

Corrosion and Corrosion Mitigation of Rebar in Concrete Exposed to Marine Environment - A Review.

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Abstract -Corrosion of reinforcement steel enclosed in Portland cement is protected except when the normal passive state in the alkaline medium is being altered by the ingress of aggressive ions from the environment. Consequently, the anticipated durability of the concrete structure is truncated. Corrosion is a general phenomenon that has plagued the human economy globally since the existence of mankind. The effect is felt in every sectors of human endeavor; such effect is detrimental to both economy and sometimes could result to loss of lives if appropriate monitoring and control measures are taken for granted. In order to ensure effective control, the corrosion engineers need adequate knowledge of corrosion mechanism of reinforcement steel in concrete and all relevant available countermeasures in order to extend the life span of the structures. This paper reviews the basic corrosion mechanism of reinforcement bar embedded in concrete exposed to aggressive environment and appropriate mitigation measures to ensure concrete structures reliability.

Keywords: *Cathodic, Concrete, Steel, Coating, Corrosion, Chloride.*

I. INTRODUCTION

The degradation of reinforcing steel due to corrosion is prevalent in concrete structures all over the planet. Corrosion of reinforcing steel emanates from mainly carbonization and chloride penetration effect. Generally, most structures are contaminated with chloride as a result of deicing during the winter and chloride laden environment such as marine for offshore and coastal structures [1]. Corrosion is the deterioration of materials especially metals by chemical or electrochemical reaction with the environment. Deterioration of steel reinforcement is a major degradation mechanism for concrete structures in chlorides laden and industrial environments. This natural phenomenon occurs all over the planet earth, in every continent, both in the cities and rural areas. Corrosion damage causes cracking, delamination and spalling which result to

weakening and quickens the aging process for high way structures, parking structures, concrete pavement, offshore platforms, pipelines, water front structures and waste liquid treatment structures [2], [65].

Reinforced concrete is widely used as construction materials in various fields of constructions. However due to interactions with aggressive environments such as marine and industrial zones, many concrete structures experience accelerated deterioration which shortens their life span. The corrosion of reinforcing steel seems to be one of the main contributors of such degradation [4]. The negative impact of corrosion is enormous and it's a global issue that demands great and immediate attention. Corrosion costs the earth billions of dollars yearly. Almost \$10 billion is spent yearly in the Middle East on corrosion related cost as it was revealed by President of Bahrain Society of Engineers in his address in the opening session of the 14th Middle East corrosion conference held in February 2012[3]. While the in the United States alone about \$8 billion is spent annually for highway bridges as result of corrosion [1]

In the past, most of the designs and applications of reinforced concrete materials and structures longevity were taken for granted without considering the environmental impact on them. But in recent time, engineers and researchers are so concern in search of reliable cost-effective measures to eliminate or alleviate the corrosion reinforcing steel for concrete structures durability. For examples, various measures such as; design, coating and environmental modifications are currently in place. It is globally known that structures exposed to seawater and its environment are highly prone to chloride attack that accelerate corrosion initiation in reinforcing steel, which is the main anguish behind the present anxiety regarding concrete durability. The cost of renovating or replacing deteriorated structures by government and private sectors is enormous. Therefore, a proper understanding of corrosion mechanism and mitigations are very imperative.

II. THE THERMODYNAMICS OF CORROSION OF METALS IN AQUEOUS MEDIUM

Thermodynamics explains the energy changes involved in the electrochemical reaction between the electrodes in the

electrolyte as a result of electrical connections during corrosion of metal. The energy change is the driving force that controls the spontaneous direction of a chemical reaction. It explains whether the metal will experience corrosion or otherwise under a given environmental conditions such as pH and temperature. Thus the relationship between potential and pH can be illustrated using Pourbaix diagram [5], [6], [7], [8]. However, it does not predict corrosion rate but can be used to determine whether corrosion will occur or not.

III. CORROSION MECHANISM IN CONCRETE

A. Pitting

Pitting is a form of severe non-uniform corrosion attack that results to formation of holes (pits), these holes are relatively small in most cases [10]. Pitting corrosion is a localized corrosion, its takes place over more restricted areas which develop into a pit depending on the time and corrosion rate. One likely initiation method is the buildup of chloride ions leading to a localized breakdown of passive protective oxide films at isolated locations. Metal loss from the anodic region leads to the development of pit. Unlike general atmospheric corrosion, where the corrosion product is mainly a form of insoluble iron oxide, pitting attack results in the formation of soluble ferric chlorides [7].

