PERFORMANCE OF BLENDED CEMENT CONCRETE EXPOSED TO MARINE ENVIRONMENT

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ABSTRACT

Reinforced concrete exposed to the marine environment deteriorates more rapidly. Structures constructed at or near the sea shore have to be repaired more often than comparable structures located elsewhere. This study was carried out to develop an understanding of the performance of concrete made up of cements blended by pozzolanic materials. Several mix designs were formulated, incorporating the pozzolans like slag, fly ash and silica fume and calcium nitrate as the corrosion inhibitor. Mix designs were in accordance with ACI 211-1 and pozzolanic materials were added in accordance with ACI 233 and ACI 234. A number of tests were carried out during the study to compare the performance of samples cast from concrete of different mix designs. Tests conducted during the study were Rapid Migration Test (NT Build 492), Half Cell Potential (ASTM C 876), Absorptivity of the oven-dried samples (ASTM C 642), Compressive Strength Test (ASTM C 39) and Flexural Strength Test (ASTM C 293). Results showed that in almost all cases, use of cements blended with pozzolanic materials resulted in an enhanced performance of the concrete. Use of supplementary cementitious materials (SCM) in concrete provides a sustainable and feasible solution to the durability problems in coastal areas. Replacements of OPC by the pozzolan will not only help in conservation of natural resources, but it will also contribute towards reducing pollution and energy.

KEYWORDS

Performance, Blended Cements, Marine Environment, Pozzolans, Corrosion Inhibitor.

INTRODUCTION

Deterioration of reinforced concrete (RC) structures has been one of the most extended lessons, taught to mankind. This deterioration is intensely pressing for the structures found on the coast, like Karachi's coastal belt, where structural deficiency caused by leaching is one of the most worrying causes for the engineers. Huge amount of money is being spent annually in rehabilitation and repair of deteriorated RC structures. Construction material, failing to sustain its due performance on the account of environmental aggressions, is dubitably responsible to a large extent. Role of the oceanic aggressive agents become highly undermining in marine environment. The deterioration of RC in marine environment, that may be shore decks, bridges, piles, piers or any other RC structure built in coastal areas, is predominantly because of exposure to sea water. The cost of repairing replacing deteriorated structures has become a major liability for users and different agencies. In US, as highlighted by Gannon et al. (1992), the expenditure was estimated to be more than U.S $20 billion and to be increasing at U.S $500 million per year.

Most of the onshore structures are constructed with normal carbon steel reinforcement due to it being economical compared to stainless steel or galvanic protection alternatives. As concrete bears a natural alkalinity, therefore, under normal condition, it creates a tightly adhering γ-Fe_2O_3 oxide film around the reinforcing steel that keeps it protected as long as this layer is sustained. Before the actual degradation of concrete and the air and moisture access to the reinforcement bars, the corrosion of reinforcement bar is driven up majorly due to carbonation and chloride attack, if present, which Verbeck et al. (1975) described as a unique and specific destroyer. This results in the loss of alkalinity in concrete around the reinforcement bars and also the destruction of passive layer of Fe_2O_3 leading to the initiation of actual corrosion. The volume of iron oxidation product, eventually, causes severe cracks in the concrete providing unavoidable path for oxygen and water, bridging the structure over the threshold of corrosion.

For most of the structures exposed to marine environment, however, the major extent of chlorides in concrete originates from the external sources. The penetration of this chloride occurs through various transport mechanisms depending upon the exposure conditions. Chloride ions can also be a great predator for a structure that is not at or near the coast. It can originate with different variety of reasons. In some countries, even deicing

salts, used to combat the build-up of snow and ice on transport infrastructures, are the greatest source of chloride (Cement Concrete & Aggregates Australia, 2009). Point to be noted here is that, in the case seawater exposure particularly, the chloride poses a much, in fact the sole, threat to steel in concrete than sulfate do to concrete as calcium sulpho-aluminate or ettringite (the expansive product of sulfate and tri-calcium aluminate in the cement) is more soluble in the presence of chloride and hence it does not initiate a considerable disruptive expansion.

