Comparative Review on Corrosion of Steel Embedded in Reinforced Concrete

Er R Suresh[1], Mrs. NR CHITRA[2], Dr G M Gowthama kumar[3] Mrs. A Fathima Darras Gracy[4]

[1]ME Structural Engineering, Government College of Engineering [IRTT], Erode, Tamilnadu, India

[2]Associate professor, HOD/Civil, Government College of Engineering [IRTT], Erode, Tamilnadu, India

[3]Assistant professor/Civil, Government College of Engineering [IRTT], Erode, Tamilnadu, India

[4]Assistant professor/Civil, Government College of Engineering [IRTT], Erode, Tamilnadu, India.

Abstract – The overview of corrosion of steel embedded in reinforced concrete by different forms of Induced corrosion due to aggressive environmental ions such as chlorides, carbonation, and sulphates etc., This paper gives some important corrosion assessment methods to find out the Corrosion rate and risk of corrosion are Half-cell potential measurement, concrete surface resistivity measurement, Linear polarization resistance measurement to determine the corrosion rate of corrosion depends upon time. Different applications of software modelling using chloride diffusion in concrete, such as LIFE-365, STADIUM, COMSOL and protection methods for corrosion with merits and demerits are also discussed in this paper. In the future, further research is needed on how to control corrosion and increase the resistance of steel to reduce the corrosion rate in reinforced concrete
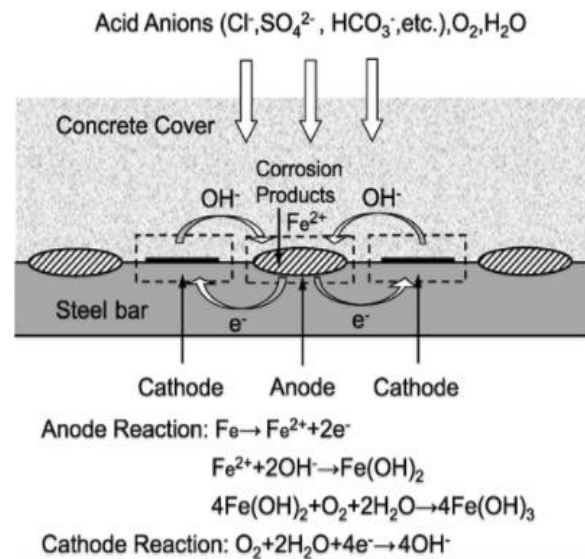
Key words – Corrosion, corrosion mechanism, chloride Induced Corrosion, carbonation Induced Corrosion, corrosion assessment procedures, corrosion protection methods.

I. INTRODUCTION

Corrosion of steel reinforcement and other embedded metals is the leading cause of poor performance and durability issues of reinforced concrete (RC) structures. It causes cracking and exfoliation of concrete, loss of bonding between steel and concrete, and a reduction in the rebar's cross-section. The loss of bond eventually would decrease members designed capacity and lead to structural failure [1]. The corrosion process is primarily driven by the interaction between the steel reinforcement and the environment. In an ideal state, the highly alkaline environment of concrete (with a pH of around 12.5) forms a protective oxide layer on the steel surface, preventing corrosion. This passive film layer, however, can be disrupted by factors such as carbonation, chlorides and sulphates and other aggressive ions are leading to the initiation

of corrosion in steel embedded in reinforced concrete. Understanding the mechanism of corrosion in reinforced concrete is crucial for developing strategies to protect and extend the lifespan of structures. It includes using corrosion-resistant materials, applying protective coatings, and ensuring proper concrete mix design and construction practices. Regular inspection and maintenance are also vital to detect early signs of corrosion and implement corrective measures before significant damage occurs. In this comparative review, the different forms of induced corrosion and their mechanisms, protective surface coatings, addition of admixtures in concrete mixes, to find out degree of corrosion using different methods and different software's to predict service life of steel embedded in Reinforced concrete as follows. The corrosion of steel embedded in reinforced concrete shown in Fig 1,

Fig 1 Corrosion of steel in Concrete [17]

$$\text{Acid Anions (Cl}^-, \text{SO}_4^{2-}, \text{HCO}_3^-, \text{etc.}), \text{O}_2, \text{H}_2\text{O}$$

