**Paper No.
RCC33**

Determination of corrosion rates by Potentiostat and weight loss measurement for steels embedded in different concretes grades developed with different cements

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ABSTRACT

Corrosion behaviour of blended cements in structural concretes under aggressive exposure condition must be established. The present investigation was mainly directed towards investigating the corrosion behaviour of blended cements such as Portland pozzolana cement and Portland slag cement in structural concretes and compare it with ordinary Portland cement. The experimental investigations were carried out to arrive at the corrosion rates on three structural concretes 25, 35, 45 MPa. 8 mm cold twisted deformed bar (Fe 500 grade) was used in this study. The investigation was carried out for steels embedded in cubical specimens for a concrete cover of 20 mm. Chloride curing and mixing was done by 5% and 1% NaCl solution respectively. The idea behind categorizing this was to simulate the marine environment condition and to take a reference for comparison. The corrosion rates were assessed both by a potentiostat and from weight-loss measurements at the end of 500 days of exposure. The studies showed that the corrosion rates determined by gravimetric weight loss were less that the values determined by potentiostat. However, the corrosion rates are in the order M45<M35<M25 for the grade of concretes and for cements the corrosion rates are in the order PSC<PPC<OPC.

INTRODUCTION

Several researchers have made contributions towards finding the effect of cement type on the rate of corrosion. Earlier, use of OPC cement in concrete could not suffice the requirement to cater the corrosion problem and hence the service life of a structure was a big issue. With growing use of different cements with partial replacement of various admixtures and pozzolanic material, researchers started to utilize them in controlling the corrosion problem. However, experimental validation was required and hence this motivated several researchers to incorporate them with experimental studies. Nowadays, a wide range of electrochemical non-destructive tests are available for determination of corrosion rate. Linear polarization technique (LPR), Tafel extrapolation method, gravimetric weight loss and electrochemical impedence spectroscopy (EIS) has now been widely used in the determination of corrosion rate.

Pradhan and Bhattacharjee (2009) conducted experimental study of corrosion on large number of slab specimen exposed to varying chloride content with three different cement embedded with reinforced steel using linear polarization (LPR) technique and electrochemical impedence spectroscopy technique (EIS). The test results showed that the corrosion rate in OPC was much higher than that of PPC and PSC. Analysis of variance (ANOVA) was carried out using various parameters to find the factors on which corrosion rate depends. It was concluded that the percentage chloride content had the strongest influence on the corrosion rate while there was no effect of time of exposure. Choi et.al. (2006) studied corrosion behavior of steel bar embedded in concrete with and without fly ash using open circuit potential, polarization resistance measurement and electrochemical impedence spectroscopy (EIS). The results obtained from electrochemical tests show that partial replacement of fly ash has led to an enhancement of corrosion resistance and a reduction of corrosion rate due to the decrease of permeability to chloride ions. There was formation of pits on the surface of concrete, the number being more in OPC based concrete and less on fly ash based concrete. In a similar kind of finding, Montemor et al. (2000) found that fly ash addition led to a raise of concrete resistivity and the time for corrosion initiation and also a decrease in corrosion rate. Arya and Xu (1995) found a similar type of behavior of corrosion rates when studied the effect of cement type on corrosion. Galvano-static measurement and pore solution analysis were performed on 1% and 3% chloride mixed samples. It was observed that chloride binding in GGBFS type cement was higher than OPC and fly ash cement. Hence large amount of free chloride were found to be present in the concrete matrix of OPC leading to higher corrosion rates. This free chloride content increased with increase in the concentration of mixing chloride solution.

Ha Tae et.al. (2007) reported the behavior of concrete against corrosion with fly ash blend. They concluded that addition of admixtures reduced the value of pH of the concrete. However, this value was above the critical value of pH required to break the passive layer around the rebars. Also, it was concluded that fly ash based concrete was more resistant to corrosion. This goes same as suggested by Choi et.al. (2006). Kelestemur and Demirel (2010) conducted similar study with finely grounded pumice (FGP) and silica fumes (SF) and found that though FGP addition resulted in decrease in compressive strength and increase in corrosion rate, addition of SF improved strength as well as corrosion rate. Dinakar et al. (2006) studied the corrosion behavior of concrete with blended cements– Portland pozzolana (PPC) and Portland blast furnace slag cement (BFSC) and compared it with corresponding ordinary Portland cement concrete. They found that both PPCs and BFSCs showed higher values for resistivity compared to their corresponding OPCs by adopting electrochemical potentio-dynamic polarization technique to measure corrosion rates. There are several supplementary cementing materials used in the past that have shown better resistance to corrosion.

