Bulletin of Electrochemistry 18 (4) April 2002, pp 159-164 0256-1654/2002/$ 3-50

COMPARATIVE STUDIES ON THE CORROSION PERFORMANCE OF STEEL IN CONCRETE IN NATURAL, POLLUTED AND MARINE ENVIRONMENTS

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[Received: 08 October 2001 Accepted: 10 January 2002]

Performance studies of two different cements were carried out by electrochemical and non electrochemical techniques on concrete specimens exposed to natural, polluted and marine environments. It was observed that ordinary Portland cement (OPC), showed better performance than Portland pozzolona cement (PPC). Microbiological examination was conducted and found that 10 micro-organisms were present in the sewage. Out of these, sulphate reducing bacteria (SRB) mainly led to deterioration in the concrete.

Keywords: Ordinary portland cement, portland pozzolona cement and sulphate reducing bacteria

INTRODUCTION

The corrosion of reinforcing steel in concrete is caused by penetration of chloride ions, carbonation of concrete or low quality of the concrete cover. The corrosion of metals in particular ferrous materials, by the sulphate reducing bacteria (SRB) is a well documented phenomenon [1]. However the corrosion of steel in concrete as a direct or indirect results of SRB activity has been little studied [2] (with the exception of the degradation of concrete in sewers). The corrosion problems relate to the production of hydrogen sulphide by SRB. The corrosion of steel reinforcements can result in the spalling and deterioration of the concrete structures.

Two types of bacteria are implicated in the degrading of reinforced concrete [3] namely aerobic sulphur oxidizing bacteria (SOB), and anaerobic sulphate reducing bacteria (SRB) [4]. The role of SOB in the corrosion of reinforced concrete is associated with problems in specific sewage conditions. The bacteria, typically "Thiobaccillus" can by oxidizing sulphur to sulphuric acid, lower the *p*H of concrete to the range 1.0 to 2.0 [5-8].

The role of SRB in the corrosion of reinforced concrete is less well defined. The hydrogen sulphide produced by SRB can be used by thiobaccillus as a substrate in their oxidation process. Once, the biogenic sulphide reacts on the surface of the steel reinforcement, it can cause corrosion [9]. The volume of the sulphide film is much greater than that of the oxide film and hence can result in the spalling of concrete.

The objective of the present investigation is to study the performance of OPC and PPC concretes in different environmental conditions such as normal tap water, sewage and sea water. Effect of microorganisms on concrete is also studied

EXPERIMENTAL

Materials used

Ordinary Portland cement	Confirming to IS - 8112 - 1989
Portland Pozzolana cement	IS 1489 Part -1 , 1991
Graded fine aggregates	Local clean river sand (fineness modulus of medium sand equal to 2.6) confirming to grading zone III of IS - 383 - 1970 was used as fine aggregates

Graded coarse aggregates	Locally available well graded aggregates of normal size greater than 4.75 mm and less than 10 mm of IS -383-1970 was used as coarse aggregates.

Composition of mix proportion used

The mix proportion used for casting was 1:1.53:1.93 (w/c = 0.53)

Constituents	Quantity used (kg/ m^3)
OPC	415
Fine aggregates	635
Coarse aggregates	800
Water	Distilled water

Systems studied: The following environments were chosen for our study:

a) Normal tap water used in the laboratory

b) Sea water is collected from Bay of Bengal, Mandapam camp, Mandapam

c) Sewage water is collected from the near by tank.

The respective environments were chosen in a separate tank and the concrete specimens were cured at different ages. Evaporation loss was compensated for throughout the exposure period.

Techniques adopted

Weight loss measurements

Cylindrical concrete specimens of size 60 mm x 55 mm were cast for OPC and PPC systems. Mild steel rod of size 6 mm diameter and 50 mm length was embedded centrally. The schematic diagram of concrete specimens are shown in Fig. 1. Initially the mild steel rebars were cleaned in hydrochloric acid, degreased with acetone and washed with double distilled water and dried. The initial weight of the rebar was taken before casting using Mettler balance for gravimetric measurement.

Cylindrical concrete specimens were prepared using 1:1.53:1.93 with a w/c ratio of 0.53. After 24 hours of setting the specimens were demoulded and cured in different environments as given in section 2.3.

Tests were conducted on a minimum of six replicate specimens and the average values were obtained.

Open circuit potential [OCP]

The OCP for different systems was monitored every month using saturated calomel electrode (SCE) as reference electrode and a high impedance voltmeter.

