Performance of Concrete Blended with Inhibitors and Slag Exposed to Chloride Environment

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Abstract. In this paper, the performance of concrete with organic inhibitor and slag on compressive strength, chloride penetration resistance and half-cell potential were studied for different water/binder (w/b) ratios and different curing ages. Organic inhibitor (Amines)was admixed with cement during the manufacturing process itself of the cement named as corrosion resistance cement (CRC). The influence of this cement on compressive strength was studied over different curing ages such as 7, 28, 56, 90, 180 and 360 days. Rapid chloride penetration test (RCPT) was conducted to explore the resistance to chloride penetration. Half-cell potential was observed for the period of one year as a measure of corrosion tendency of reinforced concrete (RC) exposed to 3%, 5% and 7.5% of sodium chloride (NaCl) solutions. The results of the concrete with inhibitor (CRC) were compared with the concrete with Portland slag cement (PSC). Significant improvement was observed in compressive strength with increase in curing ages. The performance of CRC concrete shows remarkable improvement in corrosion potential (delayed corrosion initiation) as compared to PSC concrete.

1. Introduction

The premature deterioration in reinforced concrete (RC) structures due to its exposure to chloride laden environment and it reduces the service life of structure considerably. It consumes a huge amount for repairs, maintenance and restoration of such structures. Deterioration of RC structures is more aggressive in chloride laden environment as compared to carbonation [1, 2]. The chloride induced corrosion is a major cause of deterioration of reinforced concrete. Chlorides are introduced either in fresh concrete through contaminated water, aggregate and admixtures containing chlorides or externally in hardened stage through deicing salts and also the structures exposed to marine environment [3, 4].Reinforcement in the concrete is naturally protected by a thin passive layer by the alkaline environment. This passive layer is stable till the pH of the pore solution in surrounding concrete is more than 12.5. Due to the ingress of harmful impurities like chlorides and carbonation through the cover concrete, the alkalinity of concrete get reduced which destroy the passive film. This gives access to chlorides to reach at the reinforcement level. Corrosion initiation of reinforcement takes place, when Chlorides reach to reinforcement level and exceeds the critical level[5-7]. Various researcher suggested different systems to reduce or delay the corrosion initiation periods such as use of pozzolanic, supplementary cementitious materials, admixtures for concrete and epoxy coating for steel etc. [8-10].Among the various efforts taken to reduce the corrosion of RC structures, use of inhibitors was an effective method to protect the steel embedded in concrete exposed to aggressive environment owing to its lower cost and ease in application [11,12]. Corrosion inhibitors can increase service life through prolonging the corrosion initiation time or decreasing the corrosion rate [13].

Inhibitors are classified depending on the basis of the mechanism of protection, whether it affects the anodic reaction, cathodic reaction or both are called as anodic, cathodic and mixed inhibitor respectively [14]. On the basis of application, inhibitors are either mixed into fresh concrete (mixed-in inhibitors) as admixtures or applied on the surface of hardened concrete (migrating inhibitors, MCI). The chemical nature of inhibitors defines the organic and inorganic. Though, inhibitors had great acceptance in the industries due to excellent anticorrosive proprieties, many showed up as a secondary effect, not ecofriendly. Thus the study is going on searching for environment friendly and safe inhibitors; like the organic inhibitors [15].Amine and ester are organic based admixed inhibitors have dual actions in concrete. The nitrogen (amine) compound part is responsible for its strong film formation on the metal surface by adsorption due to the strong molecular affinity for metal surface whereas the hydrocarbon (carboxylate) ester compound creates at hydrophobic layer helps to repel moisture away from the steel and acts as a pore-blocking agent which blocks the ingress of the chlorides ions ,inhibit both the anodic and cathodic processes[16-18].

Organic inhibitor also called as mixed inhibitors covers the metal surface by adsorption which is depends on type of electrolyte, surface charge of the metal and structures of inhibitors. Mixed inhibitors protect the metal in three possible ways: physical adsorption, chemisorption and film formation. Electrostatic attraction between the metal surface and inhibitor is called as Physical adsorption. These inhibitors consist of both positively charged (cations) and negatively charged ions (anions) [12, 19].