Yeau and Kim (2005) evaluated the corrosion resistance of two types of Portland cement mixed with GGBFS varying from 0 to 50% and carried out permeability, diffusivity, surface area of corrosion on embedded steel and potential measurements. It was found that the coefficient of permeability of Type I cement concrete was lower than that of Type V cement concrete. Phenomenon like corrosion is a long and slow process. Its effect on rebars looks to increase gradually. Hence a study performed in the initial days of a structure may not give a true value of factors involved in corrosion process. Thus, many researchers have studied the long term effects of various factors involving corrosion in steel embedded in concrete. Gu et al. (2000) studied the performance of reinforced concrete slabs embedded at different covers ranging from 13 mm to 76 mm. The slabs were made with and without blast furnace slag and silica fume subjected to 3.4% of chloride ponding for 6 months. The results obtained from linear polarization resistance, half-cell potential and chloride diffusion tests showed better corrosion resistance in case of blast furnace slag and silica fumes. The charge passed through silica fume and blast furnace samples were less than 1000 coulombs while it was greater than 1000 coulombs for control concrete, regardless of water cement ratio, indicating less chloride penetrability in slag and silica fume mixed specimen. Vedalakshmi et al. (2008) conducted long term study on corrosion on 3 types of concrete, M20, M30 and M40 with OPC, PPC and PSC variation using weight loss method. It was concluded that corrosion rate of rebars in OPC was 9 to 10 times higher as compared to PPC and PSC. Abosrra, et.al. (2011) studied the corrosion behavior in various grade of concrete and concluded that corrosion rate for higher strength concrete was lower. Reinforced concrete with compressive strength of 20MPa, 30MPa and 46MPa was studied under polarization technique. Test results showed lower corrosion rate for 46MPa concrete. The reason for this trend was attributed to the lower penetration of chloride due to pore refinement in higher grade of concrete.

This work comprises of measurement of corrosion rates using linear polarization measurements and weight loss methods. Slag and pozzolana materials like fly ash are industrial waste that has to be used judiciously instead of disposing them off on the ground. These materials are thus utilized in construction industry on a large scale nowadays. Pozzolana and slag based cements form hydration products that improves pore and diffusion property of a concrete matrix, thus providing enhanced resistance to corrosion. In this study, an effort has been made to study the corrosion behavior in reinforcement provided in concrete that are commonly used in structural application. The effect of grade of concrete, concrete cover to reinforcement and the effects of different types of cement (OPC, PPC and PSC) on corrosion has been experimentally investigated. Accordingly, a qualitative comment on blend effect and grade effect has been made.

EXPERIMENTAL METHODOLOGY

Ordinary Portland cement (OPC) which met the requirements mentioned in IS: 12269 (53 grade), Portland pozzolana cement (PPC) (fly ash confirming to IS 3812: 1981) and Portland slag cement were used. Crushed granite with nominal grain size of 20 mm and good quality well graded sand (4.75 mm down) were used as coarse and fine aggregates respectively. The different size fractions of coarse and fine aggregates (20 mm down, 12.5 mm down and 4.75 mm down) were taken in order to get a dense concrete. The specific gravities of OPC, PPC and PSC were 3.15, 2.90 and 3.00 respectively while specific gravity for 20 mm; 12.5 mm aggregate and sand were 2.75, 2.76 and 2.65 respectively. ACI mix design was adopted for designing M25, M35 and M45 grade concrete. Slump values obtained were in the range of 25-50 mm for all the mixes. The details of mix proportions are tabulated in Table 1.