Compressive strength test

Concrete cubes of size 100 mm x 100 mm x 100 mm were cast using 1:1.53:1.93 mix with a w/c ratio of 0.53 with OPC and PPC. During casting, the cubes were mechanically vibrated using a table vibrator. After 24 hours, the specimens were removed from the mould and subjected to curing for 3, 7, 28, 45 and 90 days. All the specimens were cured in the chosen environments contained in different tanks for the period of 3 months. After curing, the specimens were tested for compressive strength using AIMIL compression testing machine of 2000 kN capacity. The tests were carried out on a set of six specimens and the average compressive strength values were obtained.

Qualitative and quantitative examination of corrosion

At the end of the exposure period, the specimens were split open and the visual observation was made and the corrosion rates of mild steel rebars embedded in OPC and PPC concretes were determined by gravimetric method and expressed in millimeters per year (mmpy).

Chemical analysis for alkalinity and free chloride contents:

The concrete samples collected near the rebar were crushed mechanically and powdered. Then 100 gm of powdered sample was shaken with 100 ml of double distilled water in a conical flask using microid flask shaker for one hour. The extract was then filtered through a Whatman Filter paper No.42. The extract prepared from the powdered sample was then analysed for alkalinity and the free chloride contents as per the standard procedures [10].

50 cc of filtered solution was taken in 100 ml beaker and the alkalinity of the sample was measured in terms of *p*H using a standard calibrated *p*H meter. 20 cc of filtered solution was taken and the free chloride was estimated by standard silver nitrate solution using potassium chromate as an indicator. The amount of chloride present was expressed in terms of parts per million (ppm) on the basic weight of sample taken for analysis.

Electrochemical impedance spectroscopy

The A.C. impedance technique [11] allows the corrosion processes to be modeled in terms of passive electrical circuit components such as resistance, capacitance, inductance and impedance, giving an "equivalent circuit" of the corroding interface. Impedance measurements were made using electrochemical impedance analysis (Model 6310 PAR) over c frequency range of 10 KHz to 10 mHz.

Microbiological examination

Corrosion caused by various micro-organisms were tested in sewage water. Bacterial identification was carried out by the standard key described by Bergey's Manual of systemic bacteriology [12].

RESULTS AND DISCUSSION

Corrosion rate by gravimetric method

The corrosion rates calculated in mmpy for the mild steel embedded in OPC and PPC exposed in different environments for the exposure period of 6 months are given in Fig. 2. From this figure, it is inferred that the corrosion rate of OPC system was found to be 4 x 10^{-4} mmpy at the end of 6 months exposure period. But other two systems OPC + sea water and OPC + polluted water have shown higher corrosion rate than OPC normal water.

But, in PPC systems the corrosion rates were found to be 7 x 10^{-4}, 7.80 x 10^{-4} and 9 x 10^{-4} mmpy respectively for environments normal, polluted and sea at the end of exposure period of 6 months. All the PPC systems have shown more corrosion rate than OPC system.

The trend of reduction of corrosion of steel by various systems follows the order:

OPC (normal) > OPC (polluted) > OPC (sea)

PPC (normal) > PPC (polluted) > PPC (sea)

Potential vs time studies

The electrochemical characteristics of half cell potential measured periodically against a

