concrete degradation*. London: Thomas Telford Publications.

Doble, M., & Kruthiventi, A. K. (2007). *Green chemistry and engineering*. USA: Elsevier Publications.

Francis, P. E., & Lee, T. S. (Eds.). (1988). *Use of synthetic environment for corrosion testing*. Baltimore: ASTM Publications. doi:10.1520/STP970-EB

Kondratova, I. L., Montes, P., & Bremner, T. W. (2003). Natural marine exposure results for reinforced concrete slabs with corrosion inhibitors. *Cement and Concrete Composites*, *25*(4-5), 483–490. doi:10.1016/S0958-9465(02)00088-4

Lichtfouse, E., Schwarzbauer, J., & Robert, D. (Eds.). (2005). *Environmental chemistry: Green chemistry and pollutants in ecosystems*. Germany: Springer Verlag Publications. doi:10.1007/b137751

Marcus, P. (Ed.). (2012). *Corrosion mechanism in theory and practice* (3rd ed.). Boca Raton: CRS Press.

Mehta, P. K. (1991). *Concrete in the marine environment*. Oxon, UK: Taylor & Francis.

Ngala, V. T., Page, C. L., & Page, M. L. (2003). Corrosion inhibitor systems for remedial treatment of reinforced concrete. Part 2: Sodium monofluorophosphate. *Corrosion Science*, *45*(7), 1523–1537. doi:10.1016/S0010-938X(02)00248-2

Ormellese, M., Berra, M., Bolzoni, F., & Pastore, T. (2006). Corrosion inhibitors for chloride induced corrosion in reinforced concrete structures. *Cement and Concrete Research*, *36*(3), 536–547. doi:10.1016/j.cemconres.2005.11.007

Rixom, R., & Mailvaganam, N. (2002). *Chemical admixtures for concrete* (3rd ed.). London: E. & F. N. Spon Publications.

Schweitzer, P. A. (2007). *Corrosion engineering handbook* (2nd ed.). USA: CRS Press.

Siva-Araya. W. F., De Rincon, O. T., & Neill, L. P., (1998). Repair and rehabilitation of reinforced concrete structures: The state of the art. USA: The American Society of Civil Engineers.

Slater, J. E. (Ed.). (1983). *Corrosion of metals in association with concrete: A manual sponsored by ASTM Subcommittee G01. 14 on Corrosion of Reinforcing Steel, and Metal Properties Council (No. 818)*. ASTM International. doi:10.1520/STP818-EB

Stansbury, E. E., & Buchanan, R. A. (2000). *Fundamentals of electrochemical corrosion*. USA: ASM International Publications.

Tonini, (Ed.), (1977). *Chloride corrosion of steel in concrete*. Baltimore: ASTM Publications.

Zheng, H., Li, W., Ma, F., & Kong, Q. (2012). The effect of a surface applied corrosion inhibitor on the durability of concrete. *Construction & Building Materials*, *37*, 36–40. doi:10.1016/j.conbuildmat.2012.07.007

KEY TERMS AND DEFINITIONS

Cell: An electrochemical system consisting of an electrolyte in which an anode and a cathode are immersed.

Corrosion Inhibitors: A substance when added in small concentrations to a liquid / gas, decreases the corrosion rate of metal/material.

Corrosion Potential: The potential of a corroding surface in an electrolyte with respect to the reference electrode.

Corrosion: Deterioration of metal and/or material by chemical interaction with the environment.

Electrolyte: A chemical substance/mixture containing ions that migrate in an electric field.

Green Inhibitors: A non–toxic substance which is eco – friendly and biocompatible.

Passivation: A reduction of the anodic reaction rate of an electrode involved in corrosion.

Reference Electrode: An electrode with an open circuit potential that is constant under similar conditions of measurement.

Reinforced Concrete: A composite material in which concrete's tensile strength and ductility are enhanced by inclusion of steel reinforcement.

Stray Current: A current flowing through paths other than the intended circuit.