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Studies on the Corrosion Performance for Steel Embedded in Fly Ash Blended Concrete

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Abstract

The present investigation it to study the corrosion performance of fly ash blended cement concrete in chloride-contaminated environments by various electrochemical and non-electrochemical techniques. The chloride binding ability at the optimum replacement level of fly ash was also studied.

Keywords: Blended cements, Flay ash, Corrosion performance

Introduction

Mineral admixtures are finely divided siliceous materials, which are added to concrete in relatively large amounts, generally in the range of 20 to 100% by weight of Portland cement.

Power generation units using coal as fuel and metallurgical furnaces producing cast iron, silicon metal and ferrosilicon alloys are the major source of by products namely fly ash (FA), blast furnace slag (BFC) and silica fume (SF) respectively; which are being produced at the rate of millions of tons every year in many industrial countries. Dumping away these by products represents a waste of the material and causes serious environmental pollution problems. Industrial countries such as the United States, Russia, France, Germany, Japan and the United Kingdom are among the largest producers of fly ash, volatilized silica and granulated blast furnace slag. In addition to these materials, china and India have the potential for making large amounts for Rice Husk Ash (RHA).

Properties and Applications

Fly ashes are results of coal combustion in power plants. In the United States fly ash is classified by chemical composition. ASTM classifies fly ashes into two categories namely class-C and class-F. The differences between these two categories are as follows:

Class – C	Class - F
More than 10% calcium content	Less than 10% calcium content
Produced from sub bituminous coal	Produced from bituminous coat
Sum of the three components namely SiO_2, Al_2O_3 and Fe_2O_3 greater than 50%	Sum of the three ingredients namely SiO_2, Al_2O_3 and Fe_2O_3 is 70% or greater
Glassy material is often more reactive than the glass in Class -F	Glassy material is reactive
Principal active ingredient is calcium alumino silicate glass	Active ingredient is siliceous or alumino silicate glass
Contains additional reactive components such as free lime, anhydrate, C_3A, C_3S, etc.	---

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Typically 15% to 30% replacement of cements by fly ash is utilized for pavements and bridges. The performance of a blend of fly ash and Portland cement depends on:

- The performance of the Portland cement
- The ratio of Portland cement to fly ash
- Interaction specific to the fly ash

The effects of fly ash on the properties of fresh and hardened concrete are:

- Improvement in the fresh concrete workability
- Reduction in the rate of hardening and strength gain
- Reduction in heat generated in concrete
- Improvement in the concrete sulphat resistance
- Reduction in concrete permeability

The improved performance of concretewith fly ash makes them suitable for:

- Effective cost savings
- Massive placements
- Improving resistance to sulphate attack
- Improving the durability of reinforced concrete in high chloride environments
- Preventing alkali – silica reaction in concrete

Corrosion Performance of Fly Ash Blended Cements

Ashes from combustion of coal are the major industrial by-products that are suitable for use as mineral admixtures in Portland cement concretes. The utilization of fly in the construction industry is growing fast not only as blended cements but also to minimize the pollution of the environment. Earlier work reported that fly ashes accelerate reinforcement corrosion due to the presence of unburnt carbon and sulphur. Since the usage of fly ashes in the presence of unburnt carbon and sulphur. Since the usage of fly ashes in reinforcements are still questionable. In order to produce fly ashes in reinforcements are still questionable. In order to produce fly ash with stable reinforcements are still questionable. In order to produce fly ash with stable properties and adequate quality, many power plants have implemented its own sophisticated quality control measures. The property improvement of fly ash blended cements were extensively studied and reported that the physical and mechanical properties wee matched to that of ordinary Portland cement (OPC).

Although all the studies are focused on the improvement of physical and mechanical properties of concrete. So far a systematic and detailed studies on the corrosion performance of fly ash cements are very scarce. Therefore, a realistic assessment of the corrosion-resistance properties of fly ash cement is essentially needed in addition to the important physical and mechanical properties of concrete. Macro cell corrosion studies are reported to be a very aggressive technique to assess the corrosion of steel in concrete.

Recently the effect of fly ash on the corrosion of reinforcing thick and impermeable, it will normally provide adequate protection against corrosion. The protective effect of the concrete cover is of both a physical and a chemical nature and functions in three ways.

1. It provides an alkaline in the immediate vicinity of the steel surface.
2. It offers a physical and chemical barrier to the ingress of moisture, oxygen, carbon-di-oxide, chlorides and other aggressive agents.
3. It provides an electrically resistive medium around the steel members.

Under alkaline conditions (pH higher than ~ 11.5), a protective oxide film will form on a steel surface, rendering it passive to further corrosion.

When concrete carbonates and the depth of carbonation reaches the steel concrete boundary, passivation may be reduced and corrosion may occur if sufficient oxygen and moisture reach the metal surface. Chlorides or other ions may also undermine the protective effect of passivation and encourage corrosion.