The main factor that causes and hastens the initiation and propagation of pitting is electrical contact between non-similar metals or between corrosion cells. These couples cause a difference of potential that result in an electric current flowing through the water or across the moist steel [9]. The pH of the concrete plays a vital role in pitting initiation, pitting potential tends to be more negative when there is a decrease in passivation as a result of reduction of pH value, which may lead to high pitting tendency in rebar [11]. Studies have shown also that at pH 12.50, rust formed at rebar in concrete is more stable and impermeable compared to pH < 12.5, hence pitting tendency is high at this level. Pitting initiation is slowed down in a fine grained rebar than in rough surface rebar [12] [13].

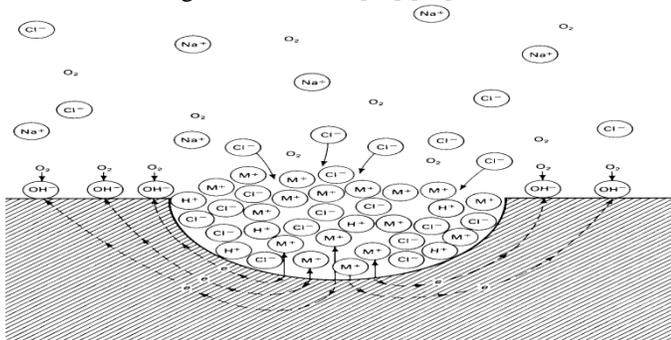
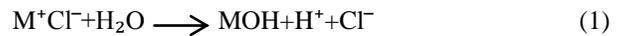


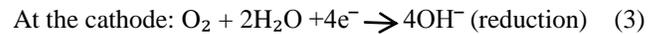
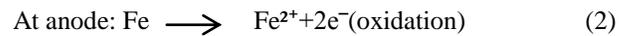
Fig. 1: Autocatalytic processes occurring in corrosion pit [10]

B. Crevice

Crevice corrosion is a localized form of corrosion that occur within or adjacent to narrow gaps or opening within a joint in a metal or metal-to-nonmetal interface. It is as a result of local differences in oxygen concentrations. Carbon steel will in chloride contaminated solution will suffer more crevice corrosion when the crevice is narrow enough so that the exchange of ion species between the external and the internal solutions is difficult, thereby accelerating the aggressiveness of the crevice solution.[9] Oxygen depletion has a vital indirect influence because after the depletion of oxygen present, the dissolution of metals proceed, this result to the formation of excess positive charged ions in the solution which necessitate the migration of chloride ions into the crevice in an attempt to balance the reaction. In several aqueous environments, the solution within the crevice has been found to develop high concentration of hydrogen ions and chloride ions, which are so corrosive. Many alloys that passivate are prone to this form of corrosion because protective films are usually destroyed by the presence of H⁺ and Cl⁻ ions.



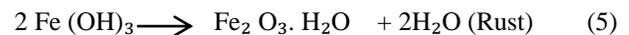
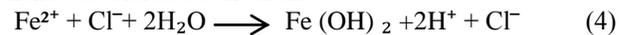
Four stages could be recognized [14] in the formation of crevice corrosion .Stage 1: Corrosion occurs as usual both inside and at the exterior part of the interface. This involves both anodic and cathodic reactions. At the anode, electrons are released which make the metal becomes positively charged. The positively charged metallic ions are counter balanced by the hydroxyl ions from the cathodic reactions at the cathode.



Stage 2: at this stage, the depletion of oxygen occurred in the crevice due to the reaction at the cathode region.

Stage 3: Chloride ions and hydroxyl ions migrate into the crevice by diffusion mechanism to compensate the absence of oxygen as a result, chloride salt is formed which when combined with water results to metallic hydroxide and hydrochloric acid.

Stage 4: At this stage, more chloride ions combined with the metallic ions; thus lowering the pH in the crevice and consequently lead to more dissolution of the metal (Fe) hence accelerates corrosion.