Since the relationship between the durability and the strength remains unsettled, the durability of concrete is subordinated with numerous factors and measures. A significant function for durability indexes is the water to cement ratio, lesser the pores, denser the microstructure, lesser penetration of water and ionic aggression and in turns lesser chance of deterioration. Another renowned way of mitigating the degradation of concrete, under the attack of ions, is the replacement of OPC by supplementary cementitious material as explained by Philip et al. (2007), slag (ground granulated blast-furnace slag), silica fume and fly ash. These fine particles of pozzolans help in densely packing up the pores leading to permeation and also give rise to formation of excess ultra-stable calcium-silicate-hydrate (C-S-H) through pozzolanic reaction.

Corrosion inhibitors like calcium nitrate can be used in reinforced concrete which does not actually stop corrosion, but delays its initiation. Calcium nitrate in concrete oxidizes the part of the passive layer of ferrous oxide (+2 oxidation state) into ferric oxide (+3 oxidation state). This ferric state is stable to chloride as compared to ferrous state and keeps the steel passive. This anodic effect on steel reinforcement bars protects it from the degradation by chloride attack. Air-entrainer reduces the probability of segregation and bleeding, ensuring a uniform paste of concrete and improving durability. The microscopic air bubbles can act as a barrier for the water and also provide chemical resistance. External waterproofing membrane can also be used to hinder the penetration and absorption of water to a great extent. Membrane system can be categorized as asphalt-impregnated fabric, cementitious, polymer, elastomeric and asphalt-laminated. The initiation of corrosion of steel reinforcement can also be delayed by coating the reinforcement bar with the referenced anodic zinc. Zinc has more electronegative potential than steel that means it is more sensitive to corrosion. Zinc puts steel in the cathodic state, and it being anodic, exposes itself to the oxidation rather than the steel.

This research is aimed to study the performance of reinforced concrete, made up with different proportions of pozzolans in the mixes along with calcium nitrate dosing and external waterproofing applications, exposed to marine environment. Performance of different mix designs was determined by using several performances related tests available in the literature. Tests conducted during the study were Rapid Migration Test (NT Build 492), Half Cell Potential (ASTM C 876), Absorptivity of the oven-dried samples (ASTM C 642), Compressive Strength Test (ASTM C 39) and Flexural Strength Test (ASTM C 293). Results showed that in almost all cases, use of cements blended with pozzolanic materials resulted in an enhanced performance of the concrete exposed to marine environment.

EXPERIMENTAL PROGRAMME

Mix Designs

Nine different mix designs were used in the study in order to fulfill the scope of studying the performance of marine concrete enhanced by the addition of pozzolans like fly ash, silica fume and slag, along with the use of corrosion inhibitor (calcium nitrate). Details of mix designs are shown in Table 1. The water to cement ratio was kept fixed as 0.4. Proportions of the ingredients were designed as per ACI 211.1, except for mix design A. Mix design A contains the ingredients in 1:2:4 ratio (M15 nominal design), and serves as control mix design as it represents general practice in local construction industry for the construction of general residential buildings. Optimum 4% dosage of calcium nitrate was added in a mix design. Moreover, for workability and ensuring proper compaction with w/c ratio of 0.4, high-range water reducing plasticizer as well as water reducer and retarder was used. For each mix design 0.2 cubic yard concrete was prepared. Minimum cover of $3^{//}$ was maintained for the reinforcement as per specification of ACI 357.

Supplementary cementitious materials used in the study as a replacement of Portland cement in concrete were locally available slag cement containing 30 % slag, Fly ash (Class-C) with the activity index up to 88.72 %, and silica fume from BASF Chemicals & Polymers, MasterLife SF 100. Low water to cement ratio, aimed to make concrete denser and more impermeable, was achieved by the help of High-Range Water Reducer (Type-F) from BASF Chemicals & Polymers, MasterPozzolith LD10 and Super Plasticizer was used additionally for easing the workability as proposed by Plante et al. (1986). Maximum size of coarse aggregate used was ¾ inch, sand passing #4 sieve was used as fine aggregate. Air entrainer (MasterAir 720) and waterproofing membrane (MasterSeal 550) from BASF Chemicals & Polymers, were also used in the study.

