



Corrosion mitigation of steel rebars in chloride contaminated concrete pore solution using inhibitor: An electrochemical investigation

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HIGHLIGHTS

- The prepared inhibitor has worked effectively to reduce the corrosion of steel.
- Synthesized inhibitor work as anodic inhibitor.
- High concentration of inhibitor is required to mitigate the corrosion of steel.
- 96% efficiency was found for 5 v/v% inhibitor after 1 h of exposure.

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ABSTRACT

Inhibitor is one of the most accepted method to reduce, prolong the initiation of steel corrosion and increase the threshold value of Cl^- and CO_3^{2-} ions. In present study, we have mixed sodium salt of phosphate and benzoate along with benzo triazole in water to prepare the inhibitor. Open circuit potential (OCP) results show that 5 v/v% inhibitor was exhibited most positive (nobler) potential than others at its prolonged exposure in simulated concrete pore (SCP) + 3.5 wt% NaCl solution. The OCP of 3 and 5% inhibitor containing solution proved that these concentrations are away from under corrosion region of steel rebar even after 192 h of exposure in SCP + 3.5 wt% NaCl solution. Electrochemical impedance spectroscopy (EIS) results show that the charge transfers resistance (R_{ct}) to be highest for 5% inhibitor and gradually decreased once the concentration was reduced with exposure periods. Potentiodynamic studies reveal that inhibitor shows passive properties due to adsorption of inhibitor molecules on steel surface and enhance the corrosion resistance properties. The efficiency was calculated using R_{ct} and corrosion current density (I_{corr}) process and found that 3 and 5% inhibitor exhibit around 89 and 96%, respectively after 1 h of exposure in SCP + 3.5 wt% NaCl solution.

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1. Introduction

Concrete is the most widely used materials in the construction sector to erect/install the big structures such as high rise building, dam, bridge, parking etc. owing to its high compressive strength. However, the reinforced concrete (RC) structures are deteriorated due to early age corrosion of embedded steel rebar in harsh concrete environment and it is the most prospective problems of the world which becoming most frightening day by day for the society [1–3].

Generally, the steel rebars remain in passive state once adequate amount of oxygen is available in vicinity of embedded

steel rebar in concrete environment due to formation of protective film [4]. Formation of protective film depends on different parameters being adopted during erection of building and infrastructures such as aggregates, chemistry of steel rebar, temperature, humidity, composition of concrete etc. [5–8]. This film protects the embedded steel rebar against corrosion in concrete up to certain circumstances such as in virgin and uncontaminated concrete but it can also sustain up to fixed concentration of aggressive ions. The passive film may deter its protective nature due to ingress of de-icing salts and carbonation of concrete which perturb the thickness of film, causes localized attack and initiate the corrosion process [9].

Owing to high alkalinity of concrete, steel rebar forms passive film which is adherent and protective. This passive film provides the continuous protection to the steel rebar until the alkalinity is

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maintained or retained. This oxide film withstands the steel rebar from corrosion by forming stable phases of iron oxides/hydroxides such as maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and goethite ($\alpha\text{-FeOOH}$) [10]. Many researchers had reported that the alkalinity of the concrete aids the formation of protective passive film on steel surface [11–13]. The steel is unlikely to rust once the passivating condition remains unchanged.

However, the passive film is not stable once chloride ions concentration increase beyond its threshold value or at low pH value reduced below to 9 [14–23]. Du et al. (2006) have studied the mechanism for breakdown of passive film on steel rebar arises when the chloride concentration reaches 0.50–0.60 mol/L even if the pH was as high as 12.50 [24]. If the corrosion of steel rebars occurs in concrete, it increases the volume across the circumference of steels and increased the volume of corrosion products resulting cracks and spalling of the concrete due to higher tensile stresses.

Thus, the durability of RC structure is caused by corrosion. Therefore, it is required to control using different mitigation processes. These are mostly different coatings, surface treatment, corrosion resistance steel rebar and inhibitors which protect the embedded steel rebar in concrete from corrosion due to attack of aggressive ions [25–32]. Instead of these processes, only inhibitors can be used due to its minimum amount to be required for mitigation. Inhibitor is the most promising mitigation process which hinder and combat the initiation of corrosion or already corroded RC structures since it would not be harmful for concrete or human being [33]. It should be easy to application by mixing in concrete, surface applied inhibitor by roller, brush or spray process [34]. Inhibitor has migratory properties where it diffuses through the pores of concrete with solution reaches to steel rebar surface, adsorbed and form very protective film.

Inhibitors slow down or reduce the initiation of corrosion process in chloride contaminated concrete environment [35,36]. Even very little amount of inhibitor can able to reduce the corrosion phenomena by forming stable oxide film through adsorption phenomena on steel rebar surface.

