

Research Article

Critical Study on Corrosion Inhibitors in U-Shaped RCC Beams

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In most structural failures, deterioration of reinforced concrete structure is due to corrosion of reinforcing bars. Ingress of chloride ions and reaction of carbon dioxide with the cement paste due to poor-quality concrete or inadequate cover are the main causes of corrosion. Corrosion can be reduced by using high-quality concrete and providing proper cover to reinforcement. In addition, corrosion inhibitors are used to protect the reinforcement in order to extend the service life of concrete structures. This research work is focused on determining the effectiveness of corrosion inhibitors under cracked and uncracked sections of U-shaped beam. The U-shaped beam concept was used in this study, which helps to develop the crack width within 0.3 mm as per IS: 456 code provision. The two vertical stubs of the U-shaped beam were stressed in order to generate the cracks at the soffit of the beam. Then, the beams are tested for accelerated corrosion along with the half-cell potential meter calculations for the corrosion potential measurement.

1. Introduction

Calcium nitrite is an inorganic compound which is freely soluble in water with the density of 2.26 g/cm^3 and has the melting point of 390°C . Nitrite ions grant the stable passive protective film formation on metal surface in the presence of chloride ions [1]. Rust is formed between the reinforcement and concrete which in turn increases the interface pressure. At last, the spalling of concrete will be formed at the corrosion propagation period [2]. The increase in chloride ions will destroy the nitrogen ions' passive layer formed as a cover on the reinforcement [3]. The cracking associated with corrosion in concrete is a major concern particularly in marine environments. The penetration of chloride ions causes the loss of durability in the marine environment which in turn causes corrosion [4].

To detect the characteristics of corrosion, the microscopy techniques are used which give the tremendous development in the corrosion detection [5]. The effectiveness of the corrosion inhibitors will be increased along with molar ratio of $[\text{NO}_2^-]/[\text{Cl}^-]$. It develops the corrosion defiance of steel with water cement ratio below 0.5. Calcium nitrate-based inhibitors have anodic nature which raises the chloride ion initiation concentration [6]. Due to the oxidizing property of calcium nitrite, nitrite turns as a passivation agent. Corrosion rate is increased when the potential is high. This results in the leaching in the cracks of concrete [7]. The percentage of corrosion initiation is about 80% less in the carbon steel, which is mainly due to the addition of the calcium nitrite-based inhibitor which helps in preventing corrosion as its effectiveness will be higher than 0.8–1 [8]. The protection method formed by combining the galvanic anode within the

migrating nitrites will give protection against corrosion in the normally used steel bars [9].

Appreciable corrosion only starts when the relative humidity of the air exceeds around 65%. Corrosion rate is negligible in pure air and water with a temperature below freezing point [10]. Self-compacting concrete (SCC) is mainly imported for improving the durability of concrete along with inhibitor which will improve the service life of the concrete [11]. Indirect monitoring of corrosion of iron can be done by measuring pH, oxygen reduction potential (ORP), and conductivity [12]. The migrating inhibitors can penetrate into the concrete which is mainly used for the rehabilitation of the structure [13]. Inhibitors are classified as inorganic and organic based on their chemical nature. Inorganic inhibitors are further classified into anodic and cathodic inhibitors based on the mechanism of action. Absorption will come under the category of organic inhibitors [14]. It was examined and found that Mn^{2+} can promote oxygen evolution reaction (OER) and thereby weakens the oxidation efficiency of MnO_2 . In order to find the effectiveness of an inhibitor, the two most preferred methods are the weight loss method and polarization curve method.

At atmospheric temperature, the compression toughness and the bond toughness will be revised, even when the temperature is raised above 60°C. The effect of corrosion rate will be more conspicuous in weak concrete than the strong concrete [15]. Studies reported high corrosion capacity when the leachates are fresh [16, 17]. In the corrosion scales, the major elements found are Fe, C, Zn, Si, Ca, Al, and S. The composition of water also influences the presence of these elements [16]. 316 steel and A3 carbon steel weight loss is directly proportional to shell factor and surface roughness due to which scaling is reduced [18].

