

# Durability performance of rebar embedded in chloride admixed blended cement concretes

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In concrete structures, permeation of chloride ions either through the pores or by visible/microcracks or contamination of chloride along with the fine and coarse aggregates increase the availability of chloride ion at the rebar level. The reduction of  $\text{OH}^-$  ions by pozzolanic reaction and by replacement of cement by mineral admixtures may reduce the chloride ion tolerable limit of rebar in blended cement concretes. In the present investigation, the corrosion rate of rebar in 0.5 and 1% chloride admixed concrete was assessed periodically up to a period of 1765 days using electrochemical impedance spectroscopic technique. Ordinary Portland cement (OPC), pulverised fuel ash cement (PFAC) and blast furnace slag cement (BFSC) were evaluated in 20, 30 and 40 MPa concretes. The high  $R_p$  value of rebar obtained in blended cements indicates that the additional calcium hydrates maintains the pH and also contributes significantly to the inhibitive effects at the steel/concrete interface thus maintaining the passivity of rebar. The results reveal that the high chloride ion complexing ability and microstructural changes by the formation of additional calcium hydrates in the PFAC and BFSC concrete matrix enhancing the corrosion resistance of rebar by a factor of five times than that of OPC concrete in 0% chloride added concrete and three times in 1% chloride contaminated concrete. The reduction of  $\text{OH}^-$  ions did not decrease the chloride tolerable limit of rebar in PFAC and BFSC concrete; moreover they had 1.4 times higher chloride tolerance than that of OPC concrete.

**Keywords:** Blended cements, Pozzolanic reaction, Polarisation resistance, Chloride, Threshold value

## Introduction

The corrosion of steel rebar embedded in concrete structures induced by chloride ion contamination is a major problem. The high alkalinity of cement paste offers satisfactory protection against corrosion due to the existence of a self-generating protective layer  $\gamma\text{-Fe}_2\text{O}_3$  at the steel concrete interface. This protective layer forms during the initial stages of cement hydration and grows to a thickness of the order of  $10^{-3}$ – $10^{-1}$   $\mu\text{m}$  with rich lime content.<sup>1</sup> The concentration of ions present in the pore solution in concrete such as  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{OH}^-$  is  $>0.2$   $\text{mol L}^{-1}$ . It varies from 0.42 to 1.14  $\text{mol L}^{-1}$  if the w/c ratio varies from 0.7 to 0.4.<sup>2</sup> The  $\text{K}^+$  and  $\text{OH}^-$  ions are believed to be mainly contributing to the formation of passive layer. Consumption of free calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ] by pozzolanic reaction, leaching of  $\text{OH}^-$  ions and dilution of cement alkalies caused by the replacement of fly ash/slag causes the reduction of  $\text{OH}^-$  ions in blended cement concretes.<sup>3,4</sup> In aged concrete, the concentration of  $\text{OH}^-$

ions may fall to  $<0.05$   $\text{mol L}^{-1}$ .<sup>5,6</sup> The threshold ratio for initiation of corrosion of rebars is expressed in terms of  $\text{OH}^-$  ions concentration. The  $\text{OH}^-$  ions concentration depends upon the type of cement used, w/c ratio of concrete, cement content and aging of the structure.<sup>7</sup> Diamond<sup>8</sup> reported that the pH of pore solution of ordinary Portland cement (OPC) reduced from 13.7 to 13.55 in the presence of fly ash.

Berke *et al.*<sup>9</sup> reported that after three years of exposure in 3% NaCl solution, if the w/c ratio is  $>0.52$ , the fly ash added concretes showed higher corrosion rate than OPC and silica fume added concrete. Mangat and Molloy<sup>10</sup> observed that the corrosion rate of rebar in fly ash added concrete increased after long term exposure to a chloride environment if the fly ash content was  $>15\%$  whereas slag added concrete reduced the corrosion rate considerably. In contrary, Gu *et al.*<sup>11</sup> measured a corrosion current of  $55 \mu\text{A m}^{-1}$  in 55% slag added concrete and  $15 \mu\text{A m}^{-1}$  in Portland cement concrete at 13 mm cover depth. Algahtani *et al.*<sup>12</sup> concluded that 50% slag added concrete showed a 3.82–3.16 times better performance in terms of corrosion initiation time compared to OPC concrete. Glass *et al.*<sup>13</sup> characterised the inhibitive nature of cementitious binder using differential acid neutralisation technique and found that the acid neutralisation capacity was less in pulverised fuel ash cement (PFAC) and blast

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furnace slag cement (BFSC) concrete than that of OPC concrete. The presence of redox species such as  $S^{2-}$ ,  $HS^{-}$  and  $S^{n-}$  on the stability of passive layer of steel concrete interface was studied in OPC and BFSC paste.<sup>14</sup> The increase in corrosion current confirmed that the presence of reducing species influences the formation of passive layer.

From the earlier studies it can be observed that there are conflicting inferences about the corrosion resistance of rebar embedded in the blended cement concrete containing chloride. The reduction of  $OH^{-}$  ions concentration raised the concern over the long term durability of rebar embedded in it. Only limited information is available on the long term performance of rebar embedded in blended cements concrete in the presence of added chloride.