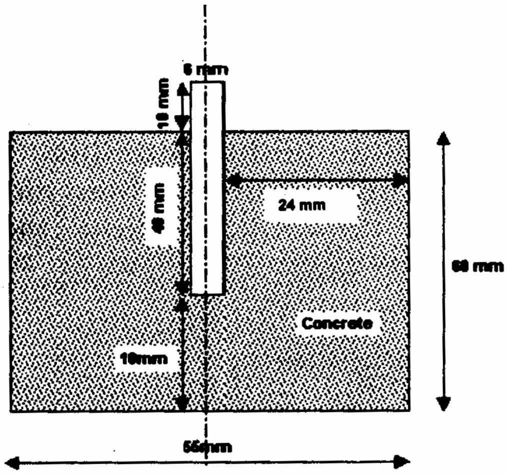

Fig. 1: Schematic representation of concrete specimen

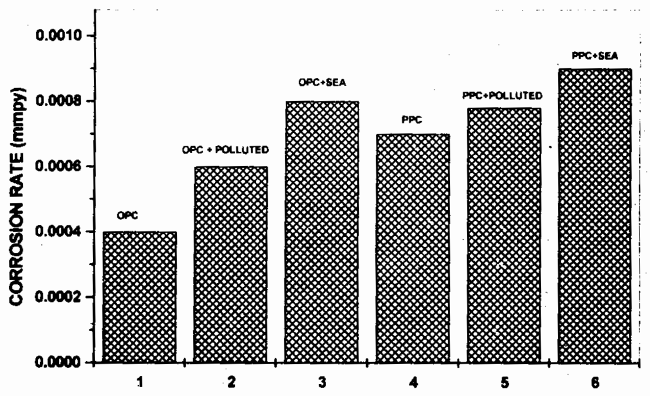

Fig. 2: Corrosion rate for various systems

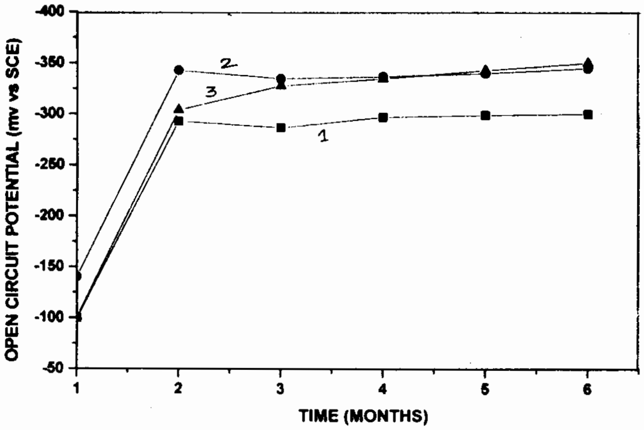

Fig. 3a: Potential vs time curves for various systems
(1) OPC (normal) (2) OPC (sea water) (3) OPC (polluted)

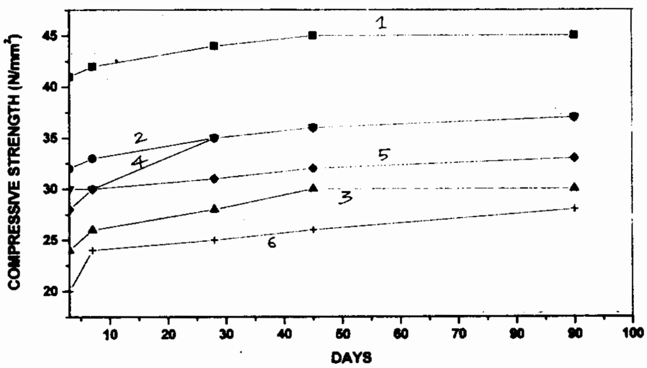

Fig. 4: Compressive strength data for various systems
(1) OPC (normal) (2) OPC (polluted) (3) OPC (sea)
(4) PPC (normal) (5) PPC (polluted) (6) PPC (sea

saturated calomel electrode with time are shown in Figs. 3(a&b).

Potential vs. time (Fig. 3a) for OPC upto 3 months of exposure, steel embedded in OPC normal showed potential values less than -275 mV vs. SCE (as per ASTM C-876 the threshold limit of potential for steel in concrete is -275 mV vs. SCE) indicating the perfect passive condition of the steel rebars. But the other two systems namely OPC (sea) and OPC (polluted) showed potential values greater than -300 mV within the 2 months of exposure indicating the active condition of rebars Interestingly OPC normal showed less negative OCP values throughout the exposure period.

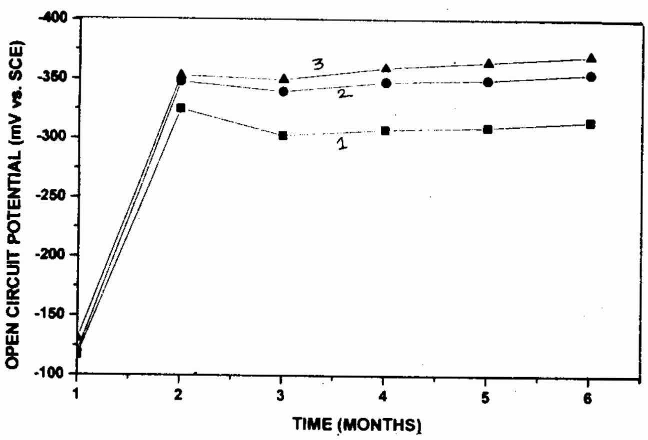

Fig. 3b: Potential vs time curves for various systems
(1) PPC (normal) (2) PPC (polluted) (3) PPC (sea)

Potential vs. time (Fig. 3b) for PPC system shows, even at 3 months of exposure, steel embedded in all the three PPC systems namely PPC (normal), PPC (sea) and PPC (Polluted) showed potential values greater than -300 mV indicating the active condition of rebars.

