

Corrosion of Reinforced Steel in Concrete and Its Control: An overview

MA Quraishi^{1*}, DK Nayak², R Kumar² and V Kumar²

¹Department of Applied Chemistry, Indian Institute of Technology, Banaras Hindu University, Varanasi-221005, India

²Department of Civil Engineering, Indian Institute of Technology, Banaras Hindu University, Varanasi-221005, India

Abstract

Reinforced concrete structures show a very good durability as it is capable of withstanding the different kind of environmental exposure. However, the main limitation of concrete, even of good quality, is that the penetration of chlorides, carbon dioxide (CO₂), moisture, etc., can cause the corrosion of reinforcement bars (rebars). Corrosion of structure can be reduced by proper monitoring and taking suitable control measures at the proper time interval. Detailed review of corrosion of reinforced steel in concrete and its control has been studied and are presented in this paper.

Keywords: Corrosion; Concrete; Reinforce; Chloride; Cement

Introduction

Strength of steel has been far much better than concrete yet later is the most widely used engineering material, this can be explained with three main reasons: One of the main reason is the excellent resistance of concrete for water which makes it a superior material than wood or steel for structural purposes. The second reason is that the concrete can be formed into different structural elements easily. Its easy availability and cost efficiency is the third and most important reason behind the popularity of concrete [1].

Reinforcement of concrete with steel is done to strengthen the structural element in tension as concrete is weak in it, but structures do fail as a result of corrosion attack on steel [2,3]. It has become a serious, widespread problem worldwide, with costly repairs now in billions of dollars annually. In addition, the numerous intangible losses such as the energy needed to manufacture replacements of corroded objects. The steel corrosion in reinforced concrete reduces its durability and can even result in failure of the structure.

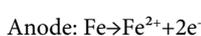
Corrosion is a phenomenon which results in the deterioration or destruction of a material when they are exposed to different environmental condition [4]. Corrosion of concrete involves an electrochemical process in which both flow of electrical currents and chemical reactions occur. The steel in reinforced concrete structures is in passive conditions and are protected by a thin layer of oxide which is due to the alkalinity of concrete (pH between 12 to 13) [2,3,5,6,7].

Corrosion Mechanism in Concrete

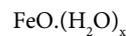
Corrosion in concrete is induced by the generation of the electrochemical potentials in following ways:

1. When two different metals are present in concrete, such as steel rebars, aluminium conduit pipes, or when significant variation exist in surface characteristics of the steel, formation of composition cell can occur.
2. Concentration cells may be formed near reinforcing steel because of the differences in the concentration of dissolved ions, such as alkalis and chlorides (Figure 1) [8].

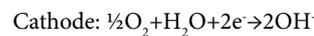
The following reactions occur at anode and cathode [9].



(Metallic iron)



(Rust)



Some parameters are essential to initiate corrosion. Presence of oxygen, humidity (electrolyte) are the two important parameters without which corrosion is not possible.[10,11,12]. The rate of corrosion is slow if the amount of water or oxygen is limited. Presence of humidity, moisture and oxygen acts as catalyst for corrosion to occur, forming more OH⁻ thereby producing more rust component Fe(OH)₂ [8,12].

Following reactions (Eq1 to 3.) represent the formation of the rust after the iron dissolution occurs at the anodic sites in the reinforcement [10] (Table 1).

