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Accelerated short-term techniques to evaluate the corrosion performance of steel in fly ash blended concrete

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Abstract

In this investigation, the influence of mineral admixture, namely fly ash (FA) on the corrosion performance of steel in mortar and concrete was studied and evaluated by some accelerated short-term techniques in sodium chloride solutions. Electrochemical techniques such as open circuit potential measurements and anodic polarization studies were carried out. An impressed voltage technique and macrocell corrosion study was also carried out to understand the optimum level of replacement of FA with better corrosion resistance properties. Results are compared with conventional gravimetric weight loss measurements. The alkalinity and the free chloride contents are estimated. The FA replacement levels namely 10%, 20%, 30% and 40% with respect to ordinary Portland cement (OPC) was chosen for the present study and the results are compared with OPC specimens without FA.

Keywords: Mineral admixture; Fly ash; Reinforcement corrosion; Accelerated techniques

1. Introduction

The development and use of blended cements is growing rapidly in the construction industry mainly due to considerations of cost saving, energy saving, environmental protection and conservation of resources. Fly ash (FA), a siliceous material obtained from different thermal power stations is now being considered as a cementitious ingredient for concrete. The use of FA in mortar and concrete, as a partial replacement of Portland cement, appears to constitute a very satisfactory outlet for this industrial by-product. The use of FA to replace a portion of the cement has resulted in significant savings in the cost of production of concrete. Mineral admixtures are finely divided siliceous materials, which are added to concrete in relatively large amounts [1,2]. 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 FA, blast furnace slag (BFS) and silica fume (SF), [3] respectively. 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 FA, volatilized silica and granulated BFS. ASTM classifies fly ashes into two categories, namely class-C and class-F according to their calcium contents. Class-C FA contains more than 10% calcium and class-F contains less than 10% calcium contents. Paya et al. [4–6] conducted studies on mortars containing 15–60% FA as a replacement of Portland cement with different particle size of FA on mechanical properties of concrete. Naik et al. [7] studied the influence of FA on chloride permeability of concrete. Thomas [8] reported that threshold chloride level decreased with increasing FA content. FA concrete was found to have increased resistance to chloride ion

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penetration and increased electrical resistance. Studies also reported that FA can accelerate the corrosion of steel in concrete [9–12]. In order to produce fly ashes with stable properties and adequate quality, many power plants have implemented their own sophisticated quality control measures. The property improvement of FA blended cements was extensively studied and it was reported that the physical and mechanical properties matched that of ordinary Portland cement (OPC) [13–16]. Corrosion-resistance properties of FA blended cement concrete are also important to consider along with the physical and mechanical properties of concrete for a durable structures. The objective of the present investigation is a systematic study on the influence of FA on the corrosion resistance of steel in concrete by various non-electrochemical and electrochemical accelerated short-term techniques in 3% NaCl solution.

2. Methods and materials

2.1. Materials used

OPC conforming to KS: L 5201:1989 was used throughout this investigation. ASTM class F-type FA was used. The composition of OPC and FA used was as follows:

Constituents	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	LOI	Others
Cement	63.8	22.8	5.1	3.7	1.7	2.0	0.8	0.1
Fly ash	3.26	51.63	30.40	5.20	2.80	0.40	5.30	1.00

Natural fine aggregates of normal gravity and maximum size of the coarse aggregate was 10 mm conforming to KS F 2526: 2002 was used.

The mix proportions used for casting is as follows:

1:1.71:3.1
OPC: 415 kg/m^3
Fine aggregates: 710 kg/m^3
Coarse aggregates: 1287 kg/m^3
Water–cement ratio: 0.50
FA: 10%, 20%, 30% and 40% replacement level of OPC by weight of cement.

2.2. Techniques adopted

2.2.1. Weight loss method

Cylindrical mortar specimen of size 55 mm diameter and 60 mm height were cast using OPC and OPC containing various FA replacement levels. A cold twisted rod of 12 mm diameter and 45 mm long was embedded centrally. Initially the rebar samples were cleaned in hydrochloric acid, degreased with acetone and washed with double distilled water and dried. The initial weight of the rebar sample was taken before casting for gravimetric weight loss measurements.