The objective of the present investigation is to determine the corrosion rate of rebar embedded in chloride admixed blended cements concrete using electrochemical impedance spectroscopic (EIS) technique. The durability factor and chloride tolerable limit of rebar in the blended cements concrete also will be arrived.

## Experimental

### Materials and mix proportions

Three mix proportions having a design compressive strength of 20, 30 and 40 MPa concrete at 28 days were used for casting the concrete specimens. The details of

mix proportions are given in Table 1. The mix proportions were kept constant for both blended cements concrete and Portland cement concrete. The same water content and coarse aggregate content were maintained in all the mixes. In this way, the variations in the mix design have been kept to be the minimum and thus the influence of each cement can be distinctly followed and analysed. Three cements namely OPC conforming to IS: 8112 (Ref. 15) equivalent to ASTM-Type-I cement, PFAC conforming to IS: 1489- (Part-I) (Ref. 16) and BFSC conforming to IS:455 (Ref. 17) were used. Chemical composition of cements used is presented as Table 2. Well graded river sand and good quality crushed blue granite were used as a fine and coarse aggregates respectively. The different size fractions of coarse aggregate (20 and 12.5 mm down graded) were taken and recombined to a specified grading. A cold twisted high yield strength deformed bar (Fe-415 grade) with a diameter of 16 mm conforming to IS: 1786 (Ref. 18) was used and its chemical composition is C-0.17%; Mn-0.66%; Si-0.115%; Si-0.017%; P-0.031 and Fe-balance. Potable water was used for casting the concrete specimens.

### Concrete specimen preparation

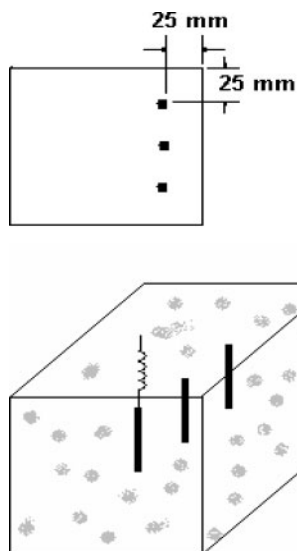
Figure 1 shows that 150 × 150 × 150 mm size concrete cubes were cast. Cold twisted deformed rods of 100 mm length and 16 mm diameter were taken and pickled in inhibited hydrochloric acid solution to remove the initial rust product. In each concrete

**Table 1** Detail of concrete mix proportion

Grade	Type of cement	W/C ratio	Cement, kg m <sup>-3</sup>	Water, kg m <sup>-3</sup>	Fine aggregate, kg m <sup>-3</sup>	Coarse aggregate, kg m <sup>-3</sup>	Characteristic compressive strength, MPa
M20	OPC	0.67	284	190	770	1026	27
	PFAC	0.67	284	190	770	1026	23
	BFSC	0.67	284	190	770	1026	28
M30	OPC	0.54	352	190	739	1026	37
	PFAC	0.54	352	190	739	1026	31
	BFSC	0.54	352	190	739	1026	39
M40	OPC	0.42	452	190	655	1026	54
	PFAC	0.42	452	190	655	1026	42
	BFSC	0.42	452	190	655	1026	48

**Table 2** Chemical composition of three types of cement

Compound	Ordinary Portland cement, %	Pulverised fuel Ash cement, %	Blast furnace slag cement, %
Silicon -di-oxide (SiO <sub>2</sub> )	20–21	28–32	26–30
Aluminium oxide (Al <sub>2</sub> O <sub>3</sub> )	5.2–5.6	7.0–10.0	9.0–11.0
Ferric oxide (Fe <sub>2</sub> O <sub>3</sub> )	4.4–4.8	4.9–6.0	2.5–3.0
Calcium oxide (CaO)	62.–63	41–43	44–46
Magnesium oxide (MgO)	0.5–0.7	1.0–2.0	3.5–4.0
Sulphur – tri-oxide (SO <sub>3</sub> )	2.4–2.8	2.4–2.8	2.4–2.8
Loss on ignition	1.5–2.5	3.0–3.5	1.5–2.5
Bogue compound composition			
Tricalcium silicate (C <sub>3</sub> S)	42–45	Not applicable	Not applicable
Dicalcium silicate (C <sub>2</sub> S)	20–30	-do-	-do-
Tricalcium aluminate (C <sub>3</sub> A)	7.0–9.0	-do-	-do-
Tetra calcium aluminoferrite (C <sub>4</sub> AF)	11–13	-do-	-do-
Physical Properties			
Pozzolan material used, %	–	Around 20% Fly ash (MetturThermal power station)	Around 50% GGBS (Vizag steel plant)
28 Day compressive strength, MPa	62	48	53
Fineness, m <sup>2</sup> kg <sup>-1</sup>	295	363	385



1 Arrangement of rebar in concrete specimen

specimen three rods of similar dimension were embedded at 25 mm cover from one side of the specimen. For electrochemical measurement, copper wire was brazed at one end of a particular rod and that was sealed. Impedance measurement was carried out over an exposed length of 80 mm and the remaining area was sealed using the epoxy compound. For determining the corrosion rate from the weight loss measurement, another two rods were embedded near to the previous one, as shown in Fig. 1. Before embedding, the initial weight of the rods was recorded. In one set of specimens, no chloride was added (0%) to the concrete and in another set of specimens, 0.5 and 1% chloride by weight of cement was added at the time of casting. While casting all the three rebars were embedded vertically with a 25 mm cover both at the top and bottom. Four specimens were cast for each grade/cement. The specimens were cured at room temperature for 28 days in potable water.