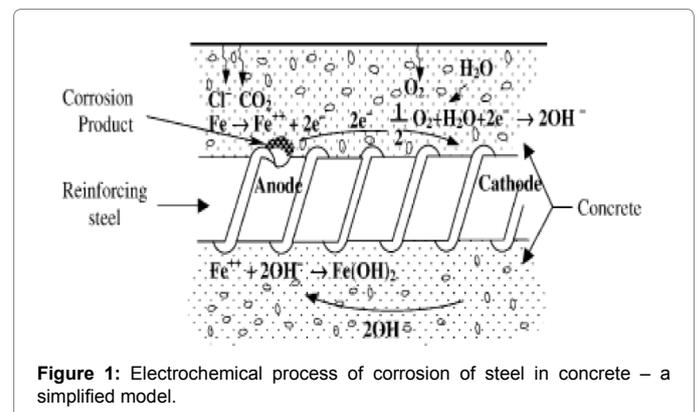


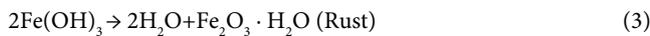
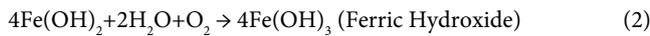
Figure 1: Electrochemical process of corrosion of steel in concrete – a simplified model.

*Corresponding author: MA Quraishi, Department of Applied Chemistry, Indian Institute of Technology, Banaras Hindu University, Varanasi-221005, India, Tel: 0542 236 8558 ;E-mail: maquraishi.apc@itbhu.ac.in

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Chloride Induced Corrosion

Chloride attack is one of the main reasons behind the corrosion of steel in reinforced concrete. Major source of Chloride ions (Cl-) are de-icing salts or seawater [5,7,13,14]. Cement, water, aggregate and sometimes admixtures can also facilitate chloride in concrete. Chlorides penetrates into the concrete through the pore network and micro cracks, forming the oxide film over the reinforcing steel and hence, accelerates the reaction of corrosion and concrete deterioration [15-17]. The passivity of steel is broken when a sufficient quantity of chlorides is present in the pore solution. The passivity of steel also depends upon the OH- concentration of the pore solution. Some author shows that the passivity is broken when the ratio of Cl-concentration to OH- concentration exceeds a particular value [7]. The mechanism of reinforcement corrosion in concrete due to chloride attack is basically an electrochemical process by which the passivating layer of steel is lost by means of formation of micro cells on the surface of steel by chloride ions. The moisture present in the pores of concrete acts as an electrolyte and the area adjacent to the concentration of chloride ions becomes cathode, thus starting the electrochemical process [13].

The bureau of Indian standard specified the maximum chloride content in cement to 0.1 percent [18].

The CTL can be defined as the maximum chloride content at the depth of steel required to sustain local passive film breakdown which promotes the corrosion process. It is usually presented as the ratio of Cl to OH [7,8].

Chlorides present in concrete in two forms, namely bound chloride and free chloride. Among bound chloride, chemically bound chlorides are utilized in the hydration product of cement and physically bound chlorides are absorbed on the surface of the gel pores. This is important as only the free chlorides are relevant to the corrosion of reinforcement. M.A Quraishi et al. [8], defined the chloride threshold level as the chloride ion concentration of steel bars in concrete provided that there are no damages at the rebar concrete interface as shown in Table 2 [8,19] (Figure 2).

Binding of Chloride Ions

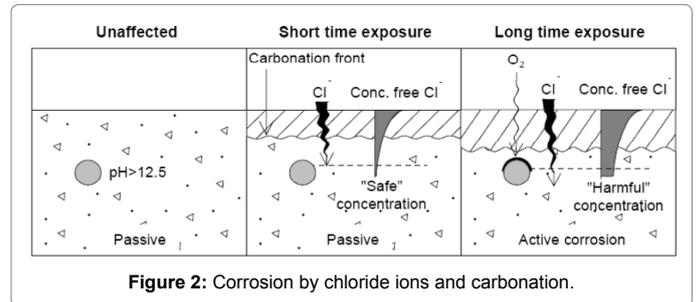
The main form of binding of chloride ions is by reaction with C₃A to form calcium chloroaluminate. Similar reaction also takes place with

Table 1: Volume variations of rust products.

Corrosion product	Colour	Volume in cm ³
Fe	Earthy	1.3
FeO	Black	1.9
Fe ₃ O ₄	Black	2.1
Fe(OH) ₂	White	3.8
Fe(OH) ₃	Brown	4.2
Fe(OH) ₃ ·3H ₂ O	Yellow	6.4
Fe ₂ O ₃	Red	2.5

Sl. No.	Risk of corrosion	Chloride Content (% wt. of cement)
1.	Negligible	0.4
2.	Possible	0.4 – 1.0
3.	Probable	1.0 – 2.0
4.	Certain	>2.0

Table 2: Corrosion risk classification at different chloride levels.