Table 1 Mix Designs

Mix Design	A	B	C	D	E	F	G	H	I
Water/Cement Ratio	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Cement (lb/c.yrd)	539.4	685.8	701	533.4	601.6	548.6	381	762	762
Slag (Replacement by %)				30%			22%		
Slag (lb/c.yrd)				228.6			168		
Fly Ash (Replacement by %)					20%	20%	20%		
Fly Ash (lb/c.yrd)					152.4	152.4	152.4		
Silica Fume (Replacement by %)		10%	8%			8%	8%		
Silica Fume (lb/c.yrd)		76.2	61			61	61		
Water (lb/c.yrd)	215.8	304.8	304.8	304.8	301.6	304.8	304.8	304.8	304.8
Fine Aggregate (lb/c.yrd)	1011.3	1005	1005	1005	1005	1005	1005	1005	1005
Coarse Aggregate (lb/c.yrd)	2022.7	1786.1	1786.1	1786.1	1786.1	1786.1	1786.1	1786.1	1786.1
Calcium Nitrate (oz)									500

Compressive and Flexural Strength

Strength has always been the most important characteristic of concrete along with durability. Reduction in compressive and flexural strengths of all mix designs used in the study was determined by exposing respective specimens to marine environment for 100 days after 28 days of curing in normal conditions. An actual splash zone near the construction site of a Quay wall at the harbor port, by China Harbor Engineering Company Group, was selected as marine environment and strength reduction was determined after 100 days. Concentration of different ions in the marine water samples from different locations of Karachi beach is shown in Table 2. China harbor port was selected due to the severity of marine environment.

Table 2 Ionic Concentrations present in different Sea Water Samples

Ions	Clifton Creek	China Harbor Port	Clifton Sea View
Sulfate	18.95 gm/10 ltr	27.7 gm/10 ltr	22.3 gm/10 ltr
Sodium	81.97 gm/10 ltr	91.96 gm/10 ltr	78.97 gm/10 ltr
Potassium	12.21 gm/10 ltr	11.65 gm/10 ltr	10.59 gm/10 ltr
Calcium	5 gm/10 ltr	12 gm/10 ltr	6 gm/10 ltr
Magnesium	15.79 gm/10 ltr	15.32 gm/10 ltr	14.39 gm/10 ltr
Chloride	229.92 gm/10 ltr	254.92 gm/10 ltr	222.43 gm/10 ltr

Compressive strength was determined by testing 6 inch diameter cylinders in accordance with ASTM C 39, while flexural strength was determined by testing 24 inch long beams with 6 inch square cross-section subjected to three-point bending, in accordance with ASTM C 293. Three (03) samples of each type were cast for testing. A set of samples was maintained in controlled non-aggressive environment, a set was coated with waterproofing membrane layer for exposure in marine environment while a set of sample were exposed to the marine environment without water proofing membrane.

Chloride Penetration (R.M.T)

Chloride induced corrosion in marine reinforced structures is a key mechanism directly affecting the durability of the structure. Thus, it can be used as an effective quantifiable durability index of concrete. Long term tests such as the Salt Ponding Test (AASHTO-T259) and Bulk Diffusion Test (NT Build-443) provides a better estimate of chloride penetration, but they consume a considerable amount of time. On a fast track, Rapid Chloride

Penetration Test (RCPT) (ASTM C-1202 and AASHTO T-277) is commonly utilized. The test is widely criticized for its flaws and the incorrect correlation with the long term Salt Ponding Test. Due to flaws in RCPT, electrically-accelerated chloride penetration testing method, known as Rapid Migration Test (RMT) or Rapid Chloride Migration Test (RCMT), was used in the present study, which quantify the ingression of chloride ions. This test was standardized in 1999 by Nordic Council Of Ministers as NT Build 492 (1999).