Table 1: Mix design as per ACI

Grade	Cement	W/C	Water	Cement	Sand	20mm	12.5mm
M25	OPC	0.61	195	312	683	582	603
M35	OPC	0.47	195	405	655	558	579
M45	OPC	0.38	195	500	624	532	551
M25	PPC	0.61	195	312	674	574	594
M35	PPC	0.47	195	405	644	548	568
M45	PPC	0.38	195	500	614	523	542
M25	PSC	0.61	195	312	679	579	600
M35	PSC	0.47	195	405	649	553	573
M45	PSC	0.38	195	500	617	526	545

Note: All quantities are in kg/m^3

For each grade, i.e. M25, M35 and M45, there were 3 blend varieties, i.e OPC, PPC and PSC. Chloride water mixing and chloride water curing (CL-CL) was adopted. Chloride curing and mixing was done by 5% and 1% NaCl solution respectively. The idea behind categorizing this was to simulate the marine environment condition and to take a reference for comparison. Tor steel bars of 8mm diameter were embedded in (150×150×150) mm cube at different covers, namely 10mm, 20mm, 30mm, 40mm and 50mm. Firstly, the wires were inserted in the grooves made in bars and sealed, so that connection could be made. Middle 50 mm of the 200mm length bar was then covered and the top as well as the bottom portion was coated with epoxy, as shown in Fig. 1. The bars were then allowed to dry for some time, and the covers were removed so that the bars were exposed in the middle 50 mm, the upper 50mm portion and lower 50 mm portion was epoxy coated. These bars were then placed in the holes, at suitable covers, made in an acrylic sheet placed over the mould (Figs. 1&2).

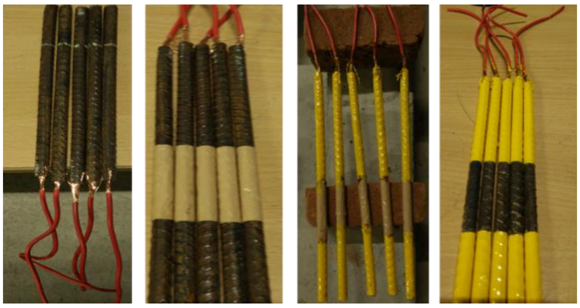


Figure 1: Preparation of bars

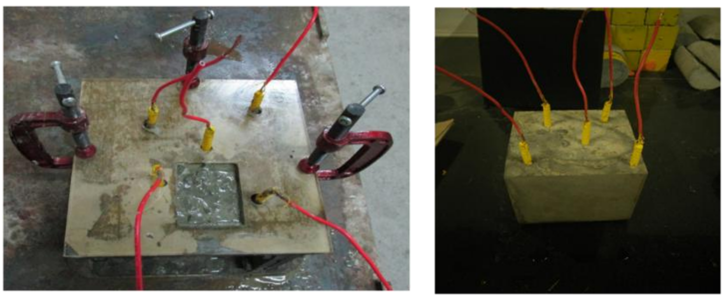


Figure 2: Preparation of samples

TEST METHODS

In the present study, compressive strength test was carried out just to ensure the concrete reaches desired strength and to observe the strength behavior with different cement type. In addition to this, corrosion rate analysis was performed to study the corrosion in different cement types.

Compressive strength test was performed to assess the early age strength properties of concrete specimen with different cement types. (150×150×150) mm cube was tested in compression testing machine at an interval of 3, 7, 28 and 56 days. It can be inferred from table

The corrosion rates were assessed both by a potentiostat and from weight-loss measurements at the end of 500 days of exposure in chloride environment. In the present study, the potential of working electrode was perturbed through counter electrode and corresponding current flow between the embedded bar and reference electrode were measured. Test was performed as per ASTM G59-97. Open sequencer (Gill AC Serial No. 1772) software was used for the analysis.

