Use of Corrosion Inhibitors for Steel Protection in Cementitious Composites-A Review

Md Daniyal[1], Md Asif Raja[2]

[1]Department of Civil Engineering, Aligarh Muslim University, Aligarh (U.P.), India
[2]School of Civil Engineering, Galgotias University, Greater Noida (U.P.), India

***Abstract*— *Steel reinforced cementitious composite is one of the most commonly used materials in construction industries. This is mainly because of its excellent mechanical properties that can withstand various types of loading conditions and low cost. But, the corrosion of embedded steel reinforcement is a main problem associated with steel reinforced cementitious composite because it shortens the life of structure. The most important causes of corrosion initiation of steel reinforcement are the ingress of carbon dioxide and chloride ions to the surface of steel. Though, the corrosion initiation of embedded steel can be delayed using corrosion inhibitors. However, after starting of corrosion, the effectiveness of corrosion inhibitor was reported to be reduced significantly and propagation of corrosion becomes more rapidly. Generally, the negative effects of the corrosion inhibitors on properties of cementitious composite were reported to be negligible. Also, the information regarding the long-term performance of the corrosion inhibitors in actual practice are very limited. Various investigations reported several types of corrosion inhibitors in order to control the corrosion of steel that were also used in construction industries commercially. However, some of the corrosion inhibitors were found to be poisonous and harmful to the environment. Therefore, there is need for more research on the corrosion inhibitors in order to find out the suitable inhibitor with low cost and without side effects to the environment.*

Keywords*— *Cementitious composite, Corrosion, Corrosion inhibitor, Steel

I. INTRODUCTION

The mixture of cement, water and aggregates is known as cementitious composite. This composite material can withstand high compressive stress but cracked or failed under the various types of stresses such as bending, tensile and shear stress. This tensile weakness of cementitious composite can be overcome by introducing steel and the resulting material so obtained is commonly known as reinforced cementitious composite and widely used in the construction of buildings, bridges, skyscrapers and many other types of structures. However, the main drawback of embedded steel reinforcement in cementitious composite is its corrosion, particularly when exposed adverse environmental conditions. Fortunately, cementitious composite is a highly alkaline material (pH ranging from 12 - 14), primarily due to its calcium, sodium and potassium hydroxide content. Because of this high alkalinity, a thin ferric oxide (Fe_2O_3) protective film is formed on the surface of steel. It is observed that when the steel is confined within low permeability cementitious composite, the steel corrosion would not occur. Unfortunately, this expectation is not completely met in actual practice and the protective film may be destroyed by ingress of aggressive agents such as oxygen, chlorides and carbon dioxide through micro pores of cementitious composite. After removing the protective layer, the initiation and propagation of steel corrosion takes place. [1-3].

It has already found that the two most important factors which cause corrosion of steel are carbonation of cementitious composite and chloride penetration. Initially, CO_2 from the air enters into cementitious composites through micro-pores and slowly dissolves in pore water to form the dilute carbonic acid as shown in (1). This acid acts as a neutralizing agent of alkalis in the pore water and does not attack the cement paste. However, after reacting with calcium hydroxide, forms calcium carbonate as shown in (2), which reduces the pH value considerably.

$$CO_2 + H_2O \longrightarrow H_2CO_3 \qquad (1)$$
$$H_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2H_2O \qquad (2)$$

This phenomenon is commonly known as carbonation of cementitious composite. After carbonation, the passive protective film of ferric oxide (Fe_2O_3) gets damaged and the steel is become bare to corrosion. Further, the rate of carbonation depends on the various factors such as relative humidity, concentration of CO_2 in air, grade of concrete, permeability of concrete, depth of cover and duration of exposure.