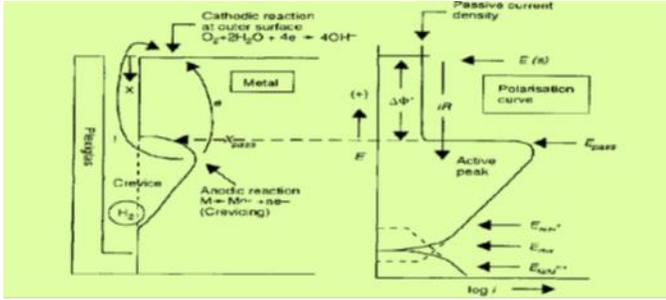


Fig. 2: Mechanism of active and passive corrosion and its corresponding anodic and cathodic reactions in crevice corrosion [14].

IV. CHLORIDE MECHANISM IN CONCRETE.

In concrete, chloride can either be dissolved in the pore solution or chemically and physically bound to the cement hydrates along the path of diffusion. Only the bound chlorides dissolved in the pore solution continue to migrate through concrete as a result of concentration difference and thus a diffusion mechanism [17, 18] as a result of this penetration at a certain concentration level, resulting to a low pH anterior [15], consequently corrosion is initiated and possible propagate if unabated. In the absence of some poisonous influences and agents, the environment provided reinforcing steel by the surrounding concrete is almost ideally suitable for preventing corrosion in rebar steel. [19] The amount of free chloride ions is lowered by the binding mechanisms; which consequently reduce the rate of migration. The most important factor that controls the penetration of chloride ions is the concrete permeability and this is sometimes dependent on the cement type, cement/water ratio, binding capacity of cement paste and environmental conditions M. Salta et al. [20].

concrete-steel interface before commencement of corrosion. Previous studies had shown that the possibility of steel corroding in chloride solution increases with $[Cl^-/OH^-]$ ratio of the solution and a threshold value of 0.61 was suggested [21]. Linhua Jiang et al [22] investigated the influence of chlorides on threshold level of reinforcement corrosion; they stated that with increase in the chloride salt in the simulated concrete pore solution, resulted to reduction in the steel potential E_{corr} and increase in current density I_{corr} which indicate corrosion initiation and consequently the corrosion potential decreased below $-350mV$ and current density greater than $0.1\mu A/cm^2$ which indicate the onset of active corrosion. The chloride threshold is dependent on the presence of macroscopic voids in the concrete near the steel surface. Usually, voids can be seen in real structure due to partial compaction may reduce the strength of the layer of cement hydration products deposited at the steel-concrete boundary [15]. Many other factors such as temperature, concrete composition, steel surface morphology or composition could affect the chloride threshold, environmental exposure [23]. The relationship of chloride threshold and other factors such as carbonation, complete compaction and humidity is shown in the figure below:

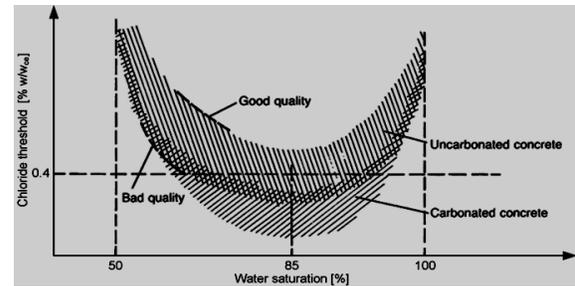


Fig. 4: The effect of concrete properties on chloride threshold [5]

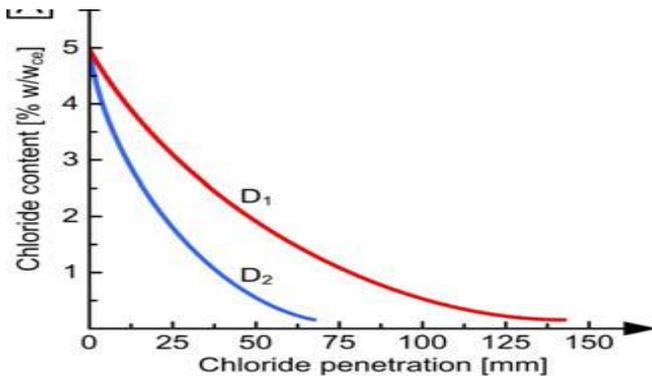


Fig. 3: Chloride diffusion model in concrete [5]