Specimen of 2 inches thickness and 4 inches diameter were prepared by slicing the 4 inches by 8 inches cylinder at their mid-height. A water-cooled diamond saw was used for this purpose. After desiccation and treatment, the specimen was fixed in a rubber sleeve with the help of a pair of stainless steel clamps that should ensure the impermeation of both NaCl and NaOH solutions to the either sides as shown in Figure 1. The stainless steel wire meshes were placed into the electrolytic solutions near the both sides of the specimen. The steel mesh inserted in NaCl solution was made cathode by connecting it with the negative terminal of the supply and the mesh in NaOH solution was made anode by connecting it with the positive terminal of the dc power supply. With the frequent monitoring of the current supplied, 60 Volts potential difference was applied across the specimen for 18 hours. After which, the specimen was axially split. Adopting the calorimetric method, the silver nitrate solution (0.1N) was immediately sprayed onto the exposed surface. The chloride ion presence was indicated by white silver precipitation separated by a brownish color of chloride absence. The average depth of the chloride penetration was noted for further calculation of Chloride-ion Migration Coefficient or Non-Steady State Migration Coefficient (D_{nssm}).
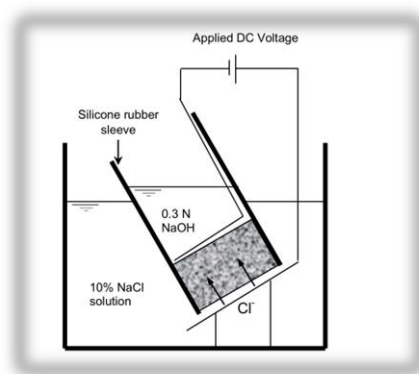

Figure 1 Schematic diagram of Rapid Migration Test Setup

Absorption Capacity Test

Absorptivity of samples cast from all the mix designs was determined in accordance with ASTM C642. Specimens were extracted from 4 inches diameter cylindrical samples by slicing them with the help of a water cooled diamond saw. Two (02) inches thick slices were obtained for the test.

Absorption of oven dried sample after immersion was evaluated as per specifications of ASTM C642. Specimens were oven dried for 24 hours at the temperature 85°C until the mass became constant and weighed. This weight was noted as the dry weight (W1) of the cylinder. After that the specimen was submerged in water at 85°C for 24 hours. Then this weight was noted as the wet weight (W2) of the cylinder. The water absorbed is simply represented in percentage of the sample's dry weight and calculated by Eq. 1 stated below.

$$\% \text{ water absorption } = \frac{(W2 - W1)}{W1} \text{ x } 100 \tag{1}$$

Where,

W1 = Oven dry weight of sample;
W2 = Wet weight of sample after it reaches a constant weight.

Corrosion Rate Test

The corrosion potential was measured by the help of copper/copper sulfate electrode. The setup was prepared in accordance with the specifications of ASTM C-876. The half-cell setup simply consisted of a container porous at the bottom consisted of the copper rod, not in physical contact with the container, filled with a saturated copper sulfate solution. A lead wire connected the copper rod to the high impedance voltmeter and also a connection is made to the exposed steel reinforcement of the specimen. The specimens were subjected to a chlorine environment of 5% NaCl solution. The corrosion potential readings were obtained weekly. The corrosion activity is evaluated in accordance with ASTM C-876. Evaluation criteria suggested by ASTM C876 when Copper/Copper Sulfate electrode is utilized is as follows:

1. If potentials over an area are greater than -0.20 volt, there is a probability greater than 90 percent that no steel corrosion is occurring in the area at the time of measurement.
2. If potentials are in the range of -0.20 to -0.35 volt, corrosion activity of the steel in the area is uncertain
3. If potentials are less than -0.35 volt, there is a probability greater than 90 percent that steel corrosion is occurring in the area at the time of measurement.