However, the most important factor which causes the corrosion of steel is due to the introduction of chloride ions into the cementitious composites. The chloride contamination of cementitious composites may be internal (use of cement or admixtures with high chloride contents, contaminated or marine water, dirty aggregate etc.) or external (atmospheric gases, marine environments, use of de-icing salts etc.). The chloride ions are found in three forms in cementitious composite namely chemically bounded, physically absorbed and free chlorides. The steel corrosion is mainly depends on the amount of free chlorides. This is because of the fact that the free chlorides only reacts with Fe^{2+} of ferric oxide (Fe_2O_3) layer over steel surface and consequently forms ferrous chloride as shown in (3). Subsequent reaction of ferrous chloride with water forms ferrous hydroxide as shown in (4) and acid containing free chloride ions, which is responsible for further attack over steel surface. Actually, the free chloride acts as a reaction catalyst.

$$Fe^{2+} + 2\,Cl^- \longrightarrow FeCl_2 \quad (3)$$

$$FeCl_2 + 2\,H_2O \longrightarrow Fe\,(OH)_2 + 2\,HCl \quad (4)$$

Subsequently, the steel gets exposed and activated locally to form the anode and the unexposed surface form the cathode initiating the electrochemical process. In this process, moist cementitious composite acts as an electrolyte. In fact, this process constitutes a red-ox reaction. In anode, oxidation (loss of electrons) and in cathode, reduction (gain of electrons generated in the anode combine with certain ions in the electrolyte) as shown in (5-6) takes place. This electrochemical process constitutes corrosion reactions that occur in steel reinforced cementitious composite and can be represented as follows (7-9) [4-7].

$$2Fe \longrightarrow 2Fe^{2+} + 4e^- \quad (5)$$

$$4e^- + 2H_2O + O_2 \longrightarrow 4OH^- \quad (6)$$

$$2Fe^{2+} + 4OH^- \longrightarrow 2Fe\,(OH)_2 \quad (7)$$

$$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3 \quad (8)$$

$$2Fe\,(OH)_3 \longrightarrow Fe_2O_3{\bullet}H_2O + 2H_2O \quad (9)$$

The volume of hydrated ferric oxide ($Fe_2O_3{\bullet}H_2O$) may have up to ten times of the volume of the original steel. This volumetric increase causes tensile pressure in the cementitious composites, which leads to cracking, spalling, delamination of the cover and leaving the reinforcing steel exposed to the environment, and resulting faster rate of corrosion. Another adverse effect of corrosion is the reduction of cross sectional area of steel reinforcement which causes weaknesses to the cementitious composite structures. Also, corrosion of reinforcement has enormous financial implications as well as social problems including endangering the safety of workers who are engaged in construction industries. Corrosion of reinforced cementitious composite structure may cause loss of lives which has to be given main concern than money. Therefore, various researches have been done in order to prevent or control the process of corrosion in steel reinforced cementitious composite structures. Some of the well known methods of controlling corrosion include use of corrosion-resistant steel, admixtures, corrosion inhibitors, thicker cover, steel or concrete surface coatings, concrete sealers, and cathodic protection [8-16].

II. CORROSION INHIBITORS

It has been found that the corrosion inhibitors were successfully used for the protection of steel tanks, pipelines etc. from deterioration for many decades. However, their use in reinforced cementitious composite for the protection of steel is more recent. They are chemical substances that when added in sufficient quantity to cementitious composite, can decrease the steel corrosion without affecting the fresh as well as hardened properties of cementitious composite. Recently, they are commonly used in order to produce high performance cementitious composite. [17].

Generally, conventional corrosion inhibitors can be classified as; inorganic (primarily nitrites) and organic (alkanolamine and their organic, inorganic acid salts) corrosion inhibitors. However, on the basis of their protection mechanisms, they can be classified as; anodic, cathodic and mixed inhibitor. Also they can be added into reinforced cementitious composite either as protective measures or restorative purposes. Therefore, on the basis of mode of applications, they can be categorized as; admixed inhibitors (added to fresh concrete for new structures) migrating inhibitors (can penetrate into the hardened concrete for existing structures) [18].