Mortar specimens were prepared using 1:3 mix with a w/c ratio of 0.45. The specimens were mechanically vibrated. After 24 h, 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 was maintained in the same condition for 15 days and then subjected to drying in open air at room temperature for another 15 days. Each wetting and drying cycle thus consisted of 30 days. All the mortar specimens were subjected to 6 complete cycles (180 days) of test period. Tests were conducted on a minimum of 6 replicate specimens and the average values are reported.

2.2.2. Open circuit potential (OCP) measurements

The rebar specimens were cut to the required size. They were polished and degreased and embedded in mortar specimens. Electrical connections were taken by screwing a 3 mm mild steel rod on the rebar. The OCP of the different systems was periodically monitored using a voltmeter with a high input impedance of 10 MΩ. Saturated calomel electrode (SCE) was used as a reference electrode. The positive terminal of the voltmeter was connected to the working electrode i.e., mild steel rods. The common terminal was connected to the reference electrode. The corresponding potentials were recorded. OCP for all the specimens were monitored over an exposure period of 180 days. In this study, specimens in triplicate were used for each system and the average of these values are reported and interpreted based on ASTM C-876-1994 [17] and the half-cell measurement set up is shown in Fig. 1.

2.2.3. Anodic polarization technique

Rebar specimens were embedded in cylindrical mortar specimens of size 58 mm diameter and 60 mm height using a w/c ratio of 0.45. The mortar specimens only with OPC (control) and OPC replaced by FA at 10%, 20%, 30% and 40% replacement levels were subjected to anodic polarization studies using a 3-electrode system which consists of embedded steel in mortar as anode, stainless steel ring electrode as cathode and SCE as reference electrode. Anodic polarization studies have been carried out in 3% NaCl solution using a Gamry Instruments, Inc., CMS 100 Framework software analyser. The currents flowing at anodic potentials, namely +300 and +600 mV were recorded for all the specimens at a fixed duration of 12 h. A duplicate experiment was made for these measurements at an ambient temperature of 25 ± 1 °C.

2.2.4. Impressed voltage technique

The impressed voltage technique is an accelerated corrosion testing technique which indirectly gives information about the permeation characteristics of the concrete. Cylindrical concrete specimens were made using 1:1.71:3.1 mix proportion with a w/c ratio of 0.5. Specimens with OPC and various FA replacement levels were made with embedded rod as an anode and cylindrical stainless steel