The new suggestion of migratory corrosion inhibitors (MCIs) provides a thin protective coating of MCI molecules around the steel bar by means of migration process into the concrete [19]. The setting times of the powdered pastes at 20°C with the effects of inhibitors mainly depend on the inclusion of inhibitor in precise proportion [20]. The concrete mixture which includes the pozzolanic material can increase the compressive strength of the concrete by more than 30%. Calcium nitrite addition will increase the compressive strength at the age of 7 and 28 days [21]. It acts as a long-term strength enhancer and also influences the early stage strength gain in concrete. Corrosion inhibitors are highly used to improve the threshold value of chloride. The time will be decreased for both the initiation of concrete and cracked concrete with increase in time for chloride contamination and the corrosion current density [22]. Increasing percentage of inhibitors from 0.22 to 1.95 increases the threshold value of chloride [23].

2. Experimental Work on U-Shaped Beam

U-shaped beam is mainly used to control the crack width less than 0.3 mm as per the IS: 456 code provision. The two stubs act as support and also help to develop the desired crack width. The two different corrosion inhibitors used in the

work were “Nitozinc Primer” (two-component zinc-enriched primer) (CH1) and “integral liquid compound” (containing 2% chloride conforming to IS2645:2003) (CH2) for the cracked and uncracked sections of the U-shaped beam. For the application of Nitozinc Primer, Nitozinc base primer was mixed equally with hardener primer to obtain a homogeneous mixture, and the mix is applied in two coats around the surface of the steel reinforcement. Other than this, there are benzoates, chromates, molybdates, and orthophosphate-based inhibitors available. For the application of integral liquid compound, the dosage of 200 ml is used for 50 kg of cement. The specimen dimensions for the U-shaped beam are as follows. The effective beam size was 600 mm × 100 mm. The size of stubs was 150 mm × 100 mm with 300 mm height. Two numbers of 12 mm diameter tie rods are used as reinforcements. Another two numbers of 12 mm rods are used outside to hold the stubs. These two rods are kept tight using 20 mm diameter bolts. The soldering work was done in the U-shaped rod which was kept in the beam for initiation of corrosion process.

The casting of U-shaped beam was done without damaging the soldered wires. M20 concrete mix (1 : 1.5 : 3) is used with 20% replacement of fly ash from cement content. For generating the cracked section, the stressing rods are inserted after the curing period of 28 days, and they are stressed to the desired crack width at the two vertical stubs which are shown in Figure 1.

The cracks are formed at the soffit of the beam which is measured using the Brinell microscope and the crack width is limited to a maximum of 0.3 mm, as the study is limited to mild exposure condition under the regulation of Indian Standard 456:2000. The upper part of the beam is referred to as A, and the bottom part of the beam is referred to as B. The cracks formed in 5 positions are named from 1 to 5 for both OPC (confirming to IS 269:2015) and PPC with corrosion inhibitors. Figures 2(a) and 2(b) show the crack details of conventional concrete specimens, and Figure 3 gives a clear idea of crack positions in beams with corrosion inhibitors.

2.1. Accelerated Corrosion Test. For the accelerated corrosion process, NaCl solution of 5% and DC meter of constant 12 V are used. The stainless-steel plate provided around the beam acts as the cathode, and the U-shaped rod acts as the anode. The anode will give off the electrons which is observed by the cathode, which will form the electrochemical process. The layout of accelerated corrosion processes for both cracked and uncracked section is shown in Figure 4. The U-beams are placed in a plastic tub with 20 mm gap from the bottom of the tub with the help of 20 mm cover block used for concreting. The level of solution is maintained above the reinforcement position inside the horizontal beam.

The NaCl solution was monitored up to the soffit of the beam, and the cathode (stainless-steel plate) and anode (U-shaped rod) were connected to the negative end and positive end of the DC meter. The manual setup for the accelerated corrosion test is shown in Figure 5. At the same time, the corrosion potential measurements are done by using manual half-cell potential meter which is prepared by



FIGURE 1: Formation of cracks due to stressing.