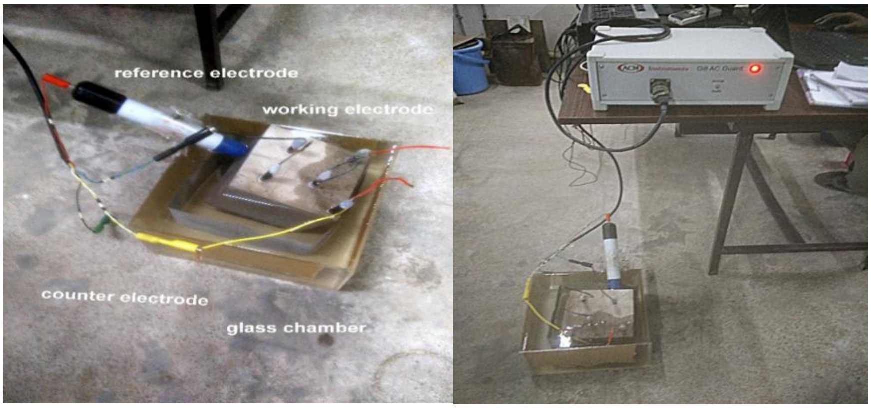


Figure 3: Experimental setup for corrosion rate test

A square mesh of size (20×20) cm and height 10cm was used as counter electrode as shown in Fig. 3. Corrosion rate test was done using AC Gill Sequencer. Cyclic sweep between the start and reverse potential was set at a rate of 100mV/min. The Tafel plots were recorded. The value of i_{corr} was obtained from the slope drawn on cathode and anode extended to intersect E_{corr} of Tafel plot in the linear region. Th corrosion rate (CR) was then calculated as per equation 1 in mm/year.

In the weight loss measurement test, the specimens were exposed to 5% NaCl solution for a period of 500 days. During the exposure to salt solution, chloride ions tend to diffuse through the cover concrete and cause corrosion. At the end of the exposure period the concrete specimens were broken open and the rebars were taken out. Then they were visually examined for the extent of rust and forms of rust. After visual examination, the top bar was pickled in inhibited hydrochloric acid as per ASTM GI standard (G1,1995) to remove the rust product and re-weighed. From the initial and final weight, loss in weight due to corrosion was determined. From this, corrosion rate in mmpy was calculated as per equation 1.

Corrosion rate was then calculated from equation using i_{corr} value.

$$CR = \frac{0.00327 \times a \times i_{corr}}{n \times D} \quad (1)$$

where,

i_{corr} = corrosion current density in μA/cm^2

CR = corrosion rate in mm/year

a = atomic weight of iron, i.e. 55.84 amu

D = density of the steel in g/cm^3, i.e. 7.85 g/cm^3

n = number of electrons exchanged in corrosion reaction, i.e. 2 in this case

RRESULTS AND DISCUSSION

The compressive strength results are included in Tables 2, 3 & 4 respectively for all the grades of concretes studied. From the results, it can be noticed that the that initial strength were more in OPC concrete specimen while strengths at later ages were more in case of PPC and PSC concrete. The reason for this kind of behavior would be high content of alite (C_3S) in OPC cement which contributes to early setting and hence early strength in concrete. The reason for higher ultimate strength in slag based cement was due to better distribution and refinement of pores. Inter-facial transition zone (ITZ) is a border line zone between cement paste matrix and aggregates. This zone is highly porous and contains more amount of water. This acts as a weak link in concrete, since it has lesser strength than cement paste and aggregates. During compressive strength test, cracks passes through this ITZ. Now in PSC and PPC based concrete, the slag and pozzolan material forms hydration products which ultimately clogs pores present in ITZ. Hence, larger size pores reduce to small and pore refinement is achieved, due to which a high ultimate strength was observed.

Table 2: Compressive strength test results for M25

Age of Concrete (days)	OPC	PPC	PSC
3	15.92	13.95	12.87
7	20.5	17.6	16.73
28	26.57	29.25	35.84
56	31.9	33.48	41.42

Table 2: Compressive strength test results for M35

Age of Concrete (days)	OPC	PPC	PSC
3	17.21	14.3	13.2
7	27.67	26.9	24.28
28	37.72	38.41	43.65
56	46.46	54.23	58.21

Table 3: Compressive strength test results for M45

Age of Concrete (days)	OPC	PPC	PSC
3 days	22.65	20.75	19.44
7 days	33.35	27.57	25.34
28 days	47.38	54.32	58.36
56 days	55.61	60.67	63.16