### Exposure condition

After 28 days of curing, the specimens were exposed in the exposure yard. Synthetic seawater was prepared as specified in ASTM D-1141.<sup>19</sup> Synthetic seawater (20 mL) was sprayed horizontally using the spray gun once in a day for five days on one side of the specimen and then the specimen was air dried for the next two days. Thus seven days constituted one cycle of wetting and drying. This test procedure simulates the atmospheric exposure of concrete structures in the marine environment. The temperature, relative humidity and other parameters prevailing at the exposure site are given in Table 3. To accelerate the corrosion process as well as to arrive at the chloride tolerable limit,  $\text{Cl}^-$  ions were added during the casting of concrete specimens.

Table 3 Meteorological data

	Max	Min
Temperature (average)	33°C	21°C
Relative humidity (average)	80	65
Rainfall (average)	180 mm	
SO <sub>2</sub>	Nil	
Salinity	38 mg m <sup>-2</sup> per day	

Since the atmospheric salinity at the exposure site was low and a considerable amount of chloride was added during casting of specimens will be bound as Friedel's salt, periodic salt spray was resorted to. The experiment was conducted over a period of 1765 days.

### Method of measurement

The potential of the rebar was measured periodically using a high input impedance multimeter. Impedance measurement was made using three electrode arrangements. Stainless steel electrode of size 10 × 80 mm was used as an auxiliary electrode and saturated calomel electrode was used as a reference electrode. The length of the counter electrode was more than the exposed length of the rebar and by means of this, current was distributed uniformly throughout the length of the rebar. The electrode assembly was kept on a wetted sponge. The rebar embedded in the concrete acted as a working electrode. Chloride was used as a contacting solution to reduce the resistance between the electrode assembly and the concrete. A small sinusoidal voltage signal of 20 mV was applied over a frequency range from 100 kHz to 10 mHz using a computer controlled electrochemical analyzer (Model 6310: E G and G Instruments, Princeton applied research). Measurements were made periodically. The impedance values were plotted on the Nyquist plot. From the Nyquist plot, using the software 'z view' the concrete resistance  $R_c$  and polarisation resistance  $R_p$  value were calculated from the diameter of the high and low frequency semicircle. For calculating  $R_c$ , the frequency range between 100 kHz and 100 Hz was used whereas for calculating  $R_p$ , 100 Hz–10 mHz has been used.<sup>20</sup> By assuming  $B$  as 26 mV (Ref. 21) the  $I_{\text{corr}}$  was calculated using the Stern–Geary relation<sup>22</sup>

$$I_{\text{corr}} = \frac{B}{R_p} \quad (1)$$

where  $B$  is Stern–Geary constant, 26 mV for both active and passive state of rebar;  $R_p$  is polarisation resistance,  $\Omega \text{ cm}^{-2}$ ;  $I_{\text{corr}}$  is corrosion current,  $\mu\text{A cm}^{-2}$ .

The corrosion rate of rebar was calculated from the  $I_{\text{corr}}$ , using the following formula

$$\text{Corrosion rate, mm per year} = 0.0116 \times I_{\text{corr}} \quad (2)$$

where  $I_{\text{corr}}$  in  $\mu\text{A cm}^{-2}$ .