RESULTS AND DISCUSSION

Compressive and Flexural Strength

The targeted ultimate compressive strength for the mix designs was 5000 psi. This was achieved by most of the mix designs except mix designs E, F and G as can be seen Figure 2. In general, all the mineral additives added advantage in the strength, except for fly ash, which caused considerable drop in strength whether it is used separately or in combination with silica fume and slag. This may be attributed to quality of fly ash used in the study, and more experimentations and testing may be needed to account for this drawback. Replacement of cement with silica fume in mix designs B and C and blast furnace slag in mix design D resulted in enhanced strength of concrete. Addition of calcium nitrate in mix design I seems to have no effect on strength and strengths achieved by mix designs H and I are almost similar to control mix design. All the samples showed reduction in compressive strength after exposure of 100 days to marine environment with mix designs B, C and D performing better than rest of the mix designs followed by mix designs A, H and I. Mix design G with all the three pozzolans depicted highest strength loss in marine environment.
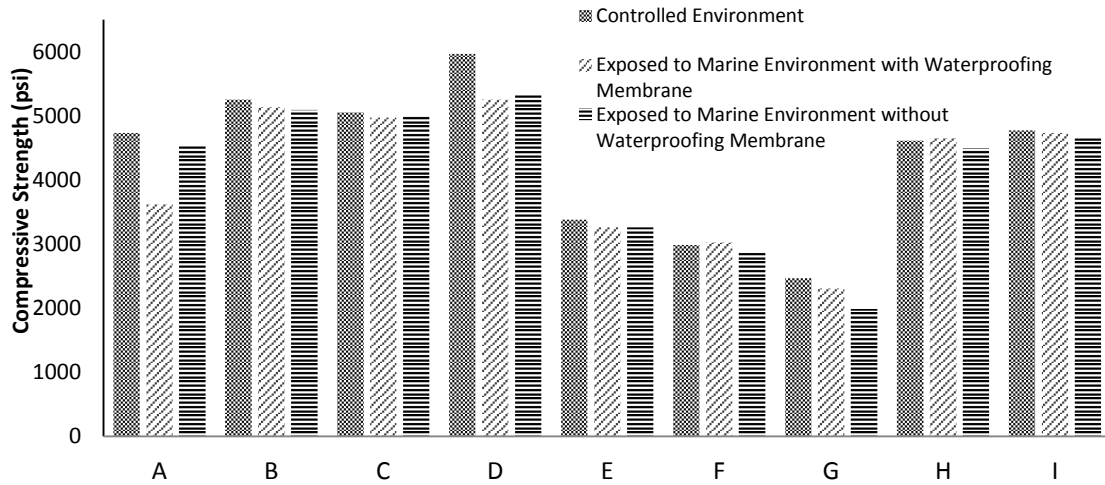

Figure 1 Compressive Strength Results of Different Mix Designs

Results for flexural strength are shown in Figure 3. A trend similar to compressive strength can be seen in Figure 3 that silica fume and slag attributed to the increase in strength while fly ash influenced a considerable loss in flexural strength as well. It is mentionable that the mix containing 30% slag showed highest value of strength and least strength degradation in marine exposure.
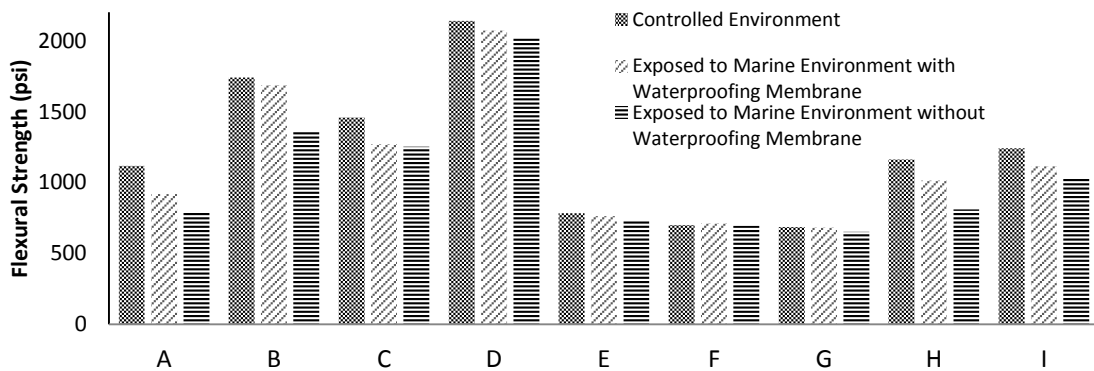

Figure 2 Flexural Strength Results of Different Mix Designs

Chloride Penetration (R.M.T)

The test was performed for Chloride-ion Diffusion Coefficient or Non-Steady State Migration Coefficient according to the specifications provided by NT Build 492. The diffusion coefficient was also calculated accordingly. The average temperature of the anolyte solution was 30°C throughout the tests. 60 volts current was supplied for 18 hours. The depth of chloride penetration indicated by silver nitrate solution was considered as mean chloride depth for each sample.