2.1 Anodic Inhibitors

When the anodic inhibitors are mixed into the steel reinforced cementitious composite, reaction between the inhibitors and metallic ions (generated on the anode due to oxidation reaction) takes place. The reaction generally produces insoluble hydroxides which are deposited on the steel surface as impermeable and insoluble film. This adsorbed film reduces the anodic reaction and passivate the steel surface. However, it is very important that the concentration of inhibitors should be sufficient in order to effective results. This is mainly because of the fact that the inadequate quantity of inhibitors forms the protecting film which will not cover the steel surface completely. Due to this, the exposed steel surface (anodic area) relative to cathodic area reduces and causes localized (pitting) corrosion. Hence, inhibitor concentrations less than the critical value are worse than without inhibitors at all. Fig.1 shows a potentiostatic polarization diagram of the steel on the solution with an anodic inhibitor and without inhibitor. The anodic reaction is affected due to the presence of corrosion inhibitors and the corrosion potential of the steel is shifted to more positive values as well as the corrosion current density decreases. Chromates, nitrates, tungstate, molybdates, phosphates, hydroxides and silicates are some examples of anodic inhibitors.

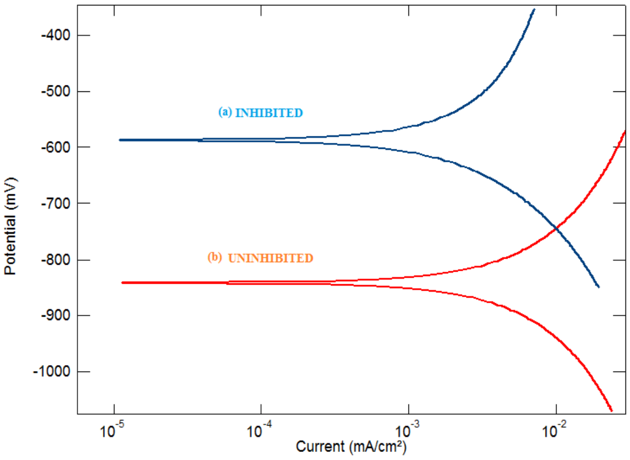

Fig.1: Potentiostatic polarization diagram of steel in (a) anodic inhibited (b) uninhibited solution

2.2 Cathodic Inhibitors

When the cathodic inhibitors are mixed into the steel reinforced cementitious composite, they are either slow down the rate of cathodic reaction or forming the insoluble precipitates over the surface of steel. For example the ions of zinc, magnesium and nickel react with hydroxyl ions of water forming the insoluble hydroxides such as $Zn(OH)_2$, $Mg(OH)_2$, $Ni(OH)_2$). Thus, cathodic inhibitors restrict the diffusion of reducing species to the surface of the steel, preventing the corrosion reaction to occur. Also, it has found that rate of corrosion reaction does not depend on the concentration of cathodic inhibitor and therefore they are considered more secure than anodic inhibitor. Hence, various types of cathodic inhibitors have been used in construction practice, which includes the ions of the magnesium, zinc, and nickel, and salts of tannins, polyphosphates, calcium and lignins. Fig. 2 shows a potentiostatic polarization curve of the steel on the solution with cathodic inhibitor and without inhibitor. When the cathodic reaction is affected the corrosion potential is shifted to more negative values as well as the corrosion current density decreases.

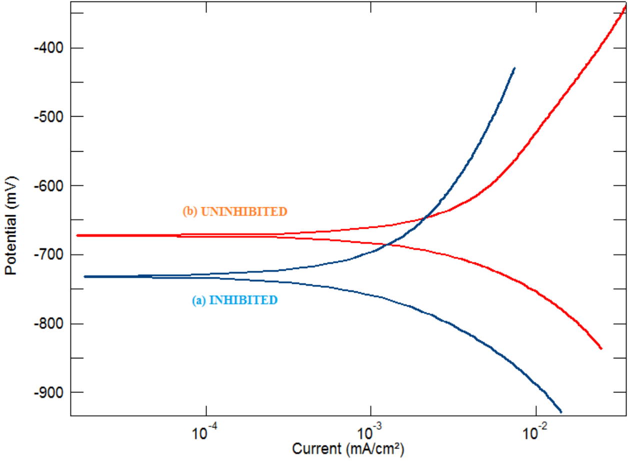

Fig. 2: Potentiostatic polarization diagram of steel in (a) cathodic inhibited (b) uninhibited solution

2.3 Mixed Inhibitors

When the mixed inhibitors are added into the steel reinforced cementitious composite, they work on both anodic and cathodic areas. They usually form precipitates on the surface of steel, blocking both anodic and cathodic sites and ultimately reducing the corrosion rate. It has found that in mixed type inhibitors, the material with hydrophobic group that contains polar groups for instance N, S, OH is more effective. Organic polymer compounds for example aminoalcohol and amine are also used. However, the most commonly used inhibitors of this category are the phosphates and the silicates. Fig. 3 shows a potentiostatic polarization curve of steel on the solution containing mixed type inhibitor and without inhibitor. It can be seen that after addition of mixed type inhibitor, the corrosion potential remains the equal, but the corrosion current density decreases [19-27].