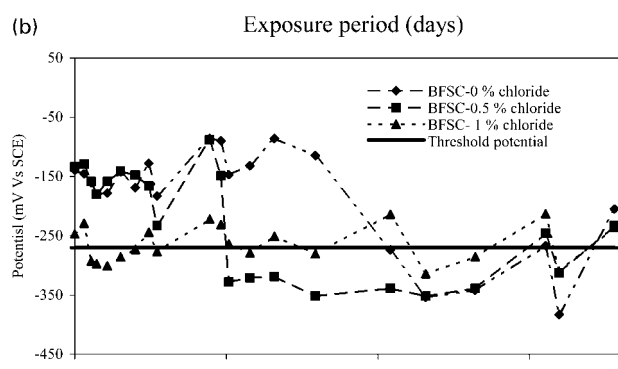
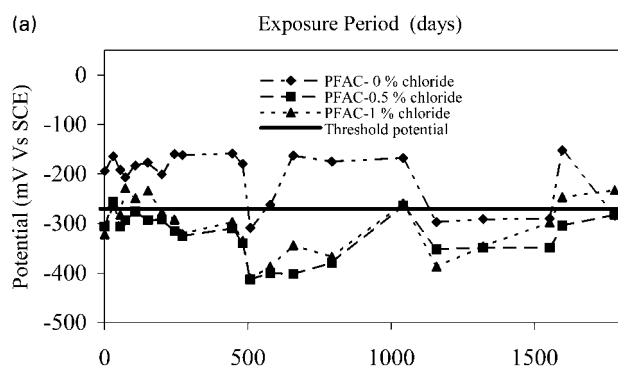
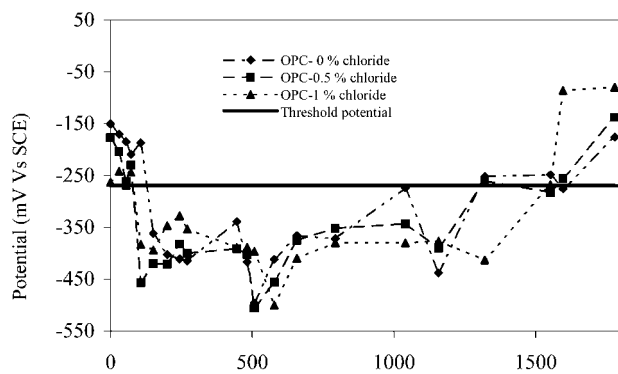
### Corrosion rate from gravimetric weight loss

At the end of 775, 1135, 1528 and 1765 days of exposure, the concrete specimens were broken open and the rods were visually examined for the extent of rust. After pickling the rebars in inhibited hydrochloric acid as specified in ASTM G1,<sup>23</sup> the final weight was measured. From the initial and final weight, the corrosion rate in mm per year was calculated as

$$\text{Corrosion rate in mm per year} = \frac{87.6w}{DAT} \quad (3)$$

where  $w$  is loss in weight, mg;  $D$  is density of Iron,  $\text{gm cm}^{-3}$ ;  $A$  is area,  $\text{cm}^2$ ;  $T$  is time, h.

At the end of 1765 days, the durability factor of rebar in blended cements concrete has been calculated by comparing the corrosion rate as follows:



a OPC; b PFAC; c BFSC

## 2 Potential time behaviour of rebar in 20 MPa concrete

Durability Factor of rebar in PFAC/BFSC concrete =

$$\frac{\text{Corrosion rate of rebar in OPC}}{\text{Corrosion rate of rebar in PFAC/BFSC concrete}}$$

## Cl<sup>-</sup> and OH<sup>-</sup> ion concentration

### OH<sup>-</sup> ions concentration

The concentration of OH<sup>-</sup> ions was determined from the powdered concrete sample by decantation method. The concrete sample near to the rebar was collected. Then the sample was powdered and sieved through a

600  $\mu\text{m}$  sieve. Then this powder was mixed with distilled water at the ratio of 1:3 by weight respectively. This mixture was taken in a closed glass tube and shaken for 10 min and kept for 48 h. After 48 h, the solution was filtered and used to determine the OH<sup>-</sup> ions concentration. A known amount of solution was titrated against 0.1 N H<sub>2</sub>SO<sub>4</sub> using phenolphthalein as an indicator and from the titrated value, the OH<sup>-</sup> ion concentration was calculated.

### Cl<sup>-</sup> ions concentration

The water soluble chloride content was determined by volumetric analysis using the silver nitrate method.<sup>7,24</sup> The decanted solution filtered for OH<sup>-</sup> ion concentration was used for chloride determination also. A known amount of solution was titrated against 0.01 N silver nitrate using potassium chromate as an indicator. The Cl<sup>-</sup> ion concentration was determined from the titre value.

## Results

### Potential time behaviour of rebar in chloride contaminated concrete

#### Concrete of 20 MPa

As per ASTM C 876,<sup>25</sup> Table 4 shows that criteria have been applied while interpreting the data.

The potential time behaviour of the rebar embedded in M20-OPC, PFAC and BFSC concrete is shown in Fig. 2. It can be seen that (Fig. 2a) the rebar in 0% Cl<sup>-</sup>-OPC concrete initially shows a potential value of -151 mV and attains an active potential value of -352 mV at the end of 151 days. In 0.5% Cl<sup>-</sup> added concrete, the initial potential value is -171 mV and it is -263 mV in 1% Cl<sup>-</sup> added concrete. The potential tends to become more active with time to reach a value of -457 and -383 mV at the end of 107 days. Compared to 0% Cl<sup>-</sup> added concrete, the active potential is reached very earlier in 0.5 and 1% Cl<sup>-</sup> added concrete. More negative potential is observed up to a period of 1158 days in all the three chloride levels and thereafter the potential tends to move towards the more positive direction so as to attain a value of -176, -138 and -60 mV in 0, 0.5 and 1% Cl<sup>-</sup> added concrete respectively at the end of 1765 days. The corrosion product formed on the rebar surface might have caused the shift in the potential to less negative direction after 1158 days.

