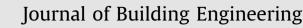
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Electrochemical process to improve the durability of concrete structures

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ARTICLE INFO

Article history: Received 3 November 2015 Received in revised form 5 July 2016 Accepted 5 July 2016 Available online 6 July 2016 Keywords:

Corrosion mitigation Electrochemical injection of corrosion inhibitor Durability Inhibitor formulation

1. Introduction

Reinforcing steel embedded in a chloride-free Portland cement concrete exhibits a high degree of resistance to corrosion. The cement paste in the concrete provides an alkaline environment that protects steel against corrosion. This corrosion resistance is due to passivating or protective ferric oxide film that forms on the steel when it is embedded in fresh concrete. This film is stable in the highly alkaline concrete environment that has a pH of approximately 12-13. In the passive state, steel is protected by the naturally high pH and availability of oxygen in the concrete. The corrosion rate of steel in this state is negligible. The factors influencing depassivating forces are carbonation and penetration of chloride ions [1–3]. Corrosion steel is an electrochemical process. Two requirements are necessary for the development of a corrosion cell. Sufficient dissolved oxygen is required for reaction at the cathodic sites and moisture is required to maintain low electrical resistivity in the concrete between the anode and cathode. Anodes and cathodes on either a macro or micro scale develop, creating a corrosion cell. Micro cells occur within millimetres of each other, while macro cells may be upto several metres apart. In a corrosion cell, metallic iron corrodes or oxidizes at anodic sites to form ferrous ion with the release of two electrons and the reaction is shown in Eq. (1).

 $Fe \rightarrow Fe^{2+} + 2e^{-} \tag{1}$

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http://dx.doi.org/10.1016/j.jobe.2016.07.005 2352-7102/© 2016 Elsevier Ltd. All rights reserved.

ABSTRACT

Chloride induced corrosion of steel in concrete is a major threat to the construction industry leading to the premature failure of concrete structures. Electrochemical injection of corrosion inhibitor (EICI) into concrete is a promising technique for existing concrete structures, which can serve as a rehabilitative measure to retard or reduce rebar corrosion. An attempt has been made to evaluate the effectiveness of a hybrid inhibitor formulation injected into chloride contaminated concrete. The optimised current density of 0.5 A/m² was found to be a minimum requirement with maximum efficiency. During EICI, the amount of free chloride removed from cover concrete was also tested. The mechanism of inhibitive action was established through FTIR, SEM, EDAX and MIP studies.

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Electrons flow through the steel to combine with oxygen and moisture at the cathode to form hydroxyl ions as shown in Eq. (2).

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$
 (2)

Hydroxyl ions then combine with a ferrous ion at the anode to form ferrous hydroxide as shown in Eq. (3).

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2 \tag{3}$$

This ferrous hydroxide can react to form ferric hydroxide Fe $(OH)_3$ and ferric oxide Fe₂O₃ in the presence of water along with other species. The implication of these reactions is that the corrosion products occupy a greater volume than does the original steel. The resulting tensile stress may be sufficient to cause cracking or spalling if these stresses exceed the tensile strength of the concrete. The effect of chloride inclusion in concrete is two fold: it increases the conductivity of the concrete and acts as a catalyst in the oxidation of iron. In the presence of chloride ions, intermediate reactions may occur involving iron chloride.

Chlorides are not consumed in the corrosion process but simply act as catalysts at the anode. The corrosion reaction rate is therefore controlled by the supply of water and oxygen to the cathode. Thus, even though a concrete deck may be sealed to prevent new chloride ingress into the slab, continued chlorideinduced corrosion may occur. The reaction produces hydrogen ions at the anodic site resulting in a lowering of the pH and creating more favourable corrosion conditions by destroying the passive layer. Under these conditions the presence of molecular oxygen is not a requirement since the oxygen needed to develop ferrous oxide may be developed from the water itself. Again, the ferrous





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oxides developed may continue reacting to form other products such as ferrous and ferric chloride. These products may occupy an even greater volume than those of the ferrous and ferric hydroxides. At the cathode, different reactions may occur depending on the availability of oxygen. The balancing reaction that occurs at the cathode for corrosion in the absence of oxygen is as shown in Eq. (4).

$$2H^+ + 2e^- \rightarrow H_2 \tag{4}$$

In the presence of oxygen, the reactions at the cathode are shown in Eqs. (2 and 5).