2. Experimental Procedure

2.1. Materials and mix proportions:

For the present investigation, Corrosion resistant Cement (CRC) and Portland slag Cement (PSC) confirming to IS 455-1995 was used [20]. The physical test such as blain surface area, specific gravity confirming to IS 2720-Part-3and loss on ignition(LOI) for both the cements were carried out as per Indian Standard (IS) 1727-2004. The oxide elements in both the cements were analyzed by XRF (X-ray fluorescence) as presented in table 1. The Properties of C.A, F.A and concrete mix design are similar to authors' previous work [21].

Table 1. Chemical and Physical Properties of Binders.

Comp-ound	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O_3	K_2O	Loss on Ignition (%)	Specific Gravity	Blain Surface Area (m^2/kg)
CRC	32.47	13.31	3.14	44.61	1.79	3.49	0.28	0.89	0.8	2.8	408.97
PSC	25.53	12.89	1.53	48.17	5.29	5.44	0.42	0.79	1.8	3.0	361.8

2.2 Methods

2.2.1.Compressive strength. In order to study the influence of inhibitors (CRC) and PSC on compressive strength of concrete, concrete cube specimens were prepared as given in table 2. The specimens were vibrated mechanically for proper compaction. To avoid the evaporation of moisture from the wet concrete, the specimens were covered with plastic sheet. After 24 hours of setting, the specimens were demoulded and cured for the different curing ages in normal tap water. Results were reported for average of triplicate specimens for each variable.

2.2.2.Rapidchloride ion penetration test (RCPT). The rapid chloride penetration test was used to assess the permeability of concrete mixed with corrosion inhibitors. For RCPT measurement cylindrical specimen were cast as mentioned in table 2.After 28 days of curing the concrete cylinders were sliced to 100mm diameter and 50mm thick disc specimens. The disc samples were preconditioned confirming as per ASTM C 1202-12 [22]. For measurements, two sides of the disc were sealed in Plexiglas containers with silicon sealant. One side of the container is filled with 3 % sodium chloride (NaCl) solution (cell connected to the negative terminal) and the other side is filled

with 0.3N sodium hydroxide (NaOH) solution (cell connected to the positive terminal) as shown in figure 1.
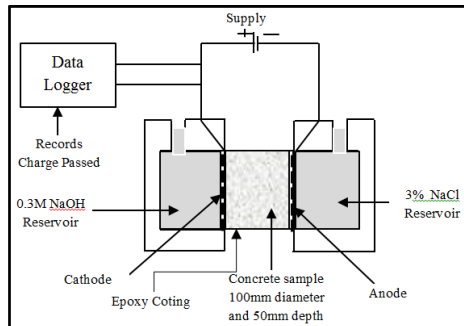

Figure1.ASTM C1202-12 line diagram.

Figure 2. Typical laboratory test setup for RCPT.

The specimen subjected to RCPT by impressing a 60 V potential and current was measured at every 30 minutes over the period of 6 hours. The total charge passed through the cell at the end of 6 hours was then calculated in order to determine the penetrability. A higher level of charge passed indicates higher permeability of the concrete. The typical laboratory test set up is shown in figure 2.

Table 2. Details of Test Specimen.

Sr. No	Specimen	Size	Test	Quantity (No.s)
1	Cube	150 x 150 x 150 mm	Compressive Strength	180
2	Cylinder	Dia=100mm, L=200mm	Rapid chloride Penetration	24
	(Disc)	Dia=100mm, L=50mm	Test (RCPT)	(72)
3	Beam	280 x 115 x 150 mm	Half Cell Potential (HCP)	54

2.2.3.Half-cell potential (HCP) measurement. The tendency of any metal to react with an environment is indicated by the potential it develops in contact with the environment. The half-cell potential (HCP) is an electrochemical technique most widely used for the assessment of corrosion risk the reinforced bars in concrete. This technique is based on measuring the electrochemical potential of the steel rebar with respect to a standard reference electrode placed on the surface of the concrete and can provide an indication of the corrosion risk of the steel as shown in figure 3.