In the case of PFAC concrete (Fig. 2b), the rebar shows a potential value is in the range of -164 to -262 mV up to the period of 1041 days which is less than the threshold potential value of -270 mV as given in ASTM C876. In 0.5 and 1% added concrete the rebar shows an active potential which is in the range of -257 to -413 mV throughout the exposure period.

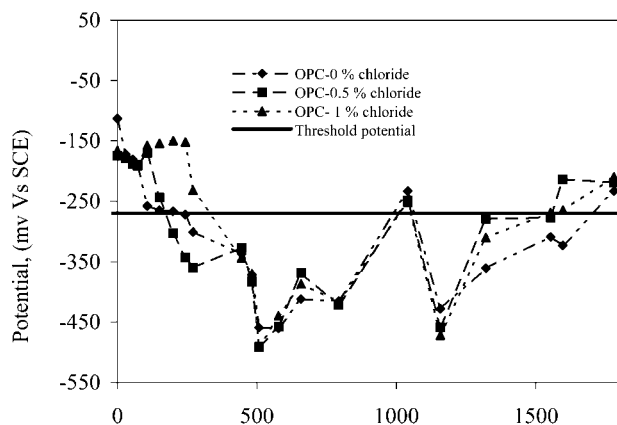
The rebar in BFSC -0% Cl<sup>-</sup> concrete attains an active potential value of -354 mV only at the end of 1158 days whereas 0.5 and 1% Cl<sup>-</sup> added concrete the active potential value of -328, -279 mV is attained at the end of 508 and 578 days respectively (Fig. 2c). When compared to OPC concrete, in blended cement concretes the time to reach the active potential was invariably delayed at all the three chloride levels.

#### Concrete of 30 MPa

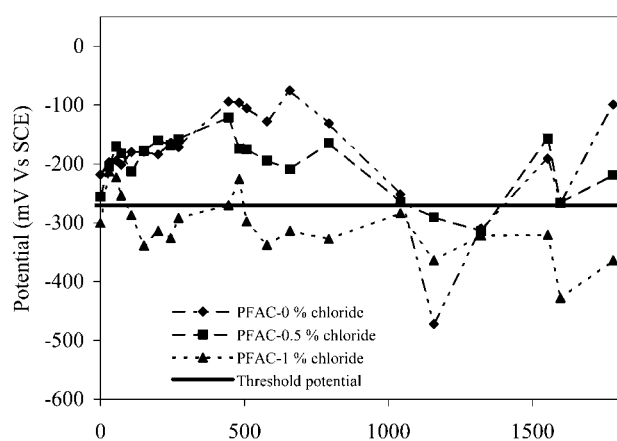
It is clearly seen from Fig. 3a, up to the period of 244 days, the potential value of the rebar in OPC

Table 4 Criteria applied showing data

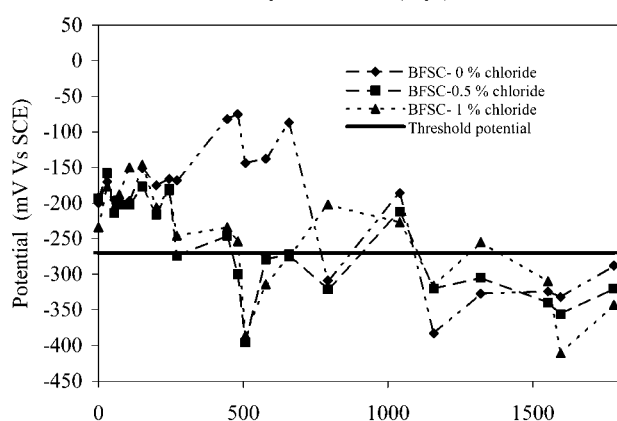
Potential, mV versus SCE	Probability of corrosion, %
More -ve than -275	>90 (active)
Between -275 and -125	Uncertain
More +ve than -125	<10% (passive)



(a) Exposure Period (days)



(b) Exposure Period (days)



(c) Exposure Period (days)

a OPC; b PFAC; c BFSC

### 3 Potential time behaviour of rebar in 30 MPa concrete

concrete is in the range of  $-113$  to  $-272$  mV which indicates that the rebar is in passive condition. Thereafter up to the period of 793 days, potential value moves towards more negative direction to a value in the range of  $-301$  to  $-460$  mV which indicates that the rebar reached active condition. This behaviour is maintained up to the period of 1593 days and thereafter it returns to a value of  $-233$  mV at the end of 1780 days. In 0.5 and 1%  $\text{Cl}^-$  added concrete, the rebar attained a more active potential value of  $-303$  and  $-344$  mV at the end of 200 and 445 days respectively. When exposed further up to 1158 days, the rebar

maintains the active potential which is in the range of  $-343$  to  $-459$  mV. In 0.5%  $\text{Cl}^-$  added concrete and in 1%  $\text{Cl}^-$  added concrete it is  $-344$  to  $-472$  mV. Formation of corrosion products on the rebar may reduce further dissolution of the rebar in presence of chloride and thus the potential is shifted to passive values of  $-219$  and  $-210$  mV in 0.5 and 1%  $\text{Cl}^-$  added concrete at the end of 1780 days.