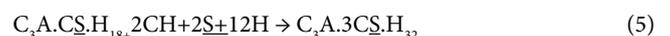
C₄AF to form calcium chloroferrite. Studies show that more chloride ions are bound when cement contain higher C₃A content and also when cement in the mix is higher. It is also reported that slag cement or concrete with GGBS binds more chloride ions. Corrosion can still occur in the absence of chloride at a pH value less than 11.5.

Sulphate Induced Corrosion

Most soil contains some sulphate in the form of gypsum CaSO₄·2H₂O, other sulphate in the form of calcium, magnesium, sodium and potassium[20-21]. Sulphate in the form of solid does not attack the concrete severely but in the solution form it can penetrate through concrete pores and react with hydrated products of cement. Due to sulphate attack cement paste expand in concrete or mortar. Sulphate salt reacts with aluminate present in concrete in the form of calcium aluminate hydrate gel (C-A-H) and form calcium sulphoaluminate (also known as ettringite) within the hydrated cement paste. As a result of this subsequent expansion of the solid phase concrete deterioration takes place. Cement contains some amount of alumina in the form of C₃A and little amount in the form of C₄AF. C₄AF shows higher resistance to sulphate attack compared to hydrate of calcium aluminate[21-23].

Chemical Reaction in Sulphate Attack

When C₃A is more than 5% in portland cement, hydration product contain alumina in the form of monosulphate hydrate, C₃A.CS.H₁₈. And if C₃A content of the cement is more than 8 percent, the hydration product will also contain C₃A.CH.H₁₈. When hydration takes place in the Portland cement calcium hydroxide generated. This calcium hydroxide reacts with sulphate and both the alumina-containing hydrates form high sulphate named ettringite (C₃A.3CS.H₃₂) as shown by equation below[21].



Calcium sulphate attack only calcium aluminate hydrate producing calcium sulphoaluminate (3CaO. Al₂O₃. 3CaSO₄. 32H₂O) known as ettringite. Water molecules may be 31 or 32.

- Methods of controlling sulphate attack
- Using sulphate resisting cement
- Quality concrete
- Use of air-entrainment
- Use of pozzolana
- High pressure steam curing
- Using high alumina cement

Delayed Ettringite Formation

Delayed ettringite formation mainly occurs due to internal sulphate attack in concrete. Delayed ettringite formation (DEF) has been reported with steam cured concrete product at high temperature. DEF causes expansion of hardened concrete due to ettringite formation leads to cracks and causes serious damage to the structure. Due to the DEF, transition zone between aggregate and cement paste shows microcrack and bonding between aggregate and cement paste are reduced which leads to strength loss of hardened concrete. Calcium silicate hydrate adsorbed sulphate ion released by the decomposition of ettringite in early stage of concrete hardening process.

Condition necessary for DEF

- Released sulphate ion from hydration product
- Free moisture content in concrete.
- Microcracks resulting from alkali-silica reaction, higher permeability of concrete, due to fatigue.

Chemical composition of Portland cement on DEF is not clearly understood. Some factors correlate strongly but the causes are not clear. Figure 3 showing the factored influences of DEF.

Corrosion Evaluation

Weight loss method

Weight loss due to corrosion of steel rebar can be calculated as the loss in weight over the initial weight.

The efficiency of inhibitor will be calculated from the weight loss (i.e., reduction in corrosion) by using the given formula.

$$\text{Weight loss (\%)} = [(W_1 - W_2) / W_1] \times 100$$

Where,

W_1 = Initial weight of rebar.

W_2 = Weight rebar after removal of corrosion products.