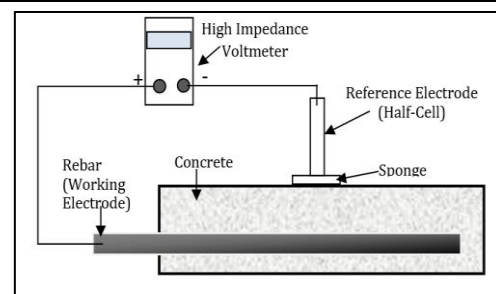|	**Table 3.** Conditions of Reinforcement Corrosion Related to Half-cell Potential (mV) Measurements to Relative Reference Electrodes [23].	
Sr. No	Hg/HgCl2 (SCE)	Likely Corrosion Condition
1	< -426 mV	Sever corrosion
2	< -276 mV	High (< 90% risk of corrosion)
3	-126 to -275 mV	Intermediate corrosion
4	> -126 mV	Low (10% risk of corrosion)

Figure3. Schematic representation of Half-cell potential (HCP) measurement.

The measured values are influenced by concrete cover, concrete resistivity (moisture content) and oxygen availability. It should be noted that it only indicate the probability of corrosion and not the actual corrosion rate. The measurement of corrosion potential is the primary step to understand the

corrosion tendency. From the measured HCP risk of corrosion can be categorized as per ASTM C876-2007 [23]which is reproduced in table 3.

For corrosion potential measurement ASTM G109 [24]RC beam specimen were prepared for the same concrete mixture with thermo-mechanically treated (TMT)reinforced bar of 12mm diameter confirming to IS 1786 [28]. The composition of steel was same as previously reported work [21].The reinforced bar is preconditioned before casting. The details of prepared steel specimen is explained schematically in figure 4. The preconditioning of bar was carried out as per the procedure mentioned in ASTM G1-03 [25] was also explained in figure 4.
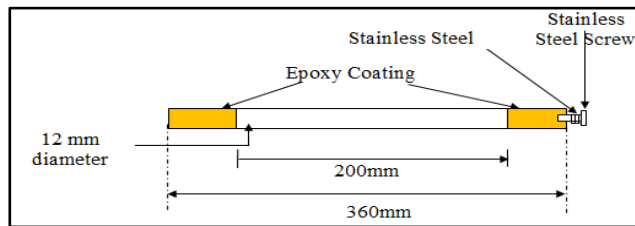

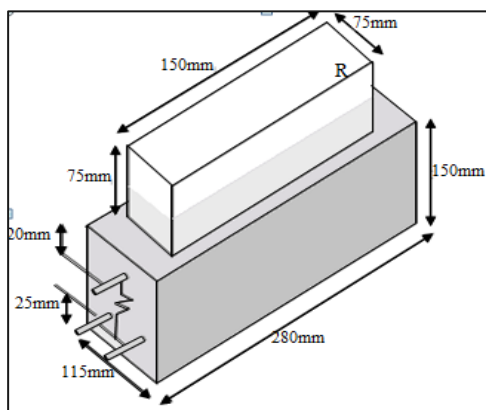**Figure 4.** Line diagram of preconditioned steel specimen.

Figure 5. Line diagram of ASTM G109-2007 beam specimen.
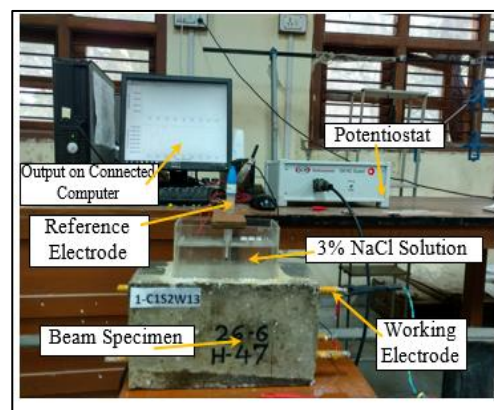

Figure 6. Typical laboratory Set of corrosion potential measurement ofASTM–G109 beam specimen.