The behaviour of rebar in PFAC and BFSC concrete is different from OPC concrete (Fig. 3b and c). In PFAC concrete (Fig. 3b) after 1158 days of exposure, the rebar attains an active potential value of  $-339$  and  $-291$  mV in 0 and 0.5%  $\text{Cl}^-$  added concrete respectively. The value indicates that the initiation of corrosion has started only after 1158 days. In 1%  $\text{Cl}^-$  added concrete, the rebar attains an active potential value of  $-287$  mV at the end of 107 days and attains more negative potential value of  $-438$  mV at the end of 1597 days.

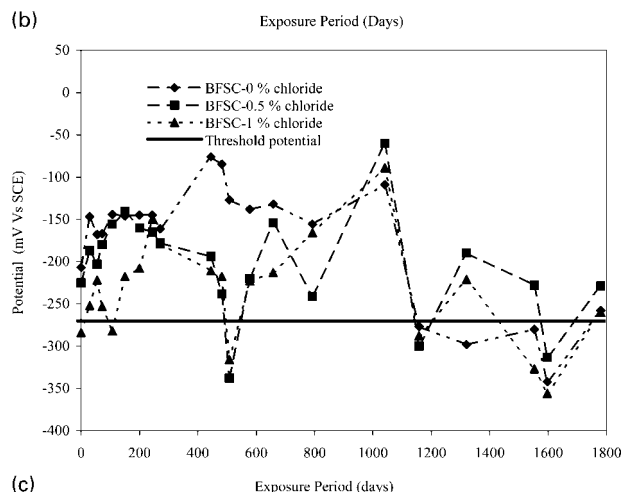
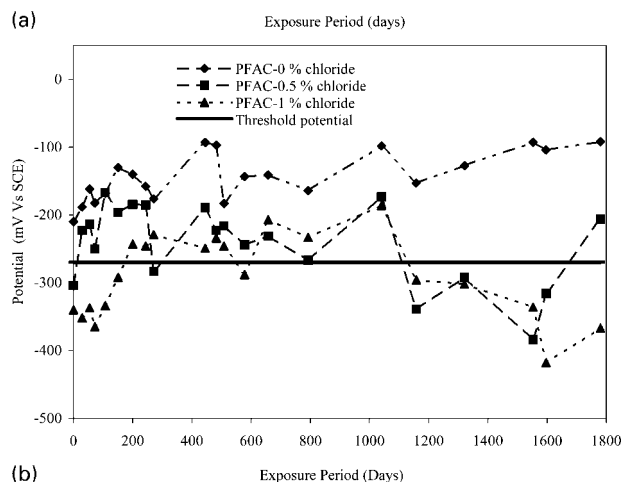
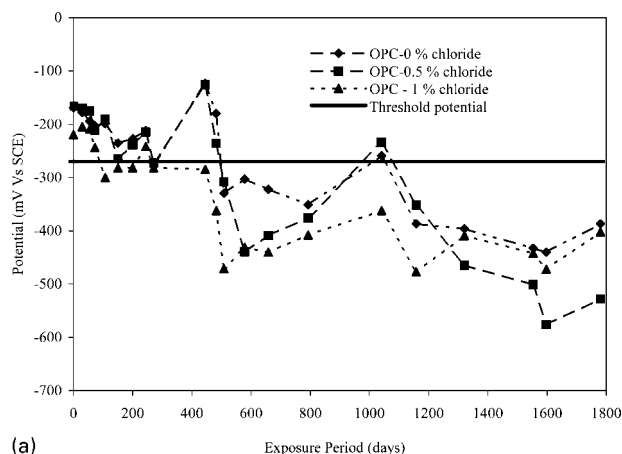
Similarly in BFSC -0%  $\text{Cl}^-$  added concrete, an active potential value of  $-309$  mV was attained after 793 days of exposure (Fig. 3c). The value is increased with time and finally reaches a value of  $-332$  mV at the end of 1593 days. The presence of chloride, initiated the corrosion very early in 0.5 and 1%  $\text{Cl}^-$  added compared to 0%  $\text{Cl}^-$  added concrete; It is 482 days in 0.5% and 508 days in 1%  $\text{Cl}^-$  added concrete respectively. Compared to OPC concrete, the time taken to corrosion initiation in 0%  $\text{Cl}^-$  added concrete is delayed by six times in PFAC concrete and three times in BFSC concrete.

### Concrete of 40 MPa

From Fig. 4a, it is observed that when compared to 20 and 30 MPa concrete, in 40 MPa OPC concrete, the reduction of w/c ratio and higher cement content retains the passive condition of rebar up to a period of 482 days. Reduced permeation of chloride and higher  $\text{OH}^-$  ion concentration near the rebar delayed the initiation of corrosion by 1.97 times compared to 20 and 30 MPa concrete. The same trend is observed in 0.5 and 1%  $\text{Cl}^-$  added concrete. After 482 days of exposure, the potential value moves towards the more negative direction to a value in the range of  $-329$  to  $-387$  mV till the end of the exposure. The potential value is more negative at both the chloride levels compared to that of 0%  $\text{Cl}^-$  added concrete. The potential value is in the range of  $-308$  to  $-528$  mV in 0.5%  $\text{Cl}^-$  added concrete, and  $-361$  to  $-477$  mV in 1%  $\text{Cl}^-$  added concrete respectively.