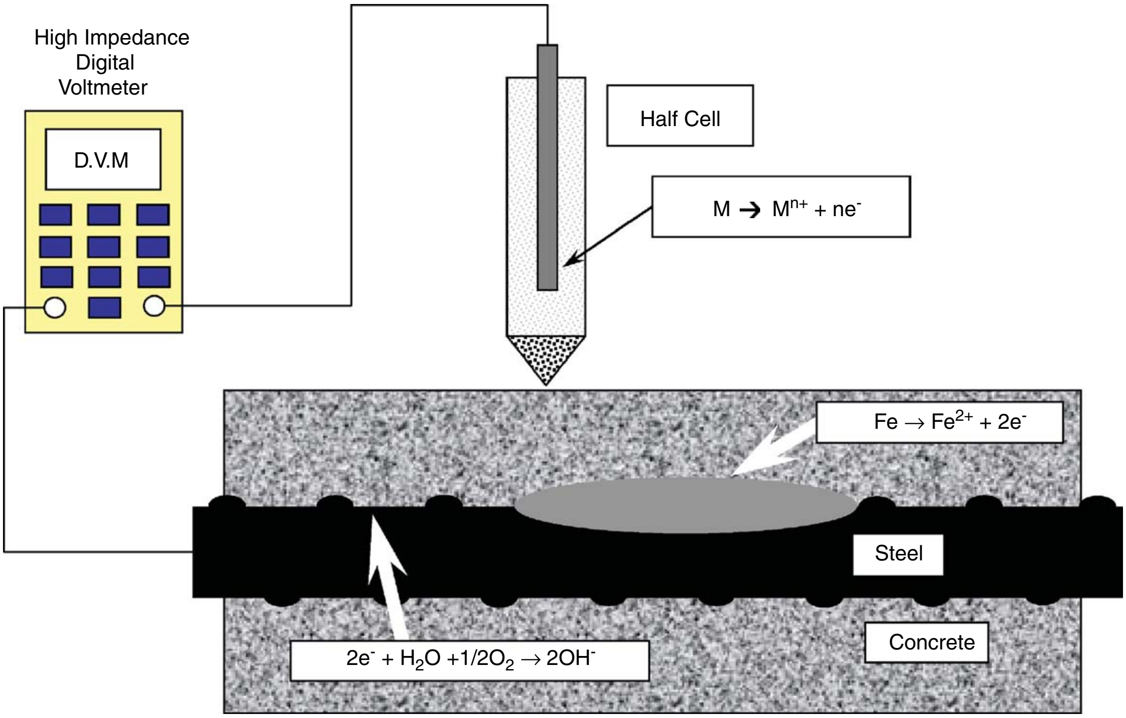

Fig. 1. Half-cell potential measurement.

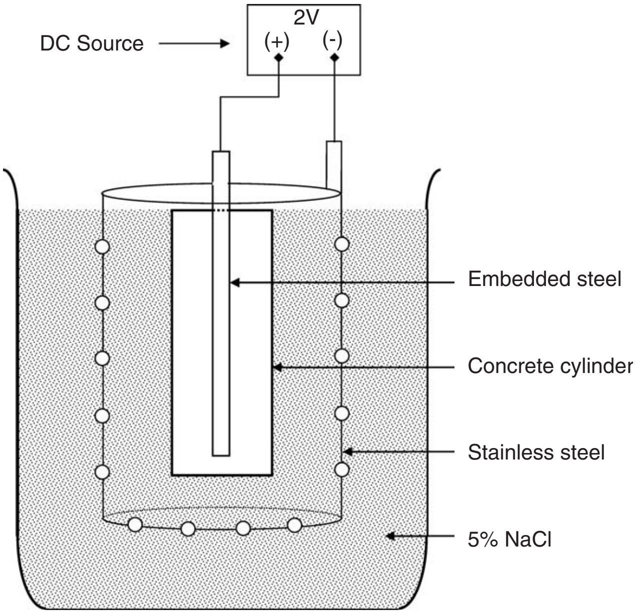

Fig. 2. Set-up for impressed voltage test.

electrode acts as a cathode and the electrolyte is 5% sodium chloride solution. A constant voltage of 2 V is applied from the external DC source between anode and cathode. The time to initiate a first crack on the concrete was observed and the corresponding anodic current was noted at an ambient temperature of 25 ± 1 °C. The schematic of the test arrangement is shown in Fig. 2.

2.2.5. Macrocell corrosion studies

A rectangular concrete specimen of size 279 × 152 × 114 mm was designed as per ASTM G 109-92 for macrocell corrosion studies. A cylindrical rod of size 12 mm diameter, 300 mm length was used as both anode and cathodes in the same concrete. Initially the rebars were cleaned in hydrochloric acid, degreased with acetone and washed with double-distilled water. The top mat of the rebar acts as anode and the bottom mat of rebars acts as cathode. The anode to cathode ratio was maintained as 1:2 in order to induce accelerated corrosion. The configuration of macrocell specimen used is given in Fig. 3. In both the anode and cathode, exposed length was 190 mm. The remaining length was used for taking electrical connections and properly insulating from the aggressive environment.

Concrete specimens were prepared using 1 : 3 : 4.5 mix with a w/c ratio of 0.6. The specimens were mechanically vibrated. After 24 h of setting, the specimens were demolded and cured in double-distilled water for 28 days. Then, all the concrete specimens were subjected to 3% NaCl wetting cycle immediately after curing. One alternate wetting and drying cycle consists of 15 days wetting with 3% NaCl solution and 15 days drying. Measurements were carried out during wetting cycles as macrocell current showed maximum magnitude due to the low resistivity of concrete. All the concrete specimens were subjected to 6 complete cycles of test period.