Anode Reaction: $Fe \rightarrow Fe^{2+} + 2e^-$

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

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

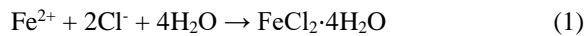Cathode Reaction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

II. DIFFERENT FORMS OF INDUCED CORROSION

There are three different forms of Induced Corrosion of steel embedded in Reinforced concrete such as a) Chloride Induced Corrosion b) Carbonation Induced Corrosion.
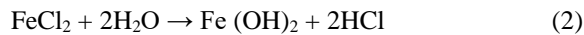
a) Chloride Induced Corrosion

Chloride-induced corrosion of RC structures is common for structure's exposed to marine environment or de-icing salt. The role of chloride ions during the anodic reaction is shown in Eq. (1). The cathodic reaction is demonstrated by Eq. (2). These equations imply that chloride ions neither participate in reaction nor are consumed during the reaction, while they catalyze the corrosion reaction and act as carriers to transport the corrosion product.

Anodic Reaction:
$$Fe^{2+} + 2Cl^- + 4H_2O \rightarrow FeCl_2 \cdot 4H_2O \qquad (1)$$
Cathodic Reaction:
$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl \qquad (2)$$

Chlorides exist in concrete in either "free" or "bound" form. It is also commonly accepted that only the free chloride ions in concrete pore solution are responsible for the initiation and propagation of corrosion while the bound chlorides can be regarded as harmless [2]. Besides chlorides from raw materials of concrete, chlorides are also present in concrete commonly by penetration from the exposed environment. This process is governed by the chloride diffusion coefficient of concrete and concrete cover thickness [3,4]. In this regard, chloride-related corrosion could be retarded through controlling concrete quality (both chloride content in raw materials and concrete mix design) and ensuring concrete cover thickness. The proportion of concrete repairs required for damage to bridges and even necessary demolition of structures as a result of chloride-induced reinforcement corrosion is the highest compared to other damage mechanisms Fig 2 shows Distribution of causes of damage to concrete surfaces from bridge structures in the German federal trunk road network [Schiesl, P. & Mayer, T. F-2007]
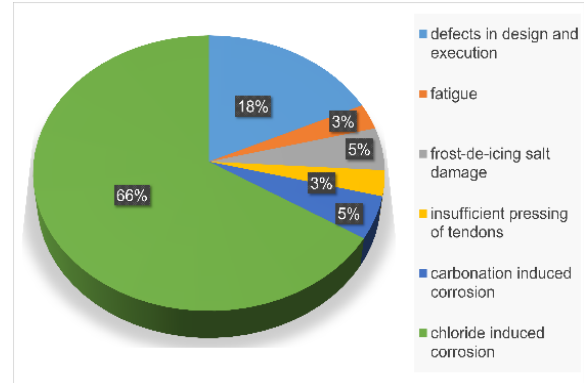

Fig 2 Distribution of causes of damage to concrete surfaces from bridge structures

b) Carbonation Induced Corrosion

Tricalcium silicate ($3CaO.SiO_2$), dicalcium silicate ($2CaO.SiO_2$), tricalcium aluminate ($3CaO.Al_2O_3$), and calcium aluminoferrite ($4CaO.Al_2O_3.Fe_2O_3$) are the common components of cement in concrete. These are frequently abbreviated as C_3S, C_2S, C_3A, and C_4AF. Whenever cement combines water, the hydration procedure creates crystalline calcium hydroxide, or portlandite $Ca(OH)_2$ (CH), as well as a gel of hydrated $CaO.SiO_2nH_2O$ (C-S-H) and other heat-evolving compounds. Carbonation in the concrete is primarily produced by the entry of atmospheric CO_2, particularly when relative humidity levels are 50-70%. Whenever pH level of concrete falls below a threshold level, the carbonation process begins, resulting in corrosion, cracking, and spalling, etc., [5]. Carbonate is formed when carbon dioxide combines with CH and CSH, which lowers the pH magnitude of the concrete and removes the passive layer. Carbonation causes shrinkage and a drop in pH magnitude to a critical level, which causes corrosion to begin. Carbonation is related to the water/cement ratio and occurs in proportion to the square root of time (Wang et.al-2010). Concrete carbonation is a neutralizing reaction that occurs between carbon dioxide absorbed from the surrounding atmosphere and alkaline hydration products (e.g., calcium hydroxide) for concrete originating from air. Carbonation of concrete is induced by a metathesis event between the bicarbonate ion (HCO_3^-) in seawater and alkaline hydration products, as detailed through Equations [6]. 1.Dissolution of CO_2 in the sea water (Eq.3), and in the fresh water (Eq.4),

$$CO_2 + H_2O + CO_3^- \rightarrow 2HCO_3^- \qquad (3)$$

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (4)$$

2.Metathesis reaction between HCO_3^- (with concentration of 140 mg/L in seawater) and OH^- (Eq.5), and precipitation reaction in between CO_3^- and the calcium ion Ca^{2+} (Eq.6).