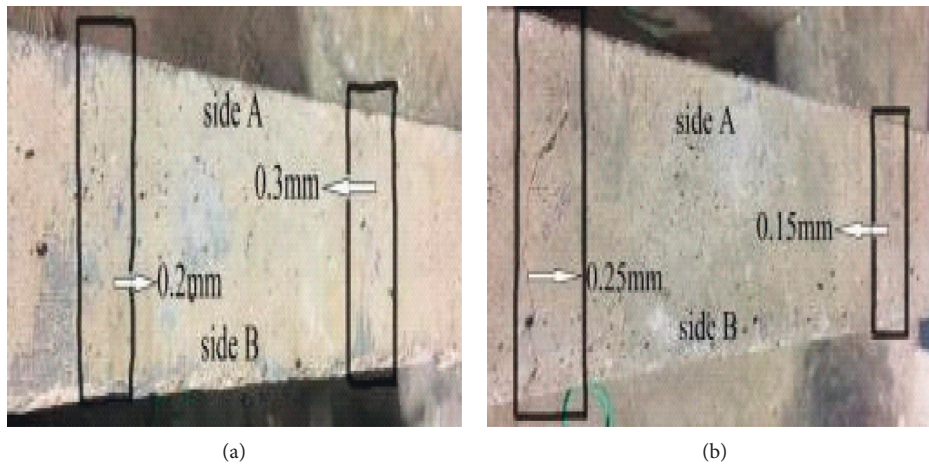


FIGURE 2: Details of cracks for conventional specimens. (a) OPC concrete mix. (b) PPC concrete mix.

connecting the reference electrode and voltmeter to the concrete surface and the U-shaped rod, respectively.

PVC pipe was used in the container, and sponge was used at the top. The copper rod played a major role in the electrode which was connected to the closing lid of the PVC pipe. The copper sulphate solution is prepared up to the saturated state which is poured into the electrode before starting the measurements, and the arrangement is shown in Figure 6.

The electrical wire which is soldered to the U-shaped rod is connected to the positive end of the voltmeter, and the electrical wire which is soldered to the copper rod in the electrode is connected to the negative end of the voltmeter. After the connection is made, the half-cell potential reading is taken at the marked section on the surface of the U-shaped beam individually. The corrosion potential obtained from the half-cell potential meter gives the conditions of concrete whether it is a carbonated concrete or chlorine contaminated concrete. The variation in

temperature has no practical influence on reference electrodes [24]. Friedel's salt in the form of deposition layer of excess chloride and hydroxide anions helped to generate excess positive charges.

3. Results

The corrosion potential measurements for various intervals were taken for the 6 sets of U-shaped beams including the cracked and uncracked sections. From all the beam results, it is evident that the concrete was wet inside and contaminated with chloride. For the conventional beams with OPC, the potential value seems to be significant at 264 hours as there is a sudden variation after 264 hours in both the positions, whereas in PPC beam, the potential variations were significant in the shear crack after 204 hours. The readings will vary depending upon the electrolytic and electrical conductivity between the reference electrode, rebar, and voltmeter. The potential values for the OPC and PPC

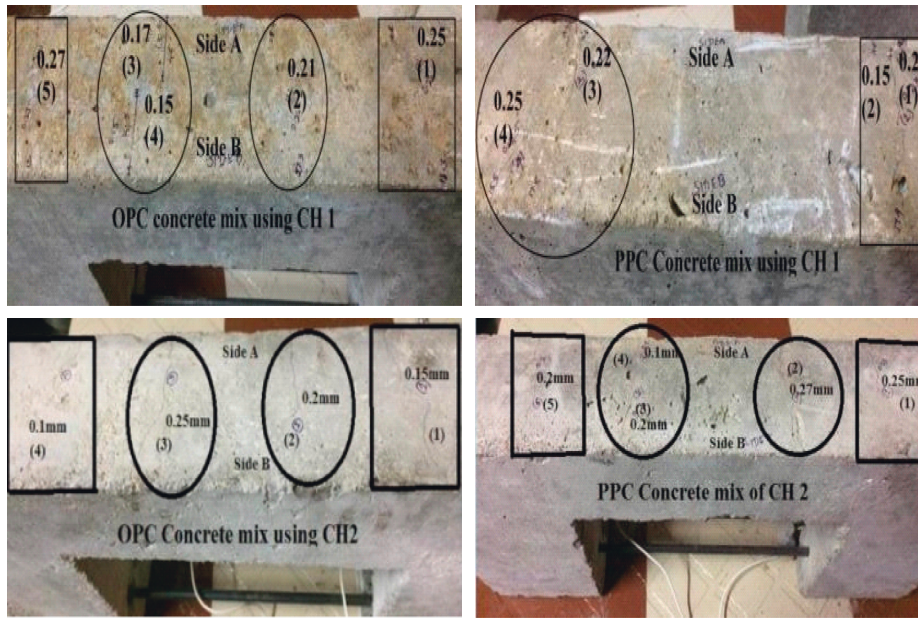


FIGURE 3: Details of cracks in beams with corrosion inhibitors.