2.2.6. pH measurements

The pH of the extracts derived from the OPC and FA admixed systems was measured. Concrete samples

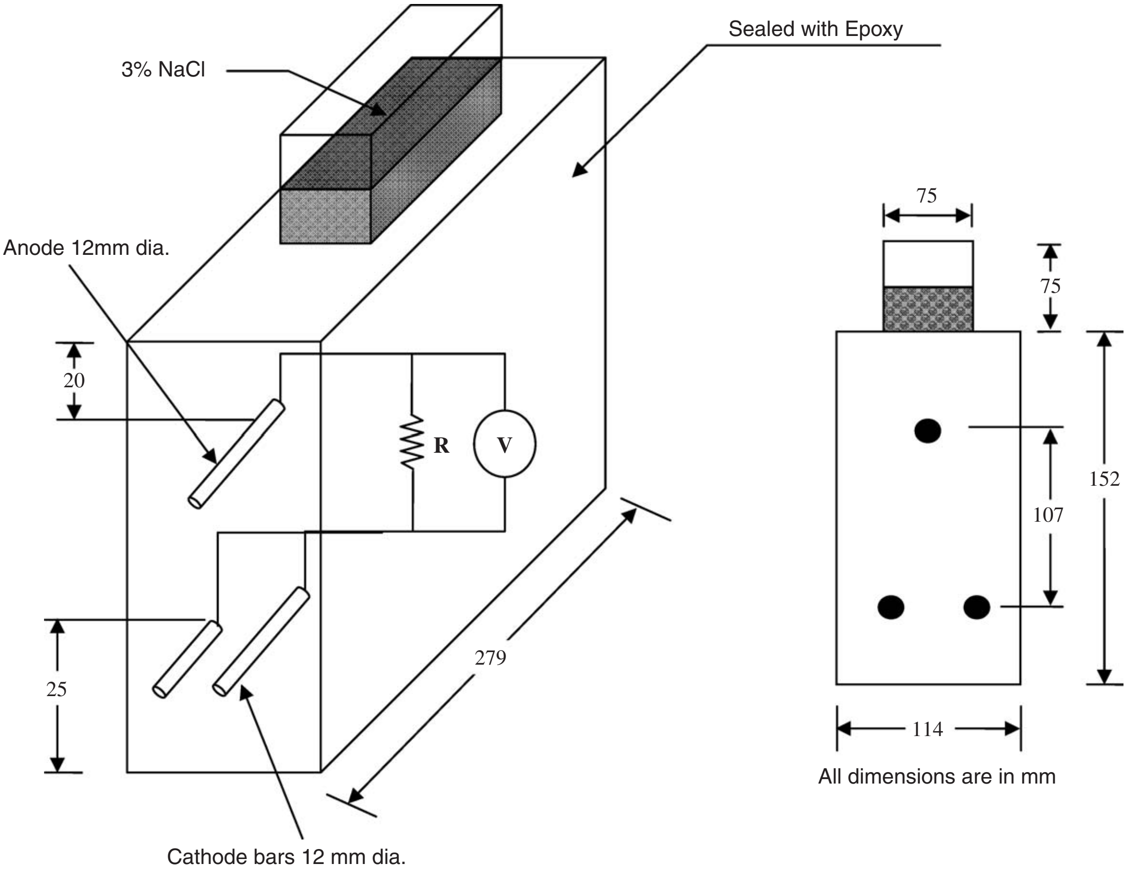

Fig. 3. Schematic view of the macrocell specimen.

collected from the various systems was powdered and then passed through the sieve of 80 μm. Then 5 g powder was added to 50 ml of distilled water. After 2 h, the solution was filtrated. The pH of the filtrate was measured using a portable Istek Inc. (Model 76 P) pH meter. The pH meter was calibrated using pH solutions more than 12. Minimum of 3 readings was noted for each system and the average pH value was reported.

2.2.7. Estimation of free chloride contents

The extract prepared from the powdered sample was then analysed for free chloride contents as per the procedures reported elsewhere [18]. Twenty cc of filtered solution was taken and the free chloride content was estimated by standard silver nitrate solution using potassium chromate as an indicator. Titrations are repeated until the concordant values were obtained. The amount of free chloride content calculated was expressed in terms of parts per million (ppm) on the basis of weight of sample taken for analysis.