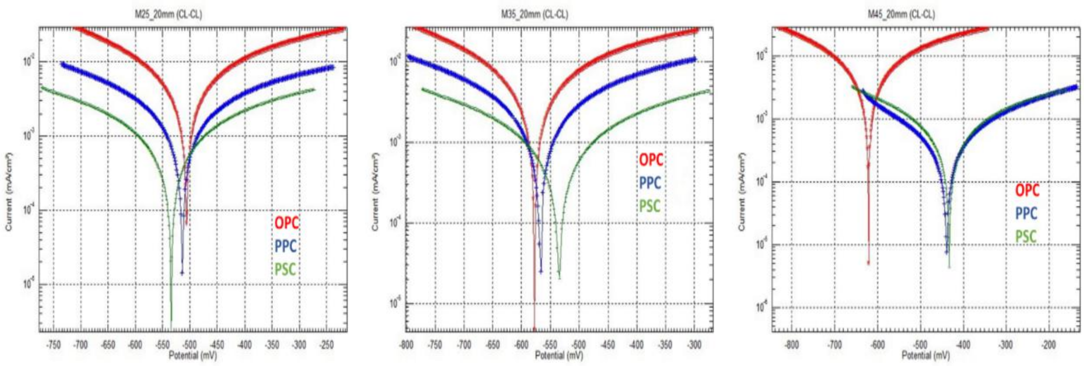
Corrosion rates were obtained for different covers with different grades i.e. M25, M35 and M45 and OPC, PPC and PSC cements. Results are organized into blend effect with different type of cement used with different types of grade of concrete taken. All the corrosion rate results determined both by the potentiostat and the weight loss methods were presented in Table 5.

Table 4 : Corrosion rate comparison showing blend and cover effect in CL-CL

Grade of concrete	Cover	CR_OPC (mm/y)	CR_PPC (mm/y)	CR_PSC (mm/y)	Ratio (OPC/PSC)	Ratio (PPC/PSC)
M25	20 mm*	0.220	0.026	0.011	20.00	2.361
M35	20 mm*	0.041	0.035	0.015	2.73	2.33
M45	20 mm*	0.050	0.018	0.012	4.16	1.50
M25	20 mm#	0.200	0.023	0.009	22.22	2.55
M35	20 mm#	0.037	0.031	0.013	2.84	2.38
M45	20 mm#	0.046	0.016	0.010	4.60	1.60

*Corrosion rates determined based on potentiostat, #Corrosion rates determined based on weight loss method

It was observed that PSC based concretes showed lesser rate of corrosion. Hence, corrosion might be prolonged in case of PSC based concretes. However, results of PPC based concrete were comparable. This fact was evident from the tafel plots where the value of polarization resistance in case of PSC and PPC was significantly greater than that of OPC. Corrosion rates when compared for OPC, PPC and PSC based M25 concrete showed that the corrosion rate for OPC based CL-CL specimen increased at a faster rate. It can also be concluded that corrosion rates for OPC was 9 times higher than PSC based concrete except for CL-CL specimen, where corrosion rate for OPC was highest. However, corrosion rates for PPC and PSC were comparable. Hence, one can infer that the service life of a structure will increase by 9 to 10 fold by using PPC or PSC based concrete (Table 5).



It was also evident from the results that the corrosion rates also depend on the exposure condition and concrete pore solution. The reason for lesser corrosion rate in PSC could be lower amount of free chloride in the concrete pore solution. The chloride binding property for PSC is higher than OPC and hence lesser free chloride is expected in PSC chloride mixed sample. Variation in concrete grade was also observed with respect to corrosion rates in different covers. It was observed that corrosion rate was in the order M45<M35<M25. The results also show effect of grade on corrosion for different types of cement. The lesser value of corrosion rate in M45 in grade effect and PSC in blend effect was further validated by low value of i_{corr} and high value of polarization resistance in them. i_{corr} was obtained by drawing tangent in the linear region of cathode and anode and by extrapolating it to cut the E_{corr} value given. It is evident from Fig. 4 that the value of i_{corr} in case of M45 was less which in turn made the value of polarization resistance greater and hence the corrosion rate was lesser.

CONCLUSIONS

1. PSC concrete showed better performance than OPC. However comparable results were obtained for PPC concrete. OPC showed risk of corrosion at an early age.

2. Corrosion rate analysis after 500 days showed that corrosion rate for OPC concrete can be 9 times higher than PSC and PPC concrete, determined both by the potentiostat and the weight loss methods. Hence, the service life of a structure can be increased by approximately 9 to 10 times with the use of PSC concrete. Corrosion rate was also affected by the grade of the concrete. It was observed that the corrosion rate was in the order M45<M35<M25. However, the corrosion rates analysed based on weight loss method were lesser than the ones analyzed based on potentiostat.

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