$$HCO_3^- + OH^- \rightarrow CO_3^- + H_2O \qquad (5)$$

$$CO_3^- + Ca^{2+} \rightarrow CaCO_3 \downarrow \qquad (6)$$
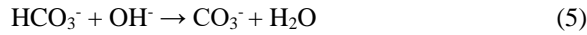
In figure 1, the carbonation Induced Corrosion having 18% causes damages to the structures during corrosion takes place. Carbonation inducing from the environmental and other way of attacking is the Second reason for initiating the corrosion in steel embedded in Reinforced concrete.

III. METHODS OF EVALUATE CORROSION IN RC STRUCTURES

a) Half-cell potential Measurements

Corrosion of reinforcement is associated with the anodic and cathodic areas along the reinforcement with consequent changes in electro-potential of the steel. Half-cell potential is an electrochemical method and is one of the most widely used methods for the detection of the probability of corrosion in steel reinforcement in concrete. The technique based on the measurement of the potential difference between the reinforcement and a reference electrode in the form of a half cell [7]. It is a simple device consisting of an electrode and electrolyte. The electrolyte is normally made from a soluble salt of the electrode metal i.e., the reference electrode is a piece of metal in a solution of its own such as copper/copper sulphate ($Cu/CuSo_4$), mercury/mercury chloride (Hg/Hg_2Cl_2) and silver/ silver chloride ($Ag/AgCl$). Half-cell measurement is based on the electrical and electrolytic continuity between the embedded steel, reference electrode and concrete are established by the movement of ions. This can be ensured by placing a wet sponge between the reference electrode and the concrete surface shown in Fig 3. The numerical value of the measured potential between the embedded rebar and the reference electrode depends on the types of reference electrode used and corrosion condition of the steel in the concrete. It indicates the importance of reference electrode being used for half-cell potential measurement. The half-cell potential measurement evaluates the probability of corrosion before damage is evident at the surface of the RC structure i.e. it gives an indication of corrosion risk of rebar and are linked empirically to the probability of corrosion. The criteria for the probability of corrosion are given in Table 1 as per ASTM C 876-15 [8].
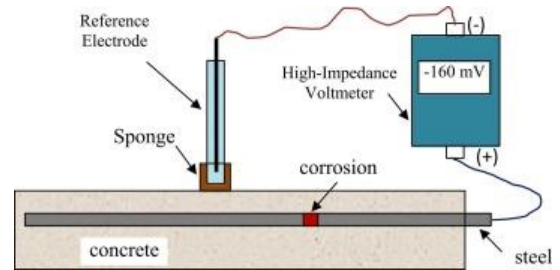

Fig 3 Half-cell potential measurement [10]

Table 1 criteria for the probability of corrosion

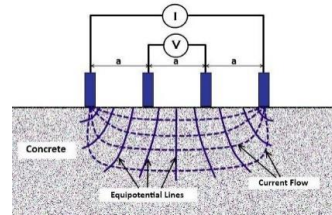| $Cu/CuSo_4$ electrode	Hg/Hg_2Cl_2 electrode	$Ag/AgCl$ electrode	Corrosion condition
> -200mV	> -126mV	> -106mV	Low (10% risk of corrosion)
-200mV to -350mV	-126mV to -276mV	-106mV to -256mV	Intermediate corrosion risk
< -350mV	< -276mV	< -256mV	High (>90% risk of corrosion
< -500mV	< -426mV	< -406mV	Severe corrosion

b) Concrete surface Resistivity Measurement

Fig 4 Wenner Four-probe Resistivity meter [12]

The Wenner four- probe system (see Fig 4) is a commonly used device to measure resistivity and consists of four equally spaced probes, which contact with the concrete surface. In this method, a low frequency alternating current is passed between two outermost probes and the resulting potential difference between the inner two probes is measured. The resistivity depends on the moisture condition of the concrete, permeability ad diffusivity of concrete and on the concentration of ionic species in the pore water. The resistivity values are dependent on moisture content of concrete and therefore may vary from time to time. And it should not be seen as definitive measures of corrosion activity but rather be used to complement with other techniques [9]. Table 2 shows the empirical interpretation of resistivity

measurements from the Wenner four-probe system [1].