3. Results and discussion

3.1. pH measurements

Table 1
Initial and final pH values for various systems

S.no.	System	pH	
		Initial	Final
1	OPC	13.00	12.90
2	OPC + 10% FA	13.00	12.90
3	OPC + 20% FA	12.90	12.80
4	OPC + 30% FA	12.80	12.50
5	OPC + 40% FA	12.00	11.50
6	OPC + 50%FA	11.10	10.00

The average pH values measured for plain cement extract and various FA replacement levels initially and at the end of exposure period are given in Table 1. From this table, it was found that the pH of the plain cement extract was 13.0. The initial pH values measured for various FA replacement levels were in the range from 13.00 to 11.10. Interestingly not much variation was observed between initial and final pH values upto 30% replacement levels. On the other hand, there is a drastic decrease in the alkalinity was observed when the replacement level is increased beyond 30%. This is to be observed both at initial and final exposure periods. This reduction in pH values can be attributed to the fact that mineral admixtures absorbed some CH through the pozzolana reaction, and in addition the relative content of cement was also reduced when mineral admixtures were employed. Since, the relative

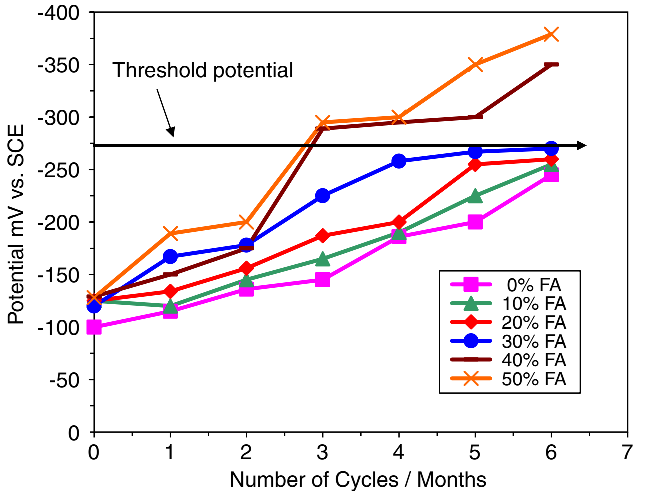

Fig. 4. Potential vs. number of cycles of exposure for various FA systems in 3% NaCl solutions.

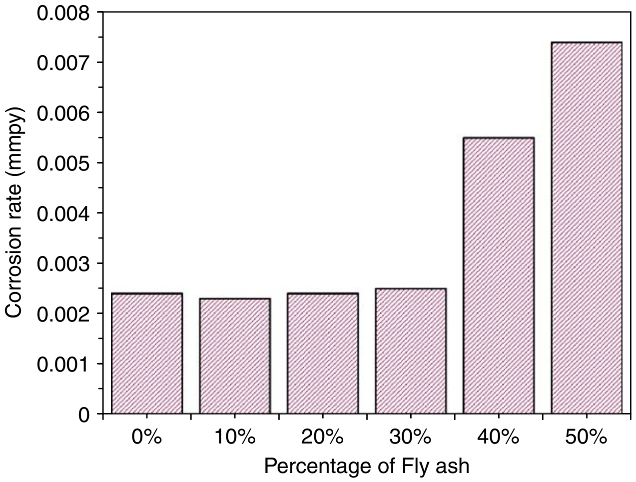

Fig. 5. Corrosion rate of mild steel embedded in FA admixed mortars in 3% NaCl solutions.

amount of cement was reduced by the addition of FA, therefore the amount of CH produced by the cement hydration was decreased.

3.2. Potential-time behaviour studies

The potential-time (in months) behaviour of steel in OPC and with various FA replacement levels are shown in Fig. 4. From this figure it was inferred that initially up to 3 cycles of exposure, almost all the systems showed potential values ranging from 0 to −275 mV vs. SCE which reflected the passive condition of embedded steel anode. After that, higher replacement levels, namely 40% and 50%, showed potential values ranging from −275 to −350 mV vs. SCE indicating the 90% probability of depassivation of steel embedded in concrete. On the other hand, rebars embedded in 10% and 20% FA replacement levels do not cross the threshold limit even after 6 cycles of exposure period and thereby maintaining of the perfect passive conditions of rebars. From the potential-time behaviour studies, it can be observed that upto 30% FA replacement level, there is no cautious to steel rebars under aggressive alternate wetting and drying conditions in 3% NaCl solutions.