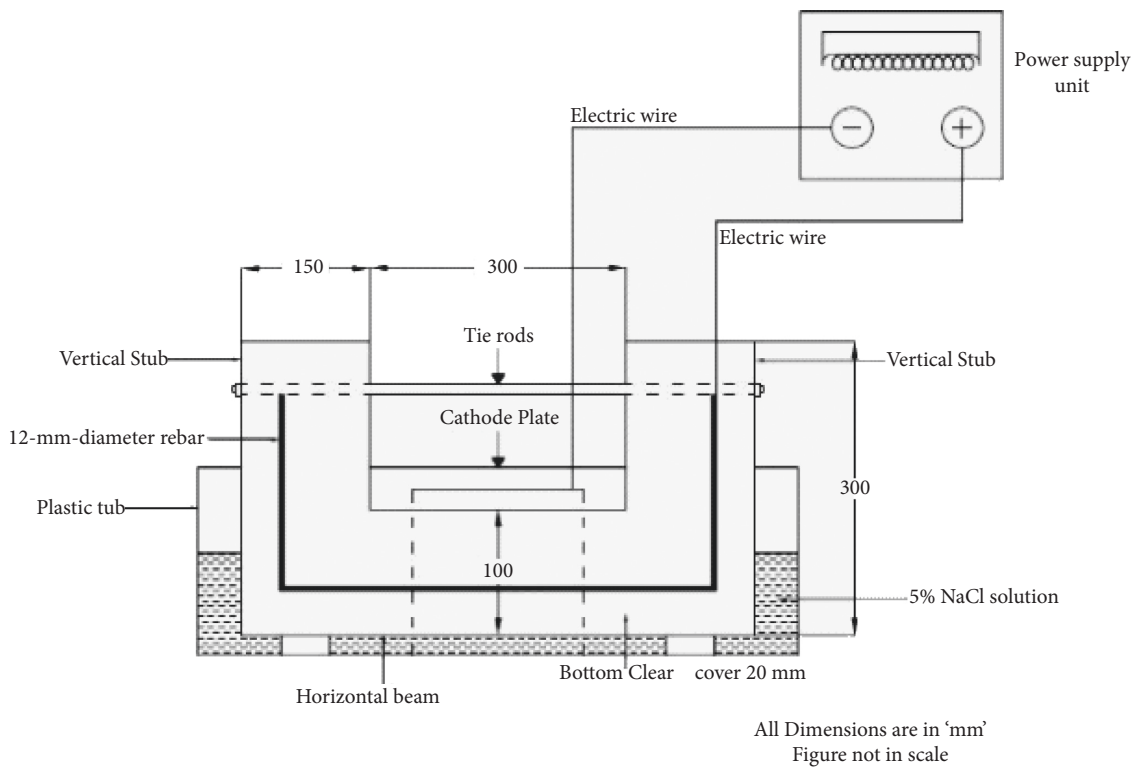


FIGURE 4: Layout of accelerated corrosion test of U-shaped beam.

conventional cracked U-shaped beams are given in Figures 7 and 8. It was noted that the change in potential was more or less stabilized after 480 hours. In the cracked section, the conventional OPC mix showed higher potential value at the early stage which shows that the cracked OPC concrete mix has higher possibility of corrosion rate. The shear cracks showed high potential readings when compared to flexural cracks. This indicates that the position of cracks influences

the steel corrosion. Corrosion pits were observed in anodic areas of steel.

The potential values are taken for 5 constant positions marked in all six sets of U-shaped beams for about 0 to 480 hours. From the results, it is clear that PPC's resistivity is much better from the initial stage itself. This may be due to the influence of more powered particles, which in turn create better compacted concrete. Dense concrete



FIGURE 5: Accelerated corrosion test setup.