Table 2 corrosion rate based on concrete Resistivity

Resistivity of concrete (k Ω-cm)	Likely corrosion rate
< 5	Very high
5 to 10	High
10 to 20	Low to moderate
> 20	Low

c) Linear polarisation Resistance technique

LPR technique is one of the main electrochemical methods for the measurement of corrosion rate, by applying stepwise potentio-static polarization or the potentio-dynamic procedures. The ASTM G59 – 97 [11] test method includes an experimental process for polarization resistance measurements that can be utilized for equipment calibration and experimental methodology verification. Additionally, reproducible corrosion potentials and potentiodynamic polarization resistance measurements are provided in it. In both procedures mentioned above, the experiment begins at the negative potential and progresses to the positive potential through the corrosion potential. The polarization resistance (R_p) value can be calculated from the slope of the potential-current plot as in Eq. (7). An instant reading on the corrosion rate can be obtained by LPR probes and instruments; and can qualitatively analyze the pitting tendency of metals in electrolytes by using the linear polarization resistance technique. For field applications, approximately all commercial LPR probes use reference electrodes made from the same metal as the sensing electrode so that the LPR probe can be installed in harsh environments such as pressurized systems, and that no special maintenance or care for the reference electrode is necessary. Thus, most commercially used LPR probes have three electrodes (the reference, sensing, and counter electrode) which are made of the same metal and in equivalent circuit solution resistance (R_s) of electrolyte between electrodes, these probes will decrease the solution resistance effect (IR drop) following its position and its proximity to the test electrode. A typical three-electrode polarization resistance probe, with an equivalent circuit, is shown in Fig. 5 The electrode configuration enables the use

of this technique in combination with other electrochemical measurements such as the zero-resistance ammeter (ZRA) or electrochemical current noise (ECN) to evaluate the stability of an inhibitor film and/or the initiation of localized corrosion on the metal's surface [12].

$$Rp = \frac{\Delta E}{\Delta i} \qquad (7)$$

Where R_p designates polarization resistance, ΔE represents the potential difference, and Δi signifies current passing through the metal. The corrosion current density is then determined using the Stern–Geary formula Eq (8):

$$Icorr = \frac{B}{Rp} \qquad (8)$$

Fig 5 Schematic diagrams of a typical three electrode polarization resistance probe [13]
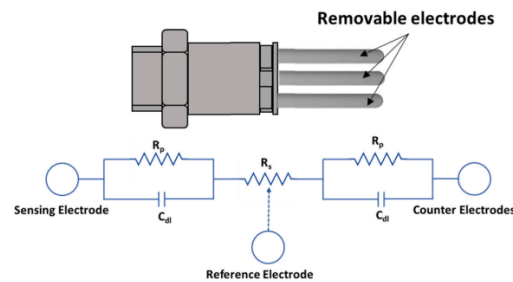
where I_{corr} denotes corrosion current density in $\mu A/cm^2$, R_p is the polarization resistance in k Ω cm^2 and Stern–Geary coefficient (B-value) can be calculated by the following relationship Eq 9:

$$B = \frac{\beta a \text{ x } \beta c}{2.303 \ (\beta a + \beta c)} \qquad (9)$$

where, β_a and β_c are the anodic and cathodic Tafel slopes/parameters in mV/decade, respectively. Generally, from the Tafel plot, the Tafel constants are obtained. Furthermore, the LPR is connected to the corrosion current density by an inverse proportional relationship. Thus, a high corrosion rate can be the indicator of low polarization resistance value and vice versa. Depending on Faraday's law, the corrosion rate (CR) can be calculated by using equation (10),

$$CR(mmpy) = \frac{3.27 \text{x} 10^{-3} \text{x Icorr x EW}}{A \text{ x d}} \qquad (10)$$

Where, I_{corr} in μ A, EW denotes equivalent weight (mass in grams that will be oxidized by the passage of one Faraday of electric charge); A represents

corroding electrode area in cm^2, and d represents corroding metal density in $gm/cm3$.