Corrosion control measures

Corrosion control is usually handled in design codes in the form of minimum concrete cover, minimum grade of concrete, maximum

allowable crack width, etc., when exposure conditions are particularly harsh, there is a need to apply special measures beyond the minimum provided in the design codes. These include both passive and active measures. The passive measures refer to the improvement of durability of concrete that includes the use of high quality concretes produced by the incorporation of various chemical admixtures (e.g. plasticizers, superplasticizers, shrinkage reducing admixture corrosion inhibitors) and mineral admixtures. Active corrosion system, on the other hand, directly reduces the corrosion rate, which include cathodic protection and galvanization. Some of the commonly used corrosion control measures are summarized as follows

- Good quality concrete with low W/C ration
- Use of superplasticizers
- Provision of adequate concrete cover
- Use of pozzolans
- Use of corrosion inhibitor
- Use of stainless steel (very high Cr) that produces a stable passivating film

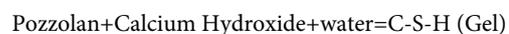
For better understanding of some of the above measures, a brief review of the use of superplasticizers, mineral admixtures and corrosion inhibitors are provided below.

Superplasticizers

Superplasticizer is the high range of water reducer. Superplasticizers can reduce the water requirement up to 30 percent without affecting workability. Superplasticizers act as a dispersing agent, with the use of superplasticizers. Superplasticizers do not chemically react with hydrated product, they affect the microstructure of cement gel and concrete mainly due to the reduction of water. SPs cannot improve the workability of zero slump concrete, mix should have an initial slump of about 20 to 30 mm. Maximum slump up to 250 mm or more depending upon the initial slump can be achieved with the help of SPs [24]. Dhir et al. [25], Salahaldeen Alsadey [26] and Collepardi et al. [27] summarized the importance of superplasticizers and presented the properties of concretes in terms of permeability, strength development, pore structure, microstructure and carbonation. It can be said that SPs reduce the porosity and permeability of concrete; hence can reduce the ingress of corrosive elements.

Pozzolanic or mineral admixture

Admixture such as fly ash, rice husk, silica fume, air-entraining admixture, surkhi, metakaolin, ground granulated blast furnace slag (GGBFS), alccofine etc. can be used as partial replacement with ordinary portland cement (OPC) to improve the properties of concrete and further reduce the use of raw material. Mineral admixture compound can have cementitious value in finely divided form in the presence of moisture, else it has no cementitious value. It is observed that on hydration of C_3S and C_2S , $Ca(OH)_2$ is formed as one of the hydration product, which directly affect the durability of concrete. The study shows that $Ca(OH)_2$ on reaction with pozzolanic materials results into an insoluble cementitious material [28-31].



Pozzolanic reactions are initially slow, hence the heat of hydration and strength development will also be slow. Passivity of steel in reinforced concrete is reduced due to the reduction in $Ca(OH)_2$ because of pozzolanic reaction and at the same time the additional

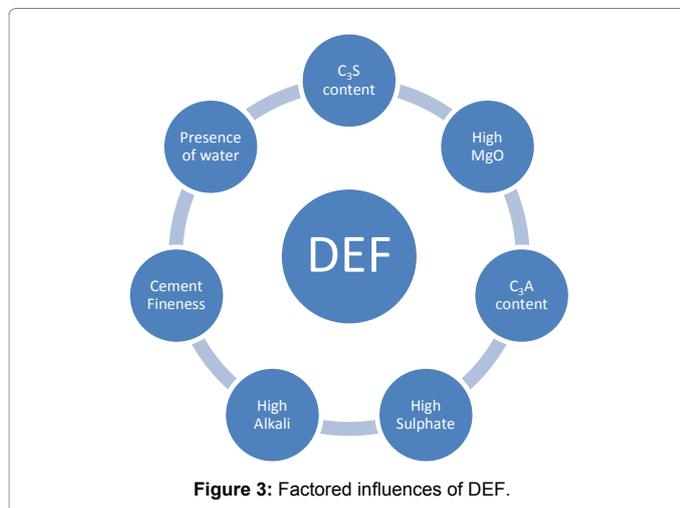


Figure 3: Factored influences of DEF.