3.3. Weight loss measurements

The corrosion rate calculated in mmpy for rebars embedded in OPC and with various FA replacement levels are shown as a bar chart in Fig. 5. From this figure it was observed that the corrosion rate for OPC system was found to be 0.0024 mmpy. Systems showing a corrosion rate equal to or less than 0.0024 mmpy may be considered as improving the corrosion resistance of steel in concrete. In the case of FA system, the corrosion rate is found to be less at 10% replacement level. Comparable corrosion rate with OPC was observed upto 30% replacement level. For example, at 20% and 30% the corrosion rate was found to be 0.0024 and 0.0025 mmpy, respectively, which represent the tolerable limit of replacement with better corrosion resistant properties. After that, the corrosion rate is drastically increased while increasing the FA levels indicating the most inferior corrosion resistant properties. The improved corrosion resistance of concrete upto 30% replacement level is due to the pore filling effect of FA during cement hydration reaction and making the concrete impermeable and thereby maintaining the perfect alkalinity near the steel anode.

Even though, there may be a decrease in the pH of the solution, it is expected that the increased density of FA cement inhibits the ingress of oxygen and moisture that are essential for the cathodic reaction, as a result the rate of corrosion is decreased due to the incorporation of FA.

3.4. Anodic polarization technique

Anodic polarization test can rapidly give the judgment about the system whether the steel is in passive condition or in active condition. The relation between anodic current vs. various FA replacement levels is shown in Fig. 6. It was inferred from this figure that in the case of 0% FA added system, the anodic current measured was found to be 0.40 and 1.00 mA, respectively, at +300 and +600 mV vs. SCE. But for FA systems, upto the 30% replacement level the anodic current measured was lesser than OPC indicating the superior performance of the system with better corrosion resistance properties. Above the 30% level, the passivity was destroyed; as a result large anodic currents in the range 0.44–1.26 mA at +300 mV vs. SCE and 1.09–2.5 mA at +600 mV vs. SCE was measured. Anodic polarization data confirmed that the integrity of passivity was maintained by the incorporation of FA upto the 30% replacement level. This is supplementary data for the optimum level of replacement with better corrosion resistance properties.

3.5. Impressed voltage technique

The impressed voltage data for OPC and various FA admixed concrete are reported in Table 2. It is found from Table 2 that the time to cracking and the maximum anodic current for plain OPC system was found to be 170 h and 85 mA, respectively. It is a hypothesis that admixed systems having equal to less than OPC data are considered to improve the permeability characteristics of concrete. Interestingly, FA systems, namely 10%, 20% and 30% showed impressed voltage data values when compared to OPC indicating their better corrosion resistance properties. On the other hand, beyond 30%, there is earlier cracking of concrete and the larger anodic current was measured indicating the inferior properties at this level.

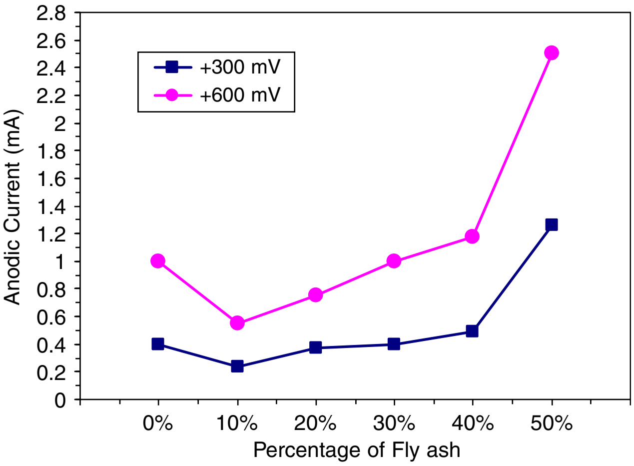

Fig. 6. Relation between fly ash replacement levels vs. anodic current.

Table 2
Impressed voltage data for OPC and fly ash admixed systems

System	Time to cracking (h)	Maximum anodic current (mA)
OPC	170	85
OPC + 10% FA	176	80
OPC + 20% FA	170	82
OPC + 30% FA	172	85
OPC + 40% FA	110	134

The improvement in the permeability characteristics of FA admixed system is due to the main hydration reaction as follows:

In OPC and FA admixed system, the primary hydration reaction is

$$2\,(3CaO \cdot SiO_2) + 6H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2. \quad (1)$$

But in FA system, the additional secondary hydration reaction is

$$3Ca(OH)_2 + 2SiO_2 + H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O. \quad (2)$$

In FA concrete, the $Ca(OH)_2$ content reduction is due to the secondary hydration reaction. During hydration, in FA concretes lime is consumed but in OPC concrete lime is produced. This is the main advantage of using FA cements to decrease the permeability of the concrete and thereby increasing the corrosion resistance properties.