A. Chloride Threshold

Chloride threshold is the term used to describe the maximum possible concentration of chloride in the

VI. EXPOSED STRUCTURES

Structures exposed to the atmosphere, in aerated environment where oxygen can easily reach the steel surface through the air-filled pores, the reinforcement electrochemical potential is about 0 V SCE. In real life, the risk of corrosion in non-carbonated concrete obtained with normal Portland cement for pH greater than 13 is considered low for chloride contents below 0.4% by mass of cement and high for levels above 1%. [14]

VII. SUBMERGED STRUCTURES

In a submerged reinforced concrete structure, either in ordinary water or chloride laden water the moisture content is near the saturation level, the diffusion of oxygen to the steel is limited and the reinforcement very negative potential, for example between -400 and $-600 mV SCE$. [14]. In this situation, the chloride threshold is much higher.

However, for the hollow (air-filled) structures submerged in seawater e.g offshore platform legs, tunnels, microcells between outer and inner reinforcement may cause significant corrosion [14].

VIII. CORROSION MITIGATION IN CONCRETE REBAR

The adequate performance of concrete structures in marine environment is a function of its durability against the aggressive species in the environment. A thorough knowledge of these aggressive elements and their mechanism of attack of concrete structures are very important [24] as discussed in the previous sections in order to develop the appropriate countermeasures. For many decades ago, various techniques towards corrosion control have been examined. The common protection measures against rebar steel includes; design, steel surface treatment, alternative materials, cathodic protection and the use of inhibitor. D.D.L Chung [25]. However the success achieved so far demands further investigations. Therefore this section will focus on various corrosion control measures, though the full detail is beyond the scope of this paper. The various corrosion counter measures commonly used are considered as follows:

A. Surface Modification

The surface of the reinforcement steel bar can be treated in various ways to improve corrosion resistance. One of the traditional methods that have been used over the years is surface coating. Different kinds of anti-corrosion coatings exist, such as polymer-modified slurry, non-passivating and passivating epoxy coating, zinc- rich epoxy coating and zinc-rich water based coating. According to Jorge et al [26] revealed in their investigation that coating of non-corroded rebar increases the average bond strength. However, for deformed rebars the use of coatings decreases the average bond strength of both non-corroded and corroded rebars for repair mortars. They further recommended that the applications of cementitious coating for plain rebar is necessary but not for deformed rebars. Organic coating is widely used for reinforcement steel bars all over the World because their mode of applications is not complex. Organic coatings such as coal tar, epoxy, acrylic emulsions, elastomeric, chlorinated rubber, vinyl and epoxy coatings are good barriers for preventing steel from moisture, the protection of rebar by epoxy coating is more pronounced in recent time. However, Z. Theodosia et al [27],[28],[29],[30],[31],[32] in their study, revealed that elastomeric coating can provide a reasonable level of corrosion mitigation of rebar in marine environment and that, the coating developed good balance between liquid water and water vapour penetration.

Metal (Zn, Al, Ni) coating on reinforcing bar surface improves the corrosion resistance of the rebar steel but the product being large low-value steel commodity in nature;

therefore metal coating may not be good alternative. Surface treatment using inorganic chemical such as phosphate, silicate and chromate have been investigated by researcher. Phosphate coating appear to have a better corrosion resistance than chromate [33]. However, epoxy coating and galvanized are widely used in marine and other aggressive environment, though their performances depend on the behaviours at coating break [33], [34], [35].

B. Design

Design plays a major role in controlling deterioration of concrete structures, improper design will facilitates corrosion. Experience has revealed that most of the failures and origin of corrosion are most often traced to simple errors that could have been prevented without significant additional cost [15]. A proper consideration of the structures and prevailing environmental condition at the design stage can help in checking corrosion activities. Design techniques for corrosion control in rebar can be achieved by appropriate applications of mix designs, curing and concrete thickness cover [15],[24], [36], [37], [64]. Concrete depth of about 7cm and 10cm was recommended for concrete structures in marine environment and w/c of 0.4 or less [39],[40], [41], though w/c ratio has a greater influence on chloride attack than concrete thickness [42].