secondary cementitious material is formed which fills the pores of concrete making it dense and thereby gives more resistance to the corrosion of reinforcement. Further, it is observed that with the increase in pozzolan content in concrete amount of water required also increases. With the use of microsilica characteristic compressive strength increases up to 60-80 MPa. Keeping the compressive strength of concrete constant, elastic modulus of concrete with microsilica is less than that of without microsilica. Partial replacement of cement by GGBFS (50% or more) results into the reduction of available C_3A content, preventing the sulphate to form delayed ettringite in concrete, preventing the concrete against sulphate attack. GGBFS offers resistance to chloride penetration [32-34].

Corrosion control by inhibitors

A corrosion inhibitor is either liquid or powder chemical additive that reduce the rate of metal wastage on mixing to a corrosive aqueous condition [10], [20], [30]. In ideal condition, corrosion inhibitor prevents corrosion in reinforced steel without adversely affecting properties of concrete. Inhibitors are uniformly distributed throughout the concrete matrix hence protecting the entire steel surface [30].

Corrosion inhibitor may include materials which mitigate reinforcement corrosion by one of the following mechanisms: (i) Oxidation by passivation of the surface; (ii) Formation of barrier layers; (iii) Influencing the environment in contact with the metal.

Following are the requirements for effective corrosion inhibitor [19]:

- The solubility should be such that rapid saturation of the corroding surface occurs without being readily leached out.
- The molecules should possess strong electron acceptor or donor properties or both.
- Induce polarization of the respective electrodes at relatively low current values.
- Be compatible with the intended system so that adverse side effects are not produced.

Inhibitors can be used by adding in concrete or applying externally on existing structures, the former type comes under the category of Corrosion Inhibitor Admixtures (CIA), CIA can mainly be classified as, anodic, cathodic or mixed organic inhibitors [5,8].

Types of Inhibitors

Corrosion inhibitors are characterized in following types: Cathodic, Anodic and Mixed, depending on whether they hinder the corrosion reaction at the anodic or cathodic sites or whether both are involved [5,35].

Anodic inhibitors

Anodic inhibitors form a protective oxide film on the surface of the metal, promoting a large anodic shift of the corrosion potential which forces the metallic surface into the passivation region. The film initiates at the anode although it may eventually cover the entire metal surface. They are also sometimes referred to as passivators. An anodic inhibitor hinders the anodic process.

Cathodic inhibitors

Cathodic inhibitors are generally less effective than the anodic inhibitors. Cathodic inhibitors function by: a) or selectively precipitating on cathodic areas to limit the diffusion of reducing

species to the surface. The cathodic inhibitors reduce the corrosion rate indirectly by reducing the cathodic process in which they itself slow the cathodic reaction or they precipitate selectively on those areas which are cathodic to reduce the diffusion of reducing species to the surface.

Mixed inhibitors

Mixed inhibitors is a combination of both anodic and cathodic processes, as there is danger of pitting while using anodic inhibitors. Therefore, it became common practice to use mixed inhibitors instead of using both anodic and cathodic inhibitors at a time in concrete [4].