In PFAC 0% chloride added concrete (Fig. 4b), the potential value of rebar is in the range of  $-92$  to  $-210$  mV throughout the exposure period which is less than the threshold potential value of  $-270$  mV and indicates that the rebar is in passive condition. In 0.5 and 1%  $\text{Cl}^-$  added concrete, the passive condition is maintained up to the period of 1041 days. In both 0.5 and 1%  $\text{Cl}^-$  added concrete, the chloride ions shifted the potential of rebar to more negative values of  $-316$  and  $-418$  mV at the end of 1597 days.

It can be seen from Fig. 4c that the rebar in BFSC 0%  $\text{Cl}^-$  added concrete maintains a passive potential value which is in the range of  $-76$  to  $-210$  mV up to a period of 1041 days. With the exposure to chloride environment, the rebar slowly corrodes and shifts the potential to a more negative potential value of  $-342$  mV at the end of 1593 days. In the case of 0.5%  $\text{Cl}^-$  and 1%  $\text{Cl}^-$



(c) Exposure Period (days)

a OPC; b PFAC; c BFSC

#### 4 Potential time behaviour of rebar in 40 MPa concrete

added concrete, the rebar attains active potential values of  $-316$  and  $-338$  mV at the end of 508 days. In the subsequent period, in both 0.5 and 1%  $\text{Cl}^-$  added concrete, the presence of oxygen and moisture in the cover concrete at the time of measurement shifts the potential randomly both to passive and active direction and finally the rebar reaches active potential values of  $-353$  and  $-313$  mV respectively at the end of 1593 days.

#### Nyquist Behaviour of rebar in chloride contaminated concrete

The Nyquist plots of rebar in 20 MPa concrete containing 0, 0.5 and 1%  $\text{Cl}^-$  added concrete are given in Fig. 5. Invariably in all the plots, two arcs are present. One at

the high frequency region (100 kHz–100 Hz) and the other at low frequency region (100 Hz–10 mHz). The high frequency arc is contributed by the solid phase of the concrete and free ions in the pore solution.<sup>26</sup> The low frequency arc is contributed by the Faradaic corrosion process occurring on the embedded steel.<sup>27</sup> If pitting or generalised corrosion is occurring on the rebar the low frequency arc becomes much flatter and deformed.<sup>28</sup> From all the plots (Fig. 5) it is observed that initially up to the period of 80 days, the slope of the low frequency arc is greater than  $-1$ . This represents the non-ideal capacitance behaviour of rebar when the rebar is under perfect passive condition. After 80 days, if the corrosion is initiated due to the permeation of chloride, the slope of the low frequency arc reaches to  $-1$  and indicates that the rebar is under diffusion control. When corrosion spreads uniformly the curves become flattened. The passivation, initiation and uniform corrosion is distinctly followed by the defined Nyquist plot. The time taken to reach the deformed curve in PFAC and BFSC concrete is more than that of OPC concrete in all three chloride levels as can be seen from Fig. 5d–i.