The beam specimens size and quantity as specified in table 2 [24] were prepared with TMT two steel bars embedded at bottom with a cover of 25mm and one steel bar centrally at the top with the clear cover of 20mm from top. After 28 days moist curing the specimens were removed from tank for the further preparation. A Plastic reservoir of 150mm x 75mm x 75mm was centrally fixed on the top of the beam with silicon sealant to pour the NaCl solution during exposure. Epoxy coating was applied on four vertical faces of beam and on the top the portion outside of reservoir to restrict the entry of contamination from the surrounding throughout the measurements. Before the specimens subjected to chloride ingress, a wire was connected through lugs to bottom bar. Top bar was connected by a 100 Ohm resistor to bottom bars through common terminal of bottom steel bars in each specimen as shown in figure 6.The beam specimens then subjected to alternate wetting and drying i.e. 3 %, 5% and 7.5 % NaCl solution in order to accelerate reinforcement corrosion. One cycle consists of seven days ponding in respective NaCl solution and fourteen days drying in an open atmosphere. This wetting and drying cycle were chosen so that the specimens remain partially saturated and oxygen also available in abundance. Due to this availability of sufficient oxygen, the steel reinforcement was not polarized to immune state (large negative potential) and corrosion can proceed unobstructed when initiated [26].HCP measurements were monitored using ACM Potentiostat, Model No. 1824 [23]. A saturated calomel electrode (SCE) was used as a reference electrode and placed on the surface. The positive terminal of the potentiostat was connected to the working electrode (rebar) and the common terminal was connected to the reference electrode. The typical laboratory set up was done as shown in figure 6

 HCP was measured in three different locations very near to the rebar and the average potentials were recorded. The cycle was continued for 260 days. From the results a potential vs. time plot was drawn using the average potentials obtained.

3. Results and Discussion:

Compressive strength, RCPT and corrosion potential were monitored over the period of one year. The results of the tests are discussed as below.

3.1. Compressive strength

The specimens prepared were exposed to different curing ages such as 7, 28, 56, 90, 180 and 360 days. After the curing period was over, the compressive strength was measured by using compression strength testing machine (CTM) of 3000 ton capacity at loading rate of $140kg/cm^2/min$ conforming to IS 516 [27] as shown in figure 7. It was observed that strength gaining at the age of 7 and 28 days in case of CRC concrete was more as compared to PSC. Reduction in the compressive strength was observed with increase in w/b ratio in the range of 13.07% and 42.5% for CRC whereas for PSC, it was reduced to 17.17% and 28.75% for w/b ratio 0.5 and 0.55 respectively as compared to w/b 0.45 at 180 days. This reduction was 6.39 % and 19.88% for PSC and 11.96% and 40.81% for CRC at 360 days. For CRC concrete w/b ratio affects the compressive strength considerably as compared to PSC. This may be due to hydrophobic nature of inhibitors forms micro bubbles during casting make the concrete porous reduces the strength with increase in w/b ratio.
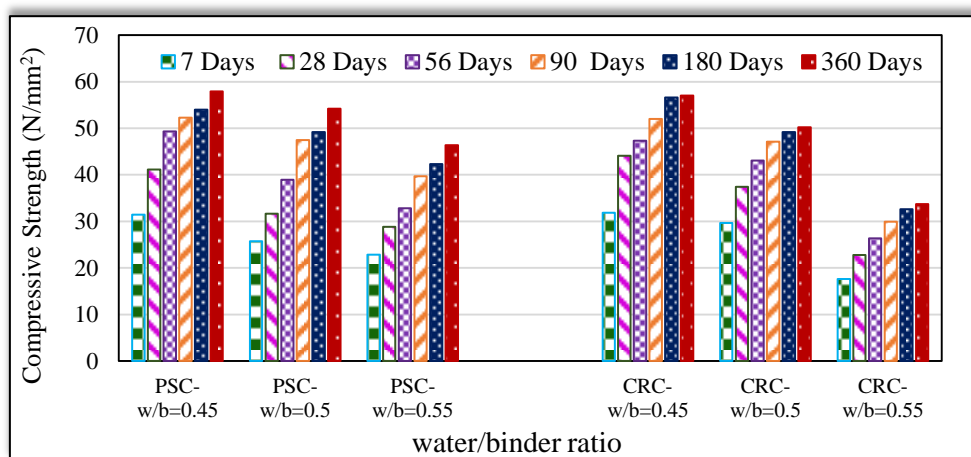

Figure 7. Compressive strength of concrete.