The trend of maintaining the passive condition of embedded steel decreases as follows:

OPC (normal) > OPC (polluted) > OPC (sea)

PPC (normal) > PPC (polluted) > PPC (sea)

Compressive strength measurements

The compressive strength values of OPC & PPC systems cured in different environments at 3, 7, 28, 45 and 90 days of exposure are given in Fig. 4.

It is a fact that compressive strength was increased with increasing of curing period.

The compressive strength of OPC was 43 MPa at 90 days. The compressive strength of OPC specimens exposed in sea water and polluted water decreased to a lower values i.e. 30 MPa and 37 MPa respectively.

The compressive strength of PPC was 37 MPa at 90 days. The compressive strength of PPC specimen exposed in sea water and polluted water decreased to a lower values i.e. 28 MPa and 33 MPa respectively.

TABLE I: Impedance values for OPC and PPC concrete exposed to different environments

System	At the initial exposure		At the end of exposure	
	R_{ct} ($\Omega . cm^2$)	C_{dl} ($\mu F . cm^{-2}$)	R_{ct} ($\Omega . cm^2$)	C_{dl} ($\mu F . cm^{-2}$)
OPC (Normal)	1410	1133	1550	710
OPC (polluted)	822	1167	515	748
OPC (sea)	650	1721	503	1537
PPC (Normal)	782	496	493	210
PPC (polluted)	697	774	300	309
PPC (sea)	526	835	299	680

The trend of reduction in strength by various systems follows the order

OPC (normal) > OPC (polluted) > OPC (sea)

PPC (normal) > PPC (polluted) > PPC (sea)

AC impedance measurements

The results obtained from the AC impedance measurements are given in Table I. The R_{ct} values for OPC systems at the initial and end of exposure period shows that, in OPC (normal) shows more R_{ct} values than other two systems. The Cdl values for OPC (normal) is less than that of other two systems.

TABLE II: Free chloride and *p*H values for OPC and PPC concrete exposed to different environments

System	*p*H	Free chloride contents (ppm)
OPC (Normal)	12.4	380
OPC (Sea)	12.4	2160
OPC (Polluted)	12.4	320
PPC (Normal)	12.3	480
PPC (Sea)	12.3	3460
PPC (Polluted)	12.3	900

TABLE III: Microorganisms present in the sewage

Sl No	Name of the microorganism
1.	Escherichia Coli
2.	Klebsiella Species
3.	Staphylocius Species
4.	Streptococius Species
5.	Bacillus Species
6.	Pseudomonas Species
7.	Vibrio Species
8.	Aeromonas Species
9.	Shigella Species
10.	Sulphate Reducing Bacteria (SRB)

Similarly the R_{ct} values for PPC systems at the initial and the end of exposure period shows that, in PPC (normal) shows more R_{ct} values than other two systems. The Cdl values for PPC (normal) is less than that of other two systems.

The trend of maintaining the passive condition of embedded steel decreases as follows:

OPC (normal) > OPC (polluted) > OPC (sea)

PPC (normal) > PPC (polluted) > PPC (sea)

The same trend was already observed in weight loss measurements and compressive strength tests.

Free chloride contents

The results of the analysis of concrete samples collected near the anode reported in Table II. From this table it is observed that in both OPC and PPC systems, there is no appreciable change in PH values. The free chloride contents estimated are also reported in Table II. For OPC (normal) the free chloride content is 380 ppm; sea water 2160 ppm and sewage 320 ppm. In sea water, chloride diffusion is more when compared to sewage water.

The free chloride from PPC normal water is 480 ppm, sea water 3460 ppm and sewage 900 ppm.

Microbiological results

Ten micro organisms were identified and they are presented in Table III. Sulphate reducing bacteria was identified in both the systems in polluted water. This micro organism is the most responsible for deteriorating the concrete Coli-form bacteria are presented which are responsible for waste pollution, pollution indicating organisms. In general, the rate of corrosion induced by SRB will take place after a long period of exposure in sewage. At earlier stage a non oxide film prevents a passive layer for interpenetrating ions. Since polluted system behave better than sea water.

CONCLUSIONS

The adverse effects of the aggressiveness of chloride ions and the microorganism on the deteoriation of concrete and the corrosion of steel have been shown.

Acknowledgements: Authors thank Director, Central Electrochemical Research Institute, Karaikudi 630 006 for his kind permission to publish this paper.

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