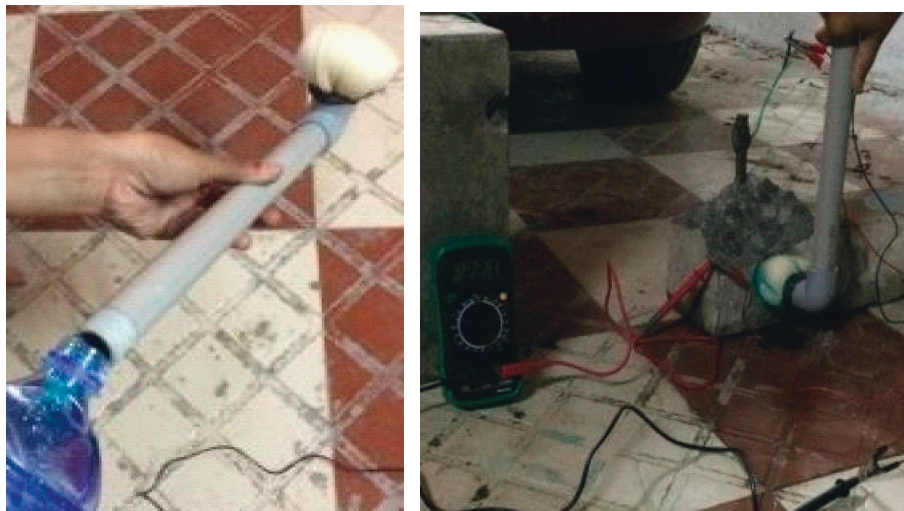


FIGURE 6: Half-cell potential measurements.

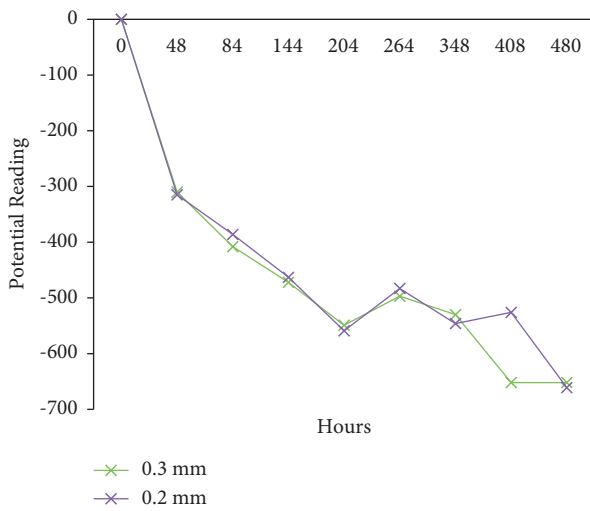


FIGURE 7: Potential values for conventional U-shaped beam (OPC).

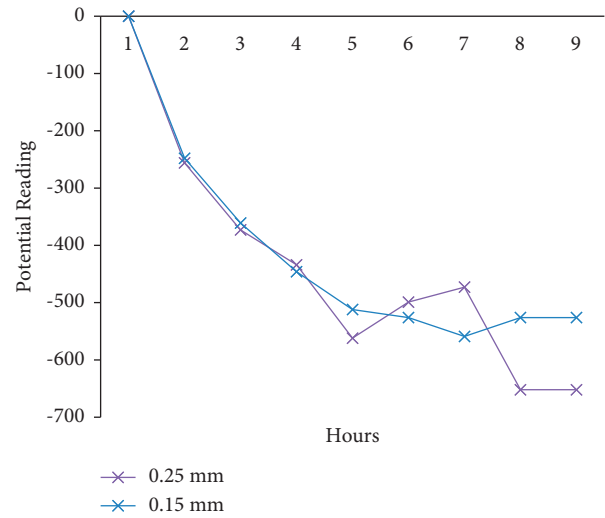


FIGURE 8: Potential values for conventional U-shaped beam (PPC).

performs better against chloride attacks. The average tabulated potential values obtained for the cracked specimens using CH1 and CH2 for both OPC and PPC

concrete mixes are given in Figures 9 and 10. The conventional specimen with OPC cement showed a shift in active direction at the early stage, whereas the PPC

specimen remained more or less constant as is evident from the plots. The CH1 behavior was superior for cracked section as the coating on bars was found to be advantageous against corrosion. The tabulated potential values obtained for the uncracked specimens using CH1 and CH2 for both OPC and PPC concrete mixes are given in Figures 11 and 12. In uncracked section, after 400 hours, the rate of corrosion became more or less stable for both OPC and PPC beams. The corrosion initiation was delayed upto the potential readings of average 48 hours. The graphs indicate that CH1 has the behavior of sudden rise and drop at the beginning stage of corrosion processes, whereas the rate of corrosion increase was constant for CH2. CH1, being the primer coated in the reinforcement, was found to be affected from the initial hours. The successful behavior of CH2 was evident in uncracked section against the corrosion.