For all w/b ratios, compressive strengths were increased with increase in curing ages as expected. The workability of concrete with CRC was increased with increase in w/b ratio which makes concrete porous and reduces the compressive strength experimentally. It was observed that reduction in the w/b ratio is possible in concrete with CRC.The rate of strength gaining at all w/b ratios was fast up to 90 days, afterward becomes slower. In the case of PSC, the pozzolanic reaction is very slow at early age, hence the rate of gain of compressive strength was lower at an early age and it was even less than CRC but after 90 days, there was not much difference in strength between PSC and CRC. It was reported in the literature that when inhibitors mixed in concrete, compressive strength is reduced, while the inhibition effect of corrosion inhibition in chloride exposure is improved [28].

3.2. RCPT

It was observed that concrete prepared from CRC was better in chloride penetration (lower coulomb charge passed) than concrete prepared from PSC at early age. With increase in w/b ratio the charge passed was increases but decreased with curing age for all cases as expected. This was because of refinement of pore structure by hydration products owing to pozzolanic action over the age in concrete

with PSC and pore blocking by inhibitors in CRC. The charge passed in coulomb in all concrete specimens was low.

From the figure 8, it is observed that the concrete mixed with inhibitor systems show lower coulomb values than the PSC Concrete. These differences refer to the difference in the electrical conductivity of concrete which is relatedto many factors such as: mix proportions, use of supplementary cementing materials, chemical admixtures etc. These factors had very significant effects on the concentration of conductive ions in the pore solution.Chloride diffusion studies revealed that the inhibitor mixed concretes exhibit very low permeability [14].
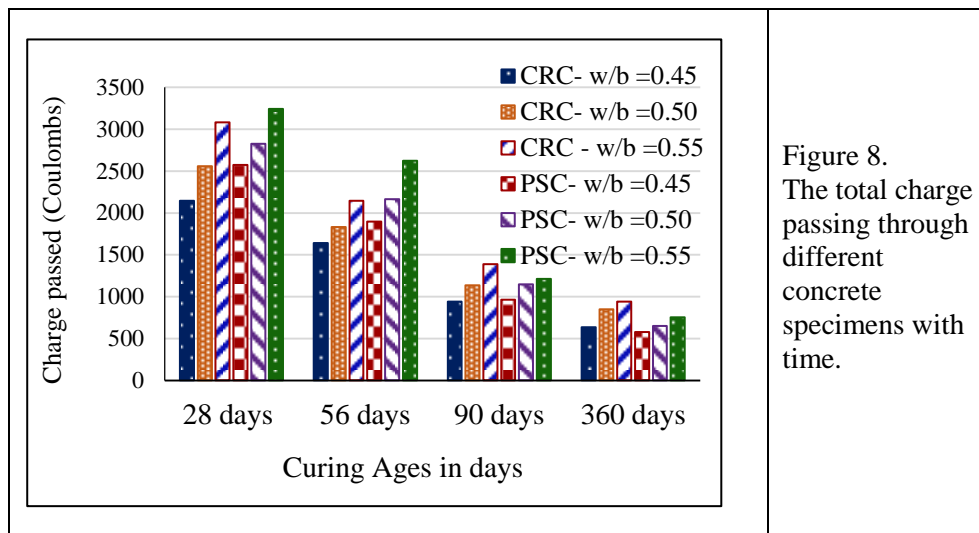

Figure 8. The total charge passing through different concrete specimens with time.

3.3 Half -cell potential measurement (HCP)

The half-cell potential of steel reinforcement in concrete measured periodically with potentiostat with saturated calomel reference electrode (SCE) is as shown in fig. 9 and fig. 10 for 3%, 5% and 7.5% chloride exposure respectively.

Corrosion potentials in all specimens were relatively negative after one week of exposure -140 mV to -200 mV versus SCE. This appears to propose that the steel in all specimens is actively corroding (HCP: -126 to -275=Intermediate corrosion) [23], whichcontradicts normal experience. From two weeks of ageonwards, potentials shifted to positive values (about -100 mV). The shift observed was more positive in CRC concrete, indicating that the steel had passivity.
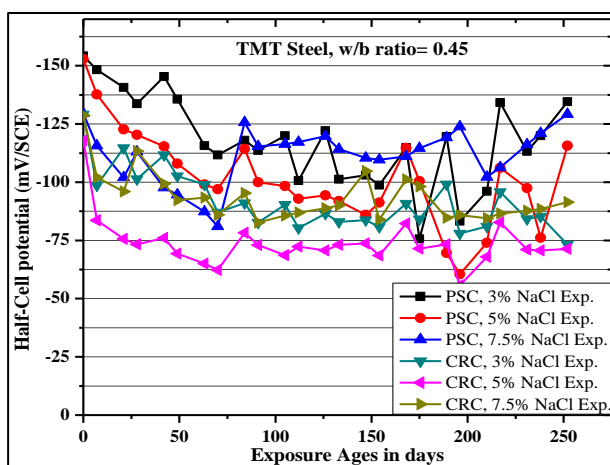