RILEM technical committee (5) on corrosion of steel in concrete made the following statements, which give perspective to this issue:

- The efficiency of the (concrete) cover in preventing corrosion is dependent on many factors, which collectively one referred to as in ‘quality’. In this context the ‘quality’ implies impermeability and a high reserve of alkalinity, which satisfies both the physical needs, and chemical requirements of the concrete cover. If the concrete is permeable to atmospheric gases or lean in cement, corrosion of the reinforcement can be anticipated and good protection should be attempted by the use of dense aggregate and a well compacted mix with a reasonably low w/c ratio.
- If chloride is expected, it is now usually agreed that carbonation of concrete cover is the essential condition for corrosion of reinforcement.

However the carbonation of fly ash concrete is not a matter of concern, provided attention is paid to obtaining adequate impermeability in the concrete mass.

The sulphur containing components of fly ash could corrode the reinforcing steel in fly ash concrete. The most of the sulphur in fly ash in present as sulphate and therefore would have an effect similar to the sulphate components in

Portland cement. Further, the corrosion of steel is greatly affected by pH at the high pH prevailing in concrete; corrosion rates would be expected to be slow.

- Sulphur compounds in fly ash are usually so limited by specifications that they are not materially different in the concrete, whether fly ash is used or not. Moreover, the alkaline condition in the concrete is unfavorable to a sulphate attack on steel.
- Carbon in fly ash would appear by theoretical considerations to be much more significant in concrete than is sulphur. The actual effect should be investigated. However, if it is kept under 3% in the fly ash, its percentage in the concrete becomes so small that if it is well dispersed, its effect on the electrical conductivity of the concrete, and therefore upon the corrosion of steel, should be quite minor (6).

These conclusions seem to be generally acceptable in the light of reported research that has shown that fly ash concrete does not decrease the corrosion protection of steel reinforcement compared with normal concrete.

RILEM technical committee on corrosion of steel in concrete, fly ash may influence both permeability and the alkalinity of the system.

The properly proportioned fly ash concrete subjected to adequate curing should in general be less permeable at later ages than the corresponding plain concrete. The danger of permeability lies in the premature exposure of fly ash concrete to agents, as a result of either inadequate proportioning in complete curing or poor fly ash quality.

Experimental Procedure

Materials used

The following materials were used for the present study.

Ordinary Portland Cement : Conforming to IS 456 – 2000

(i) Graded fine aggregates : Local clean river sand (fineness (ii) modulus of medium sand equal to 2.6) conforming to grading zone III of IS-383 – 1970 was used as fine aggregates.

(iii) Graded coarse aggregates : Locally available well graded aggregates of normal size greater than 4.75 mm and less than 10 mm having fineness modulus of 2.72 was used as coarse aggregates.

The composition of OPC used in this study was reported in Table 1. The mix proportions used in the study were reported in Table 2.

Table 1. Compositions of OPC used in this study

Constituents	OPC (%)
SiO_2	21.04
Fe_2O_3	3.35
Al_2O_3	9.93
CaO	60.68
MgO	1.30
Na_2O	0.20
K_2O	0.90
Loss on Ignition	2.60

Table 2. The mix design used for casting was as follows: 1:3.3:6.9, W/C = 50

Constituents	Quantity used (kg/m^3)
Ordinary Portland cement	215
Coarse aggregates	710
Fine aggregates	1485
Fly ash	10%, 20%, 30%, 40% and 50% replacement level

Techniques used

pH measurements

The pH values measured for plain cement extracts and cement extracts containing various fly ash replacement levels namely 10%, 20%, 30%, 40% and 50%. The p^H was measured using a standard calibrated p^H meter.

Anodic Polarization

Mild steel rods were embedded cylindrical mortal (1:3) specimens of size 58mm dia and 60mm height using w/c ratio 0.45. The mortar specimens only with ordinary Portland cement (control) and OPC replaced by fly ash at 10%, 20%, 30%, 40% and 50% replacement levels were subjected to anodic polarization studies using a three-electrode system. The embedded steel act as a working electrode, cylindrical stainless steel act as counter electrode with respect to saturated calomel electrodes (SCE) as reference electrode. The current flowing at +300 mV and +600 mV vs. SCE from the OCP values recorded for all the specimens at ambient temperature of 32± 1°C.

Weight loss measurements

Concrete cube of size 10 x 10 x 10 cm were cast from OPC and OPC containing various fly ash at 10, 20, 30, 40 and 50%

replacement levels. Mild steel rod of 1.2 cm diameter and 6 cm long was embedded centrally. Initially the mild steel rebars were cleaned in the following acid solution

HCl: 100%, $SnCl_2$: 35 gms, Sb_2O_3: 25 gms
degreased with acetone and washed with double distilled water and dried. Water and dried. The initial weight of the rebar was taken before casting using metler balance for gravimetric weight loss measurements.

Concrete cube specimens were prepared using 1:3:3:6.9 mix with a w/c ratio of 0.50. The specimens wee mechanically vibrated. After 24 hours of curing, the specimens were demoulded and cured for 28 days in distilled water in order to avoid any contamination. After the curing period was over, all the specimens were completely immersed in 3% NaCl solution. The specimens were maintained in the same condition for 15 days and then subjected to drying for another 15 days. One alternate wetting and drying cycle consists of 15 days immersion with 3% NaCl solution and 15 days drying in open air at room temperature. In order to induce the accelerated corrosion 3% NaCl solution was used.