C. Electrochemical Method

This method is generally referred to as cathodic and anodic protection. Cathodic protection technique is widely used for corrosion control in reinforcement metals by applying a smothering current by deliberately introducing external anode source, this method is referred to as Impressed Current Cathodic Protection (ICCP). It allows the electrochemical attack to be controlled because the local internal multiple anode and cathode site becomes eliminated. The most common alloys are based on Magnesium, Aluminum and Zinc depending on the environment and life span required. Discrete Zinc anodes have been used quite successful to protect reinforced concrete pipelines [7].

Catholic protection has proved to be an effective corrosion counter measure in reinforced concrete since corrosion in embedded steel bar in concrete is an electrochemical reaction; it is usually applied in the form of sacrificial anode. It can be cost effective to some extent when conductive resin or mortar is added along with corrosion resistant primary anodes embedded in the overlay. Cathodic protection in concrete deals with the application of electrical current [49],[50] to the corroding bar, if already corroding; CP abates the corrosion process and prevents further deterioration Pacheco et al [43]. However, the total homogeneous current circulation in a reinforced concrete using cathodic protection is difficult to actualize due to the complexity and variability rebar concrete structure Jing Xu et al [44]. However, cathodic protection [45], [46], [47],

[48] prove to be a sure means of corrosion counter measure in structures regardless of the chloride concentration.

D. Alternative materials

Researchers have been investigating on how corrosion problems in reinforcement could be alleviated or if possible completely eradicated. This includes the search for more corrosion resistance materials. Since the significant general review of the use of stainless steel in structure in 1993, there has been reasonable advancement [51] in the use of stainless steel as alternative to carbon steel because of its greater corrosion resistance compared to carbon steel [74-77], but lower strength [68] than traditional carbon steel, however in deicing areas, stainless steel is better [67]. Stainless steel is a corrosion resistance iron alloys that contains about 10.5% chromium. Its corrosion resistance is attributed to the presence of chromium which form passive film layer when expose to oxygen which aids corrosion resistance. However, chlorides laden environment such as marine environment is highly detrimental to its corrosion resistance [51], [69], [73]. More so, considering the cost implications of stainless steel for concrete structures, stainless steel should be considered when all possible alternatives failed. Braided reinforced composite rods that are produced from polyester fibres can be a good alternative material for steel where strength could be compromised [52], its corrosion resistance performance is high.

E. Inhibitor

Corrosion inhibitor is one of the most important corrosion counter measures used today. This method is widely used in various applications. In recent years, the use of corrosion inhibitors for corrosion control and improvement of concrete performance has tremendously increased. However, the chemical composition of a majority of these inhibitors is not unveiled to the public [53]. Corrosion inhibitor is a chemical substance organic or inorganic which when added in a required amount to corrosive environment decreases the corrosion rate. Corrosion inhibitors frequently work as either anodic, cathodic or mixed inhibitors [54, 55,56] by adsorbing themselves on the metallic surface by forming a film layer on the surface. Calcium nitrites, sodium nitrites and Sodium tungstates are anodic inhibitors that have been used in concrete structures over the years both in marine and non-marine environments. These inhibitors have the potency to inhibit initiate pitting corrosion and their efficiencies increase considerably with increase in dosage [36], [57], [58], [59], [60], [61], [62]. Some inorganic inhibitors can delay pitting initiation without any detrimental effect on the concrete [78], [79]. However, Monte et al [80] revealed that calcium nitrite is detrimental to concrete properties. Inhibitors reduce corrosion activities by; (1) Increasing the cathodic and anodic polarization behaviour (2) Decreasing the mobility of ions to the surface of the metal (3) Raising

the electrical resistance of the metallic surface (4) Creating a barrier film on the surface of the metal.

IX. CONCLUSION

Corrosion in reinforcement steel in concrete is an electrochemical reaction due to environmental interference. However, understanding the possible corrosion mechanism, and the application of appropriate corrosion counter-measure such as; cathodic protection, coating, suitable material selection and the use of admixture (inhibitors) are sure ways of minimizing its effect and enhancing concrete structures durability. However, from the review corrosion mitigation techniques have been studied using experimental approach which is expensive and time consuming. The use of computational approach proves to be more promising and efficient for corrosion mitigation studies.

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