IV. APPLICATION OF SOFTWARE IN MODELLING OF CHLORIDE DIFFUSION IN CONCRETE

Apart from the Fick's chloride diffusion mathematical models, these types of special purpose software like Life-365 and STADIUM are now also available. These software types allow the designers to perform 1D and 2D analysis of chloride exposures with a variety of user-defined parameters such as material options (inclusion of silica fume or corrosion inhibitors, etc.) and steel coating. These types of software have an extensive database for different exposure conditions and are gradually proving to be a handy tool for the design engineers [14]. Moreover, service life prediction of concrete structures subjected to chloride exposure can also be performed by general-purpose software, that is, COMSOL. These types of software are now equipped with specific modules that can simulate transport/reaction with mechanical/thermal response. Bentz et al-2014 performed 1D chloride diffusion using COMSOL, and they compared the predicted service life by the solution based on simple Fick's second law and service life obtained by using specific available modules in COMSOL for binding/reaction of ingress chlorides. The variables considered were the cover thickness, threshold chloride concentration at rebar level, and material parameters (silica fume, corrosion inhibitors, and epoxy coated reinforcing bars). It was reported that, in all cases, solution based on Fick's second law was conservative and it predicted lower service lives. For a concrete cover thickness of 50 mm, the differences were 21%, 18%, 19%, 24%, and 27% for plain cement, plain cement partially replaced by 5 and 7% silica fume, corrosion inhibitor, and epoxy coated reinforcing bars, respectively [15].

V. CORROSION PROTECTION METHODS

Different corrosion protection methods [16]

Table 3 summary of corrosion protection methods

METHODS	MERITS	DEMERITS
High Performance Fibre-reinforced cementitious composite [HPFRCC] overlay	Good durability in adverse service condition, No maintenance required, Dual function as an Anti-corrosion barrier and strengthening overlay, Suitable for corrosion damaged structures needing strengthening.	The Anti-corrosion effects are limited as HPFRCCs are still a porous material, Risk of Galvanic coupling.
Anti-Corrosion coating	Convenient application, No maintenance required.	Organic coating has problem of poor fire resistance, crack, delamination, ultraviolet ageing, uneasy to remove, Inorganic coating performs not as good as organic coating as a physical barrier, Not suitable for heavily contaminated concrete.
Corrosion Inhibitors	Convenient application, Lower cost, Multiple alternative inhibitors are available towards different corrosion mechanisms.	High Requirement of penetrability when applied to the hardened concrete surface, Dosage is crucial otherwise it will backfire sometimes.
Sacrificial Anode cathodic protection [SACP]	Simple installation, design and low maintenance, No external power source required, Low risk of hydrogen embrittlement and consequently SACP is feasible to apply to PSC structures, Availability of wide range of anodes.	Lack of control system, and knowledge of protection degrees, Limited service life, Low driving voltage, thus can be used only in less resistive concrete and may be used only in less resistive concrete & may be inadequate to provide full protection, Anodes can be large and intrusive compared to ICCP.

Impressed current cathodic protection [ICCP]	Protection current is controllable, Effective for high resistive environment like concrete, Longer lifespan, Secondary benefits such as increasing pH values near steel rebar and repelling chlorides, Low maintenance cost	The need for permanent external power source and constant monitoring, Risk of hydrogen embrittlement of steel, Concrete softening and steel/concrete bond degradation, Electrical connection of all the rebars should be insured, or rebars that are skipped will corrode more severely, Lifelong running, Anodic acidity.
Electrochemical chloride extraction (ECE)	Temporary operation, Electrolyte of ECE is variable and selectable, Available for land constructions that are contaminated by chlorides, Secondary benefits such as increasing pH values near steel rebar and densifying the concrete.	More severe negative, Consequences than ICCP of hydrogen embrittlement of steel, Concrete softening, and steel/concrete bond degradation, Chloride in concrete cannot be cleaned up entirely, Multiple times of ECE treatment may be required, Not recommended to use with prestressed RC structures.