4. Discussion

4.1. Comparison of Half-Cell Potential Results for Cracked U-Shaped Beams Using Corrosion Inhibitors. The combined half-cell potential values varied according to the corrosion rate. The cracked specimen using inhibitors showed a delay in the corrosion for both OPC and PPC concrete mixes than the conventional concrete. The cracked specimen using Nitozinc Primer exhibited a sudden drop in the corrosion rate at the beginning of corrosion process. The nitrogen-zinc layer forms a strong layer even after the initiation of corrosion. Compared to integral liquid compound, Nitozinc Primer gives the lower rate of corrosion which indicated the delay of corrosion process. Also, CH1 developed a carbonated condition in concrete which also helped to delay the corrosion, whereas the cracked specimen using integral liquid compound showed sudden variation at 408 hours. It is caused due to the potential variations during the corrosion test. The CH2 mix showed a poor performance due to its powder format and as it is mixed to cement and coated to reinforcement. But it delays the corrosion process when compared to conventional concrete. Comparing the cracked OPC mix and PPC mix, Nitozinc Primer shows higher performance in delaying the corrosion rate even in the cracked section. When the performance of OPC and PPC was compared, PPC had better resistance. AFM phase was found to be important in both OPC and PPC, and the crystalline hydrate formed due to the AFM stage also helps to delay the corrosion. Corrosion starts at 84 hours and 144 hours in OPC mix and PPC mix, respectively.

4.2. Comparison of Half-Cell Potential Results for Uncracked U-Shaped Beams Using Corrosion Inhibitors. In case of uncracked section, there is delay in the corrosion rate compared to the cracked specimens. The beginning of corrosion was almost the same for all the specimens, but after 84 hours, each specimen showed variation in their performance. The uncracked specimen using Nitozinc Primer showed a sudden drop in the corrosion rate after 84

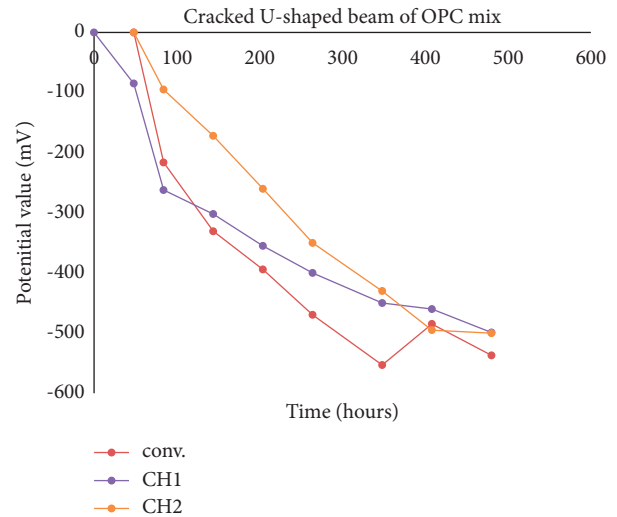


FIGURE 9: Cracked U-shaped beam of OPC mix.

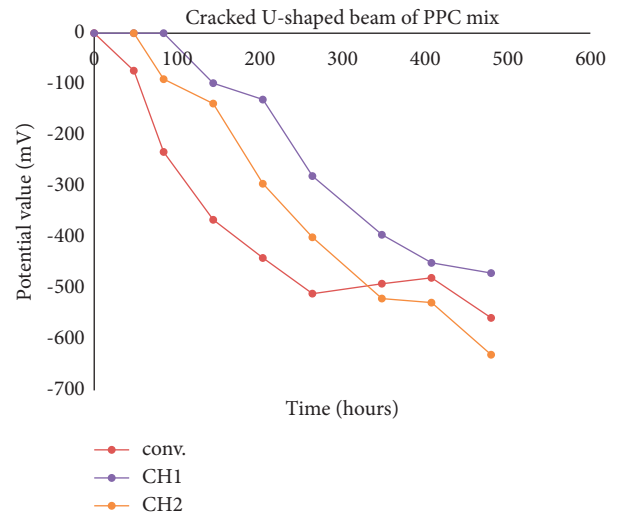


FIGURE 10: Cracked U-shaped beam of PPC mix.