The main hydrated phases produced during the pozzolanic reaction at ambient temperature are CSH, C_2ASH and C_4AH. Different factors can influence the reaction kinetics and the amounts of the phases produced, but the hydration time is the most important factor. Variation of calcium hydrates content with hydration time is important factor for pore filling characteristics. In FA concretes in presence of water, FA can react with $Ca(OH)_2$ to form secondary calcium hydrates (both aluminate hydrate and silicate hydrate). This secondary calcium hydrate fills the large capillary voids and this process of transformation is referred to as the so-called pore size refinement.

3.6. Macrocell corrosion studies

The electrochemical characteristics of half-cell potentials measured periodically against a SCE with time are given in Table 3. From this table, it was observed that initially up to 3 cycles of exposure for all the systems showed potential values ranging from 0 to −300 mV vs. SCE which reflected

Table 3
Macrocell corrosion parameters for OPC and fly ash blended system

System	Potential (mV vs. SCE)						Macrocell current (μA)					
	Cycle number						Cycle number					
	1	2	3	4	5	6	1	2	3	4	5	6
OPC	−100	−200	−225	−270	−280	−310	0	0	1	1	2	5
OPC + 10% FA	−200	−210	−250	−275	−280	−290	0	0	0	1	1	2
OPC + 20% FA	−205	−210	−260	−285	−290	−300	0	0	1	2	4	4
OPC + 30% FA	−210	−270	−275	−290	−300	−310	0	0	2	2	4	6
OPC + 40% FA	−225	−250	−280	−300	−350	−420	0	1	4	10	15	18

Table 4
Free chloride contents for OPC and fly ash blended system

S.no.	System	Free chloride contents (ppm)
1	OPC	3240
2	OPC + 10% FA	3110
3	OPC + 20% FA	3200
4	OPC + 30% FA	3300
5	OPC + 40% FA	6000
6	OPC + 50%FA	7100

the passive condition of embedded steel anode. Interestingly, FA system upto 30% replacement levels preserve the passive behaviour even at the end of 6 cycles of exposure. At 40%, specimens showed a very high negative potential of more than −400 mV vs. SCE indicated the severe corrosion of the anode. The macrocell current or galvanic current measured periodically with time are also given in Table 3. From this table, it was observed that even after 2 cycles of exposure no significant current flowed between anode and cathodes in all the systems. Plain system showed a maximum macrocell current of 5 μA whereas FA systems, namely 10% and 20% showed lesser macrocell current than control at the end of exposure. A 30% FA admixed system showed a macrocell current of 6 μA. On the other hand, at 40% level, a 3.6 times increase in the macrocell current was observed. These results agreed well with other techniques adopted in this investigation.

At higher replacement level, FA diluted the concentration of Portland cement paste and decreased the corrosion resistance of steel in concrete.

3.7. Free chloride estimations

The free chloride contents estimated are given in Table 4. Interestingly, upto the 20% replacement level, the penetration of chloride ion was found to be less when compared to control. At 30%, the estimated values are comparable with OPC. After that, as the FA replacement level increases the penetration of chloride ions also increased. Upto the 30% replacement level, the chloride binding capacity of concrete increases, since the chloride ions gets adsorbed to the surface of the pozzolanic material and enters into chemical reaction with its aluminate phase.

4. Conclusions

The following conclusions can be drawn from the present investigations:

1. The addition of mineral admixture reduced the pH values of concrete, even though the final pH values were still above the critical breakage pH values of passivation film on the steel rebar.
2. Fly ash upto the 30% replacement level improved the corrosion resistance properties of steel in concrete.
3. Fly ash improved the permeability characteristics of concrete and delayed the initial corrosion time and decrease of corrosion rate.
4. Macrocell corrosion current studies showed the better performance of fly ash in concrete and chloride binding capacity is increased when fly ash is used in concrete.
5. Some accelerated corrosion testing techniques were adopted for evaluating the corrosion resistance properties of mineral admixtures in concrete and a good agreement was noticed.

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