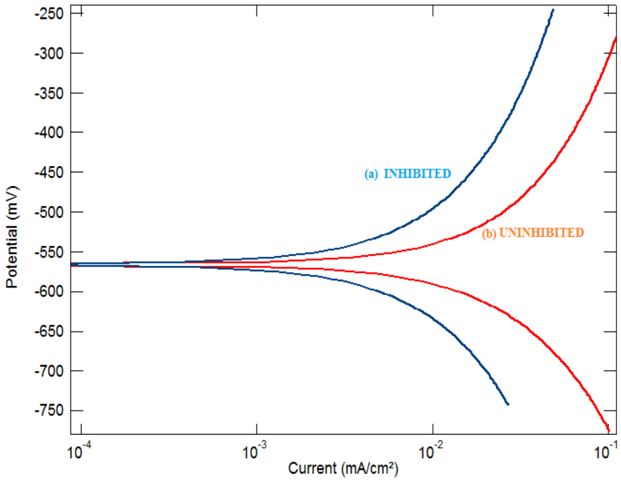

Fig -3: Potentiostatic polarization diagram of steel in (a) mixed type inhibited (b) uninhibited solution

III. EFFECTS OF CORROSION INHIBITORS

It has been found that various types of corrosion inhibitors including organic, inorganic and migratory corrosion inhibitors are reported in literature. Some of them are commercialized for steel reinforcemet protection such as nitrites, sodium mono fluoro- phosphate, amines, alkanoamines etc. However, most commonly used in the construction field are Calcium nitrite (CN), amine alkanolamine (AMA)-based inhibitors and mono fluoro-phosphate (MFP). Though, the exact method of application and proper dose for a particular exposure condition is rarely sighted.

Despite the fact that all these corrosion inhibitors offer enough steel reinforcement protection, also they have negative impacts on the human beings and environment in the form of toxicity and hazards. The toxicity may cause temporary or permanent injure or disturb to organ systems specifically liver, kidneys, biochemical processes at some position in the body. These effects may occur either at the time of synthesis or applications of inhibitors. Therefore, considering all these factors, various countries implemented environmental policy for application of corrosion inhibitors. For example, Nitrites have excellent corrosion inhibition potential but because of its toxicity, banned in Switzerland and Germany. Similarly inhibitors containing antimony, anadium, thiocyanate and copper compounds have been considered as toxic pollutants by the Environmental protection agency (EPA) of U.S.A. Nevertheless, despite of all these adverse impacts, corrosion inhibitors still play a very important role in the protection of steel reinforced cementitious composites [28- 36].

IV. CONCLUSIONS

The cementitious composite is most commonly used material in the construction industry. This is mainly because of its cost-effectiveness and load carrying capacity primarily in compression. But, it is very weak in tension or flexure. Therefore, its tensile weakness is overcome by embedding steel reinforcement. However, corrosion of embedded steel reinforcement is a major drawback. Though, it has been investigated that the corrosion of steel reinforcement can be control using corrosion inhibitors. Their use in steel reinforced cementitious composites can facilitate to delay the initiation of corrosion, particularly when exposed to carbonation and chloride attack. However, it was reported that the effectiveness of corrosion inhibitors reduces after the initiation of corrosion. Also the negative effects of using corrosion inhibitors on fresh and hardened properties of cementitious composite were found to be insignificant. However, some positive as well as negative effects were found in the various researches. Also, some of the corrosion inhibitors were found to be toxic and hazardous. Therefore, more researches are required in order to use the corrosion inhibitors effectively.

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