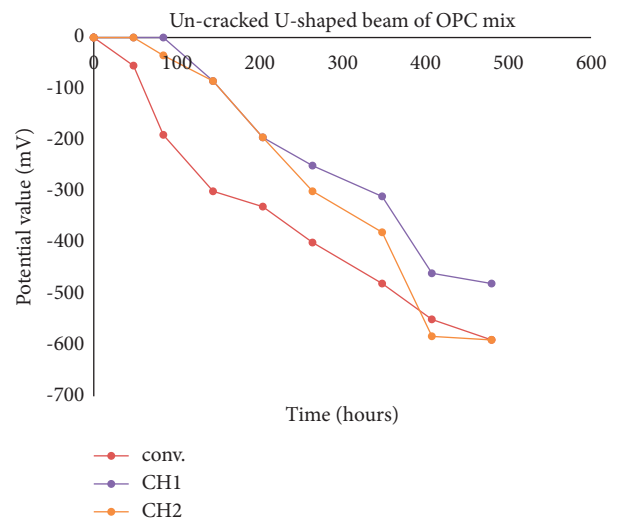


FIGURE 11: Uncracked U-shaped beam of OPC mix.

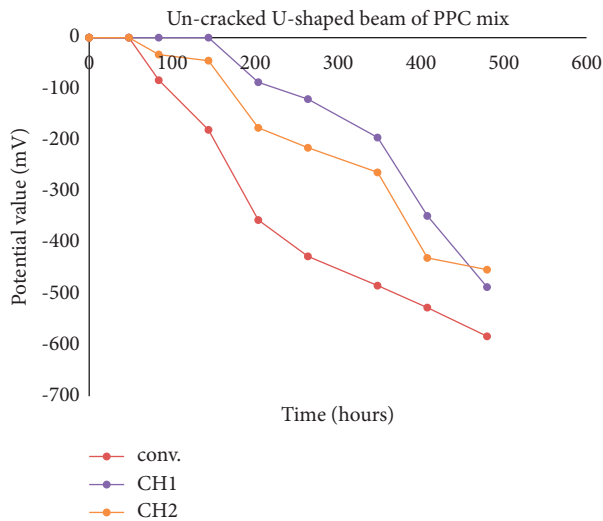


FIGURE 12: Uncracked U-shaped beam of PPC mix.

hours. The uncracked specimen using integral liquid compound shows sudden rise in the corrosion rate at 408 hours. The integral liquid compound showed lower rate of corrosion till 144 hours; after that, a sudden drop occurs in the corrosion rate compared to conventional concrete and CH1. In case of Nitozinc Primer, there was a sudden rise in the corrosion rate after 144 hours. The conventional specimen of uncracked section showed a gradual increase in corrosion rate, without any major increase or decrease. It is evident that the corrosion inhibitors had influenced the results.

5. Conclusion

- (i) For the cracked section, Nitozinc Primer makes the concrete more carbonated, and thus it delays the rate of corrosion process, whereas integral liquid compound showed sudden variation in potential values.
- (ii) In case of uncracked section, integral liquid compound delays the corrosion rate up to 144 hours. Nitozinc Primer showed a sudden increase in corrosion rate at this particular hour.
- (iii) The Nitozinc Primer has the behaviors of sudden rise and drop at the beginning stage of corrosion processes. After a particular period, the rate of corrosion becomes constant.
- (iv) Integral liquid compound also has the behaviors of sudden change at the end of the corrosion processes.
- (v) Comparing both the cracked and uncracked sections, Nitozinc Primer painted around the steel reinforcements makes carbonated concrete and protects the steel from corrosion in a better way.

Data Availability

The data used to support the findings of the study are included within the article.

Disclosure

The publication of this research work is only for the academic purpose of Jimma Institute of Technology, Jimma University, Ethiopia.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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