NT Build 492 offers a simplified formula for the Non-Steady State Migration Coefficient (D_{nssm}) defined in Eq 2.

$$D_{nssm} = \frac{0.0239(273+T)L}{(U-2)t}\left(x_d - 0.0238\sqrt{\frac{(273+T)Lx_d}{(U-2)}}\right)$$ (2)

Where;

D_{nssm}: Non-steady state migration coefficient, $\times10^{-12}$ m^2/s;
U: absolute value of the applied voltage, V
T: average value of the initial and final temperature in the anolyte solution, C
L: thickness of the specimen, mm
x_d: average value of the penetration depths, mm
t: test duration, hour

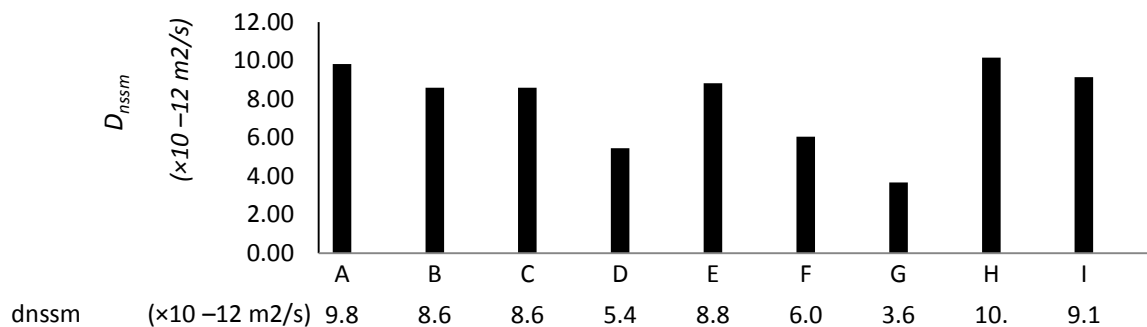| dnssm	($\times10^{-12}$ m2/s)	A	B	C	D	E	F	G	H	I
		9.8	8.6	8.6	5.4	8.8	6.0	3.6	10.	9.1

Figure 3 Chloride Rapid Migration Coefficient Results for Different Mix Designs

Chloride-ion migration test results of different mix designs are compared in Figure 3. The fact that diffusion coefficient of the same mix design did not differ by a wide scale; in a way justify the authenticity and reliability of the results. The slag cement mixes G and D, showed a much lower value of diffusion coefficient, than the mixes containing just OPC denoted as A, H and I. Fly ash and silica fume also contributed to the reduction in the diffusion coefficient's value for B, C, D, E and F mix designs. Additionally, the mix with fly ash and silica fume both in mix design F and incorporating slag along with them in G, performed best against chloride ingression and showed least chloride penetration depth as well. Dosage of calcium nitrate did not seem to offer any mentionable resistance against chloride ions induced with a potential difference.

Absorption Capacity Test

Absorption capacity of mix designs is shown in Figure 5. Percentage of water absorption of dry specimens by weight as per ASTM C-642 of all the mix designs is compared in Figure 5. Mix Design E shows higher water absorption as compared to the other mix designs. Silica fume on the other hand proved to be an effective means of reducing absorptivity, despite its small portion replacement of cement (8% to 10%). Slag, that is effective when it replaces the cement in a large proportion, also showed a considerable decrease in absorptivity. Fly ash used in combination with Silica Fume shows a reasonable lower absorptivity as compared to the Fly Ash used alone. Calcium Nitrate did not seem to affect the absorption property of concrete.

Corrosion Rate Test

The half-cell potential was noted with the half-cell submerged setup, developed in accordance to ASTM C876. The corrosion potential of steel embedded in concrete, exposed to a chloride aggressive environment of 5% NaCl for a period of 35 days, showed the mutually comparable rate of corrosion of steel in reinforced concrete due to salt attack, presented in Figure 6. It is clearly visible that the corrosion potential, that represents the corrosion activity in concrete specimen, decreased adequately with the use of pozzolans. Slag and fly ash reduced the

potential by a wider margin. Silica fume did seem to be very effective for this perimeter. Corrosion inhibitor used, which was calcium nitrate, helped in delaying the corrosion process, a great deal. A significant low corrosion activity was witnessed in the concrete samples containing calcium nitrate. The graph depicts the significance and future scope of corrosion inhibitors.
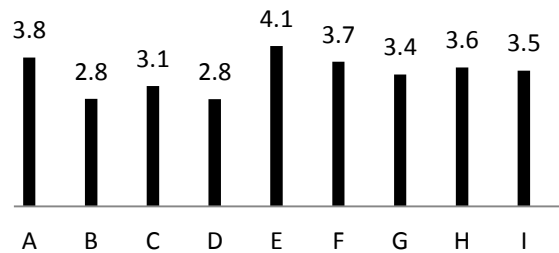
Water Absorption of different Samples (%)