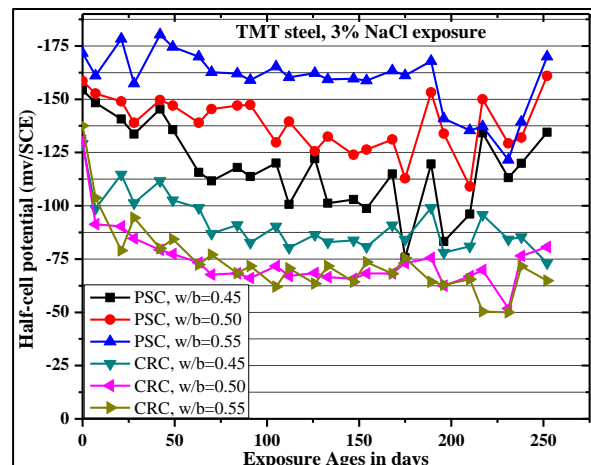Figure 9. Average HCP of ASTM-G109 beam specimen for different NaCl exposures

Figure 10. Average HCP of ASTM-G109 beam specimenfor different w/b ratio

It was observed from the figures 9 and 10 in the concrete with PSC that the increase in w/b ratio increases the negative potential. Potential values were below (-126mV) up to 60 days which indicates corrosion risk is very less [23]. Afterwards, the potential values were increased to the risk of intermediate corrosion (-126 mV to -256 mV). It was also observed that the potential values were moving toward positive side after first few cycles .This may be due to the pozzolanic activity of slag over the time refines the micro-pores, which restrict the ingression of moisture and oxygen up to rebar level. From the observation of figures 9 and 10, CRC performs better than PSC in corrosion resistance. Potential values were exhibiting in the low limit of corrosion till 200 days of chloride exposure to different chloride concentration solutions. In general, it is observed that the potential values of CRC are negative at lower w/b ratio and positive at higher w/b ratio.

In general, it was observed that the potential values of CRC are less negative at lower w/b ratio compared to higher w/b ratio. Corrosion measurements of steel in concrete normally fluctuate with time. The degree of fluctuation can depend upon the corrosion mechanism occurring [28, 29].The apparent fluctuation in potential values in summer and rainy season was observed. It was noted that the corrosion potential was affected by temperature (more negative) as well as humidity (shift to positive).

The rate of potential change was slow in CRC concrete as compared to PSC. The corrosion potential was observed for the period of 260 days from exposure (about 310 days from casting) between -90mV to -180mV for PSC whereas for CRC concrete the values were below -100mV for all concrete mixes. This shows the improvement in corrosion activity by inhibitor compared to PSC.

Improved performance is exhibited in the case of CRC concrete specimens for all the tests including compressive strength, RCPT and half-cell potential.

4. Conclusion

Based on the experimental studies on concrete with CRC and PSC the following conclusions were drawn:

1. At early ages the pozzolanic activity in concrete with PSC is very slow as it gives lower early age strength as compared to CRC.
2. Corrosion-inhibitor has no effect on strength but may influence the delayed onset of corrosion.
3. The HCP of concrete with PSC show more negative potential with the increase in NaCl solution exposure as 3%, 5% and 7.5% and decrease with increase with w/b ratio irrespective ofcuring ages. Whereas, in concrete prepared with CRC, the reverse nature was observed.
4. From half-cell potential measurements, it was observed that the concrete prepared with CRC exhibited more positive potential values as compared to concrete prepared with PSC.
5. The corrosion initiation is delayed due to use of inhibitors in concrete. Improved performance is exhibited in the case of concrete prepared with CRC concrete specimens for all the tests including compressive strength, RCPT and half-cell potential.

5. Acknowledgement

6. References

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