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
 (2)

$$4H^{+} + O_2 + 4e^{-} \rightarrow 2H_2O$$
 (5)

In both instances, steel at the cathodic site is protected against corrosion. Corrosion in concrete requires an anode, cathode and electrolyte. Chloride in concrete acts as an electrolyte, increasing the level of conductivity as chloride ions increase. It also depassivates the steel reinforcement. The level of chloride ion required to initiate corrosion in concrete corresponds to 0.15% soluble chloride ion by weight of cement. This value refers to the amount of water-soluble chloride rather than the total chloride. If chloride is present during the curing process, some chloride ions become chemically bound in the hydration products and are therefore not available in solution to act as a catalyst. Chlorides may be present in slakes where calcium chloride is used as an accelerator to setting. Also, in areas near the sea or with brackish groundwater, chloride may have entered the concrete through contamination of the aggregate. If only low chloride concentrations are present, they may become bound during the hydration process. Corrosion of steel in concrete can be mitigated by adopting various preventive measures viz., cathodic protection, using corrosion inhibitors, coating to steel rebar, coating to concrete, using blended cements, realkalization of concrete etc., [4–7]. The use of corrosion inhibitors is the more economical and appropriate method of protection for concrete structures subjected to reinforcement corrosion [8-11]. In concrete, chloride and inhibitor ions travel through natural diffusion, electro migration, and through external pressure gradient [12]. Surface applied corrosion inhibitors is relatively economical and their application is found to be very easy and efficient [13–15]. Applications of electrochemical treatments include mainly the electrochemical realkalization, electrochemical chloride extraction (ECE), electrochemical injection of corrosion inhibitor (EICI) and cathodic protection [16,17]. In EICI, a current density of $1-5 \text{ Am}^{-2}$ is usually applied between embedded steel as cathode and an external anode placed on the concrete surface in an aqueous solution containing the relevant inhibitor for a few weeks [18–21]. During the application of current, chloride ions migrate out of concrete towards the external anolyte solution, while EICI was shown to be an effective method of preventing corrosion in existing structures, and this can serve as a rehabilitative measure to retard or reduce corrosion. In the present investigation, a hybrid inhibitor formulation was designed and used for EICI studies at an optimised constant current density of 0.5 Am^{-2} . The efficiency of the inhibitor formulation was evaluated by conducting various electrochemical studies. The study showed that such inhibitor injection could provide adequate corrosion protection to rebars embedded in even chloride contaminated concrete.

2. Experimental

2.1. Materials used

Ordinary Portland cement (OPC) of grade 53 was used for the casting the specimens. Local clean river sand (fineness modulus of medium sand equal to 2.6) conforming to grading zone III of ASTM standards was used. Locally available aggregates conforming to graded aggregates of normal size greater than 8 mm and less than 20 mm of ASTM standard was used. Potable water has been used for making concrete specimens. The water is free from oils, acids and alkalies. As per IS 456-2000, the permissible limit for chloride is 500 mg/l. Thermo mechanically treated (TMT) rebar of 12 mm diameter and length 560 mm was used for weight loss and open circuit potential measurements.

2.2. Inhibitors formulation

The hybrid inhibitor formulation consists of guanidine carbonate ($C_2H_{10}N_6 \cdot CH_2O_3$), thiosemicarbazide (CH_5N_3S), ethyl acetate ($CH_3COOC_2H_5$), and triethanolamine ($C_6H_{15}NO_3$) (AR grade, Alfa Aesar was used).

2.3. Casting of concrete specimens

Concrete slab of size $60 \text{ cm} \times 60 \text{ cm} \times 10 \text{ cm}$ thickness were cast using OPC. 12 mm diameter and 560 mm length, of rebars were embedded with a concrete cover thickness of 25 mm. Concrete specimens were cast using 1:1.56:3.36 mix [cement: 372 kg/m³; sand: 580 kg/m³; coarse aggregates: 1245 kg/m³ with w/c ratio of 0.55]. During casting, the specimens were mechanically vibrated. After 24 h, the specimens were demoulded and cured for 28 days in distilled water to avoid any contamination. After curing, the chloride ion is allowed to penetrate into the concrete over a period of 90 days by means of alternate wetting and drying cycles of 3 days of wet in 3% NaCl and 4 days drying at room temperature. Concrete slab specimens were given enough time to induce accelerated corrosion of steel due to aggressive chloride ion.

2.4. Electrochemical injection of corrosion inhibitor (EICI) process

Fig. 1 shows the electrical circuit of EICI process on the concrete slab. Here rebar act as cathode and stainless steel plate act as anode. A special gauge made of sponge was placed in between

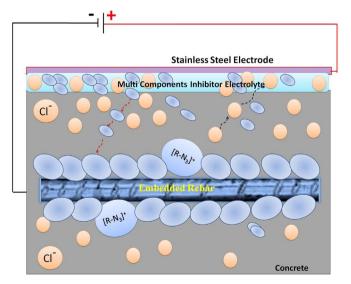


Fig. 1. Arrangement of EICI process on concrete slab.

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