VI CONCLUSION

In this paper determined Chloride Induced Corrosion having higher rate of Initiating the corrosion of steel embedded in reinforced concrete structures. The different methods to assessing the corrosion rate and degree of corrosion by half-cell potential measurement and concrete surface resistivity are the easiest method to determine the corrosion risk factor by plotting the Half-cell potentials vs time. Some precautions should be considered at taking readings such as maintaining the level of copper sulphate or any other solution in a Half-cell probe and also maintain and ensure surface wet condition it gives accurate readings. In concrete surface resistivity measurement, the resistivity of concrete gives higher value it having higher resistance and which gives lower values it has lower resistance to corrosion and it occurs and using Linear Polarization resistance technique LPR, for corrosion parameters such as corrosion rate, corrosion current density is derived. The summary of corrosion protection methods is useful for all with merits and demerits are discussed it does not enough. In the future, further research is needed on how to control corrosion and increase the resistance of steel to reduce the corrosion rate in reinforced concrete with safety and economic concerns.

REFERENCE

[1] Method of Accelerating Chloride-Induced Corrosion in Steel-reinforced Concrete- A Comparative Review Journal of Construction and Building materials in Elsevier Publications -2021.

[2] A review on Corrosion detection and protection of existing reinforced concrete (RC) structures Journal of construction and building materials in Elsevier Publications Feb-2022.

[3] Chloride penetration into concrete in marine environment—Part I: Main parameters affecting chloride penetration, Mater. Struct. 32 (1999) 252–259.

[4] Chloride penetration into concrete in marine environment Part II: Prediction of long-term chloride penetration, Mater. Struct. 32 (1999) 354–359.

[5] Degradation mechanisms and residual mechanical properties of reinforcing steel bars exposed to natural and artificial corrosion – Review & Analysis Polytechnic Journal volume 12, issue 2 article 25 – 2022.

[6] A cationic Gemini-surfactant as effective inhibitor for mild steel in HCl solutions, Journal of corrosion science in Elsevier publications April 2010.

[7] Mechanical property and microstructure characteristics of geopolymer stabilized aggregate base, Journal of construction and Building materials, in Elsevier publications Dec 2018.

[8] ASTM C876-15, Standard Test Method for Corrosion Potentials of Uncoated Reinforcing Steel in Concrete, American Standards of Testing Methods International.

[9] Thesis of Doctorate, Study of Chloride Induced Corrosion of Reinforcement steel in cracked concrete, Department of Civil Engineering, Indian Institute of Technology Madras, March-2013 by Dr Sangoju Bhaskar, Chief Scientist,

Advanced Materials laboratory, CSIR-SERC Chennai.

[10] Improving Half-cell potential survey through computational inverse analysis for quantitative corrosion profiling Journal of Case studies in Construction Materials in Elsevier Publications Dec-2021

[11] Influence of Bridge Deck Concrete Parameters on the Reinforcing Steel Corrosion Soundar S. G. Balakumaran PG thesis, faculty of the Virginia Polytechnic Institute and State University Blacksburg, VA April 28, 2010.

[12] Cathodic Protection for Reinforced Concrete: Application to Buildings and Marine Structures. Proceedings of the Fourth International Conference on Durability of Building Materials and Components 1987.

[13] Sensors in advancing the capabilities of corrosion detection: A review Journal of Sensors and Actuators: A Physical in Elsevier Publications Sep 2021.

[14] ASTM G59-97, Standard Test Method for Conducting Potentio-dynamic Polarization Resistance Measurements, American Standards of Testing Methods International.

[15] Predicting service life of steel-reinforced concrete exposed to chlorides," Article in ACI Concrete International · January 2014.

[16] Chloride Induced corrosion of steel in concrete – An overview on chloride diffusion & prediction of corrosion Initiation time, International Journal of Corrosion – 2017.

[17] Nonuniform Corrosion-Induced Stresses in Steel-Reinforced Concrete, Journal of Engineering Mechanics, Volume 138, Issue 4 in 2014.

[18] Loganathan P Thirugnananam G S, Experimental Investigation on Corrosion prevention in RC slabs, International Journal of Advanced Science and Engineering Research, volume 4, Issue 2, 2019 (pp 162-171).

[19] Dr P Loganathan, A Fathima Darras Gracy and S Mary Rebekah Sharmila, An Experimental Investigation on Corrosion Impediment in RC slabs using Anti-Corrosive agents, AIP Proceedings, Volume 2515 Issue 978-0-7354-4201-6 2022 (pp 030001-1-030001-7).