Since many decades ago, nitrite based inhibitors specially sodium and calcium nitrites have been extensively paid attention to the researchers on their use as anodic inhibitor but due to some controversial and negative impact on durability of concrete and human being, therefore now a day it has been unauthorized in European countries [20,21,37–40]. There is another phosphate based inorganic inhibitor used which control the corrosion of steel rebar [41,42]. Phosphate based inhibitor work effectively as migratory inhibitor to repair the corroded steel reinforcement bars in chloride contaminated concrete [43]. M. Vishnudevan has studied the synergistic effect of mixture of sodium nitrite, sodium citrate and sodium benzoate which effectively increase the durability of mild steel due to formation of nanosized Fe_2O_3 even in high chloride contaminated concrete environment [44]. Another alternative of nitrite based inhibitor is to use organic such as amines and alkanolamines based inhibitor which is widely used and economical [29,45]. Organic inhibitors with hetero atoms reduce the time for initiation of corrosion of embedded steel rebar in chloride contaminated concrete environment by adsorbing on steel surface [20,32].

However, from above literature search it is found that most of the studies are based on either inorganic or organic based inhibitors to mitigate the corrosion of steel rebars exposed to chloride contaminated concrete environment. Therefore, we aimed to study the effect of sodium hexameta phosphate along with sodium benzoate and Benzo triazole to mitigate the corrosion of steel rebars in aggressive solution. These are phosphate and organic compound with hetero atom which work migratory as well as adsorb on anodic site of steel rebar surface to form covalent bond with iron. The corrosion characteristics of inhibitor were assessed in simulated

concrete pore (SCP) solution with 3.5 wt% sodium chloride (NaCl) at prolonged exposure periods through electrochemical impedance spectroscopy (EIS) and potentiodynamic studies.

2. Materials and methods

2.1. Materials

The inhibitor to be studied in present investigation was analytical grade of organic and inorganic chemicals mixture. The following chemicals such as 0.01 M sodium hexameta phosphate $\{(\text{NaPO}_3)_6\}$ + 0.01 M sodium benzoate ($\text{NaC}_6\text{H}_5\text{CO}_2$) + 0.01 M 1, 2, 3-Benzo triazole ($\text{C}_6\text{H}_5\text{N}_3$) + 1 M sodium hydroxide (NaOH) were dissolved in distilled water using magnetic stirrer for 30 min at 25 °C. In present investigation, three different concentrations i.e. 1, 3 and 5 v/v% inhibitor was chosen for electrochemical studies.

The simulated concrete pore (SCP) solution was prepared by dissolving 8.33 g/L NaOH (sodium hydroxide) + 3.36 g/L KOH (potassium hydroxide) and 2 g/L CaO (calcium oxide) in distilled water at magnetic stirrer for 24 h at 25 °C [46,47]. This solution simulates the concrete environment. Thereafter, it was filtered with 5C number (110 mm) Wattman filter paper to ascertain that insoluble CaO does not come in solution then 3.5 wt% NaCl was added. The pH of this solution was 12.60 measured at 25 °C. This solution is known as without inhibitor solution. Along with this solution, three concentrations e.g. 1, 3 and 5 v/v% synthesized inhibitors were mixed in SCP + 3.5 wt% NaCl solution.

16 mm diameter of steel rebar was used in present investigation to be evaluated the effect of corrosion inhibitor in SCP + 3.5 wt% NaCl solution vis-à-vis without inhibitor. The steel rebar contains (wt.%) C:0.240, Si = 0.260, Mn = 0.950, P = 0.016, S = 0.008, Ni = 0.030, Cr = 0.040, Mo = 0.010, Cu = 0.020, Sn = 0.001 and rest was Fe. The other experimental details were explained in our recently published papers [25–27]. Prior to start the electrochemical studies, the milled scale steel rebars were pickled in 10 v/v% hydrochloric acid solutions to remove the black oxide from surface thereafter rinsed with distilled water, dried with hair drier then cut into 16 mm (diameter) \times 16 mm (length) for electro mounting. The mounting of 16 mm \times 16 mm steel rebars were carried out in acid/alkali resistance thermosetting resin. The mounted steel rebars were abraded with emery paper started from 180 to 1200 μm to ascertain scratch free surface. Finally, the polished steel rebars were degreased with acetone prior to start the electrochemical experiments.

2.2. Electrochemical studies

Prior to start the experiments, the steel rebar was exposed in inhibitor and without inhibitor containing SCP + 3.5 wt% NaCl solutions to stabilize the potential with potentiostat. The electrochemical studies were carried out with three electrode systems where steel rebar works as working electrode (WE), platinum wire as a counter electrode (CE), and silver-silver chloride (Ag/AgCl) as a reference electrode (RE). The WE and RE had been fixed in such a manner that both are close to each other, since there will be less solution resistance caused. The area of WE was 0.78 cm^2 and it was fixed for every sample [25–27]. The CE area was greater than WE which make the conducting path to flow the electrical current in solution.

The alternative current (AC) impedance i.e. electrochemical impedance spectroscopy (EIS) studies were carried out at open circuit potential (OCP) by changing the frequency of 10 mV sinusoidal voltage from 100 kHz to 0.01 Hz with exposure periods. The potentiodynamic polarization of samples were performed at 1 mV/s scan rate from -0.4 V to $+0.8\text{ V}$ vs Ag/AgCl. The potentiostat was

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