McCarthy, et al. [36] have studied the effect of Water Proofing, WP, (stearate/other water based repellent) admixtures and Calcium nitrite based inhibitors, CI, on reinforced concrete reduce chloride ingress and reinforcement corrosion. Results show that the strength of the concrete is affected by the presence of WP and a slight reduction in 28 days strength is reported, while CI added sample shows an increase in 28 days strength. It is observed that the presence of WP reduces chloride ingress rate, thus reducing the intensity of corrosion propagation. Berke and Rosenberg [37] studied the benefits of calcium nitrite inhibitor and shows that its performance increases with lesser w/c ratios, and for higher inhibiting effect, the CI/NO₂ ratio should be below 1.5. Hope [38] summarized that the combination of calcium nitrite and sodium molybdate is more efficient than calcium nitrite alone in corrosion resistance. Dhoubi et al. [39] have examined the inhibition efficiency of sodium phosphate and sodium nitrite, and found that the sodium nitrite is not effective at all if its concentration is lower than that of the chloride ions but sodium phosphate is totally effective when its concentration equals the chloride concentration. Vashi and Desai [40] have studied the effect of corrosion of zinc in hydrochloric acid containing hexamine at different inhibitor concentration and temperature. Study shows that with the concentration of inhibitor increases the inhibitor efficiency (I.E.) of hexamine increases and with the increase in concentration of acid the inhibitor efficiency (I.E.) of hexamine decreases. Al-Saade and Abas [41] have assessed the effect of hexamine as corrosion inhibitor for Galvanized Steel in Hydrochloric Acid Solution. In this the corrosion of galvanized steel in hydrochloric acid solution (pH=2) containing different hexamine concentration has been studied at temperature range (298-328) K, by using computerized potentiostat. Corrosion protection percentage of galvanized steel using different concentrations and at different temperatures reaches the range of 51-86%. The corrosion protection percent was found to increase with the increase of temperature and to decrease with the increase of hexamine concentrations. Hexamine caused to decrease penetration loss and weight loss, with it used in low concentration (7.4×10^{-5} - 3.57×10^{-4}). Erdem [42] have examined the effects of admixture such as lime, 0.1% sodium citrate by weight of cement and various super plasticizers on the hydration of perlite-gypsum plaster, perlite-perlite-white Portland cement and perlite-blended Portland cement mixtures were investigated by measurement of flexural and compressive strength by DTA-TG. Sodium Citrate was found to have negative effects. Sodium citrate causes retardation of setting time of cement and decrease the strength by more than 200%.

Quraishi et al. [43] studied the effect of sodium citrate, calcium nitrate, and hexamine on corrosion of steel. In this study, they reported the effect of inhibitor on normal consistency of cement, initial and final setting time of cement, compressive strength of cement, soundness of cement and compressive strength of concrete. The results of the study also concluded that hexamine and calcium nitrite are more efficient inhibitor. It showed 45 % and 25% inhibitor efficiency at the denseness of 0.5% hexamine and 0.5% calcium nitrite by weight of cement

respectively. Further, sodium citrate also prevents the hydration of cement, but it is not suitable as an inhibitor. The addition of Inhibitor acts as retarder for the initial and final setting period of the cement and retard the compressive strength at initial days. After 180 days strength is improved significantly.

Conclusion

The compressive strength of concrete decreases with the addition of inhibitors as observed at various curing intervals. However, with the increase in curing period the difference in compressive strength of inhibited concrete and blank sample (without inhibitor) reduces.

The size of voids in the samples of inhibited concrete is smaller in comparison to blank samples (without inhibitor). With the use of corrosion inhibitor the setting time of cement increased as compared to the blank sample (without inhibitor). It is observed that water demand increases and rate of gain of early strength decreases in proportion to the amount of pozzolan increases.

It has been amply demonstrated that the best pozzolans in optimum proportions mixed with Portland cement improves many qualities of concrete, such as: lower the heat of hydration and thermal shrinkage, increases the water tightness, reduce the alkali-aggregate reaction; improve resistance to attack by sulphate soils and sea water, improve extensibility, lower susceptibility to dissolution and leaching and improve workability.

Concrete containing microsilica showed outstanding characteristics in the development of strength, improvement in durability of concrete. With regard to whether or not, silica fume is effective for alkali-aggregate reaction, some research worker report that it is effective, other conclude that while it is effective, addition of silica fume in small quantity increases expansion.

Research works have shown that the use of slag leads to the enhancement of intrinsic properties of concrete in both fresh and hardened conditions. With the use of GGBS, reduction in heat of hydration, higher ultimate strength, improve resistance to corrosion of steel reinforcement and increased resistance to chemical attack.

It is understood that reinforcement corrosion can be solved only by a combination of good concrete quality, use of admixture, adequate cover and crack width limitation. From the review, it is very clear that a synergistic effect of mineral and chemical admixtures shall lead to significant improvement in the design life of RC structures.

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