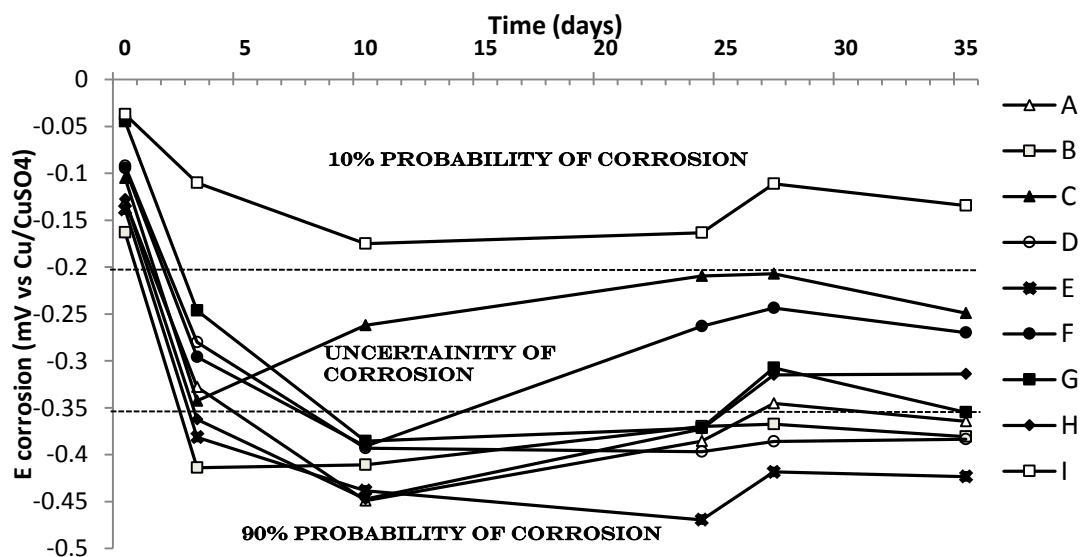Figure 5 Absorptivity for Different Mix Design

Figure 4 Variation of Half-Cell Corrosion Potential of Reinforcement versus Time of exposure to Chloride Attack (5% NaCl)

CONCLUSIONS

Following conclusions can be drawn from the study:

1. Performance of all the mix designs in terms of strength gain were better or comparable to control mix design except for mix designs E, F and G where fly ash was used separately or with silica fume and slag. This may be attributed to slow strength gain of fly ash which also affected the performance of silica fume and slag.
2. Resistance to chloride migration was best observed for the mix design G followed by D and F indicating that slag only or combination of slag, silica fume and fly ash can produce dense, impermeable and durable concrete.
3. Least absorption capacity was observed for the mix designs B and D followed by C and G reflecting better performance of Slag and silica fume as compared to fly ash which again shows highest absorption capacity which is even higher than the control mix design A.

4. Performance of mix design I, with calcium nitrate as corrosion inhibiter, was the best in Half Cell corrosion rate measurements followed by mix designs C, F, H and G. Performance of fly ash was again not comparable to mix designs with slag and silica fume.

5. As per observed durability results, use of silica fume in combination with slag would be a preferred option in marine concrete within their optimal ranges as defined in the literature. Addition of calcium nitrate as corrosion inhibitor is expected to produce better performance in resisting corrosion.
6. Use of pozzolans provides a sustainable means of construction material. Not only natural resources can be conserved by replacement of OPC by these pozzolans within their optimal ranges, but it can be a greater step for cutting down energy usage and CO_2 emission during cement production which is one of the most demanding materials being used around the world.

ACKNOWLEDGMENTS

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