All the concrete specimens were subjected to 3 complete cycles of test period. Tests were conducted on a minimum of six replicate specimens and the average values were reported.

At the end of the exposure period the concrete specimens were split open and visual observation data on corrosion were made and expressed in terms of percentage of area rusted. The corrosion rate of mild steel anodes measured by gravimetric weight loss method and expressed in millimeter per year (mmpy). The corrosion rate is calculated using the following equation:

$$\text{Corrosion rate : } 87.6 \times w/(DAT)$$

Where
W= weight loss in gm D= Density material used
A=Area of the specimen (Cm^2) T=Time duration in hours

Chemical analysis for alkalinity and free chloride contents

The core samples collected near he anodes 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 analyzed for free chloride contents as per the standard procedures. 20 cc of filtered solution was taken and the free chloride content 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 basis of weight of sample taken for analysis.

Results and discussion

pH measurements

The pH values measured for plain cement extracts and various fly ash replacement levels are given in Table 3. From this Table, it was found that pH of the plain cement extract was 13.8. The pH values measured for various fly ash replacement levels were in the range from 13.07 to 10.10. There was no After that, there was a slight reduction in pH values at 30% fly ash replacement level. Above 40% fly ash replacement level, pH value was drastically reduced to 10.10.

Table 3. Effect of different factors on fly ash replacement Levels

S.No	System	pH	Current at + 300 mV vs. SCE (mA)	Current at +600 mV vs. SCE (mA)	Corrosion rate (mmpy)	Percentage of area rusted (%)	Free Chloride Contents (ppm)
1	OPC	13.80	0.43	1.04	0.0024	No rust	3240
2	OPC + 10% FA	13.07	0.24	0.55	0.0025	No rust	4000
3	OPC + 20% FA	12.86	0.37	0.75	0.0025	No rust	4720
4	OPC + 30% FA	12.80	0.44	1.09	0.0049	5	4800
5	OPC + 40% FA	11.28	0.49	1.18	0.0055	5	5000
6	OPC + 50% FA	10.10	1.26	2.50	0.0074	12	5100

Anodic polarization technique

The results of anodic polarization data for steel embedded in 1:3 mortar specimens in 3% NaCl solution are given in Table 3. It was inferred from this Table that, in the case of OPC the anodic current measured was found to be 0.43 and 1.04 mV respectively at +300 mV and +600 mV vs. SECE. On the other hand, for fly ash systems, upto 20% replacement level the anodic current measured was lesser than OPC indicating the superior performance of the system with better corrosion resistance properties. Above 30% level, the passivity was destroyed, as a result large anodic currents in the range 0.44 to 1.26 mA at +300 mV vs. SCE amd 1.09 to 2.5 mA at +600 mV vs. SCE were measured. These results confirmed that 20% is the optimum level of replacement with better corrosion resistance properties.

Weight loss measurements

The corrosion rates calculated in mmpy for mild steel anodes embedded in various systems studied are reported in Table 3. From the table it is observed that, the corrosion rate for OPC system was found to be 0.0024 mmpy. Systems showing corrosion rate for less than 0.0024 mmpy may be considered as improving the corrosion resistance of steel in concrete. In the case of fly ash system upto 20% replacement level comparable results were obtained with OPC. But beyond 30%, inferior properties were observed. These results were concordant with the results obtained form other techniques.

Chemical analysis for free chloride contents

At the end of the test period, steel anode embedded in OPC and various fly ash system were subjected to qualitative estimations. The data calculated were reported in Table 3. From this Table, it revealed that in 100% OPC system no rust was observed at any of the surface of steel rebars. For fly ash system, upto 20% negligible red rust (less than 1%) was observed. Beyond 30% more than 5% red rust was observed.

The free chloride contents estimated were reported in Table 3. 6. Interestingly upto 20% replacement level, the penetration of chloride ion was found to be in the range 3000 to 4000 ppm. After that, the fly ash replacement level increases the penetration of chloride 9 on is also increased. The results were concordant with results obtained from anodic polarization and weight loss measurements.

Conclusions

The following main conclusions are drawn from the present investigations. Fly ash up to 20% does not affect the pH of the concrete. Comparable results on corrosion rates with OPC was obtained upto 20% fly ash replacement level from weight loss measurements. Anodic polarization data showed that, fly ash upto 20%, lesser anodic currents were observed when compared to OPC. Fly ash is not very effective beyond 30% for chloride binding capacity.

The overall conclusion is that fly ash has both positive and negative effects on the different factors governing the steel reinforcement corrosion. However, the positive factors are dominating by far over the negative factors.

Fly ash has a positive effect on the risk of corrosion and rate of corrosion, provided that normal good workmanship is carried out and that fly ash is not used in very low concrete qualities to reduce cement.

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