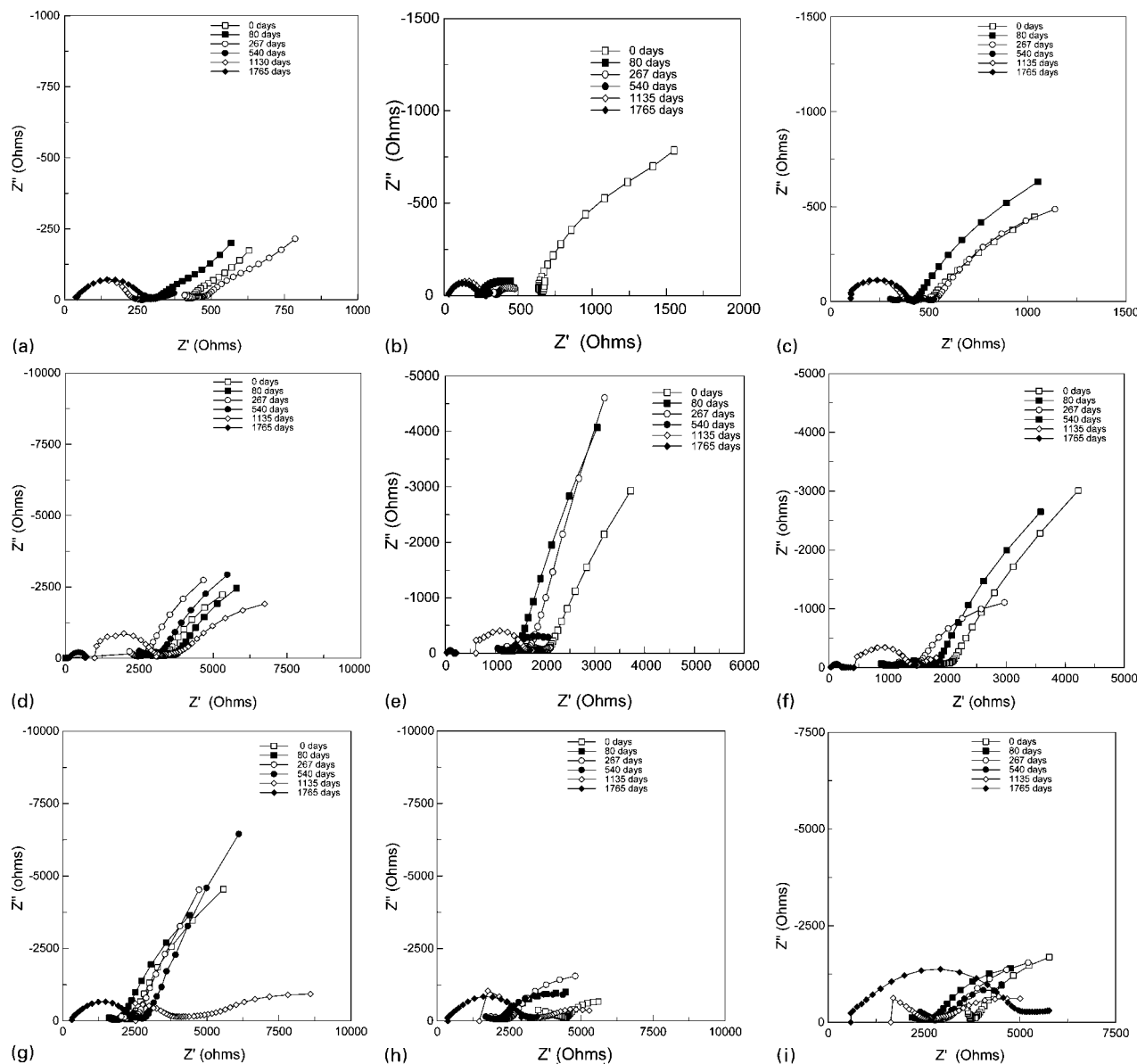
As reported in the literature, the presence of lime rich layer on the rebar at the steel/concrete interface introduces another arc in the Nyquist plot due to this interfacial film.<sup>29–31</sup> This film could be a layer of precipitated cement hydration products including calcium hydroxide and calcium silicate hydrates that deposit on the surface of the steel rebars. In the present investigation this interfacial film is not observed. Perhaps the chemical and physical properties of this interfacial layer are similar to those of the concrete matrix. This arc therefore cannot be distinguished from the matrix arc.<sup>32</sup>

#### $R_p$ measurements versus exposure period

##### Concrete of 20 MPa

Figure 6 shows the  $R_p$  value of rebar embedded in OPC, PFAC and BFSC concrete respectively. In 0% chloride OPC concrete (Fig. 6a), the  $R_p$  value decreases to  $183 \Omega$  from the initial value of  $4189 \Omega$  at the end of 1135 days. The  $R_p$  value decreases with time due to the permeation of chloride. In 0.5 and 1%  $\text{Cl}^-$  added concrete, the  $R_p$  value is lower than that of 0% chloride added concrete. In 1%  $\text{Cl}^-$  added concrete, the  $R_p$  values are higher compared to that of 0.5%  $\text{Cl}^-$  added concrete. The formation of Friedel's salt during addition of chloride releases the  $\text{OH}^-$  ions into the pore solution and increases its pH. The formation of Friedel's salts is more in 1%  $\text{Cl}^-$  added concrete than 0.5%  $\text{Cl}^-$ . The increase in pH contributes to the higher  $R_p$  value up to the period of 267 days in 1% of chloride. Thereafter the breakdown of passivity occurs due to the presence of chloride which reduces the  $R_p$  value to  $216$  and  $112 \Omega$  in 0.5 and 1%  $\text{Cl}^-$  added concrete and  $245 \Omega$  in 0% chloride at the end of 1765 days.

In PFAC 0%  $\text{Cl}^-$  added concrete (Fig. 6b), the initial  $R_p$  value is  $15410 \Omega$  which is 2.8 times higher than that of OPC concrete. The value increases to  $17998 \Omega$  at the end of 540 days. The permeation of chloride initiated the corrosion slowly after 540 days and thus  $R_p$  value gets decreased with time and reaches  $579 \Omega$  at the end of 1765 days. In 0.5%  $\text{Cl}^-$  added concrete, the  $R_p$  value increases up to the period of 267 days and thereafter it gets decreased to  $1053 \Omega$  at the end of 1135 days. In the



a M20-OPC-0% chloride; b M20-OPC-0.5% chloride; c M20-OPC-1% chloride; d M20-PFAC-0% chloride; e M20-PFAC-0.5% chloride; f M20-PFAC-1% chloride; g M20-BFSC-0% chloride; h M20-BFSC-0.5% chloride; i M20-BFSC-1% chloride

##### 5 Nyquist plots of rebar embedded in 20 MPa concrete containing 0, 0.5 and 1% chloride

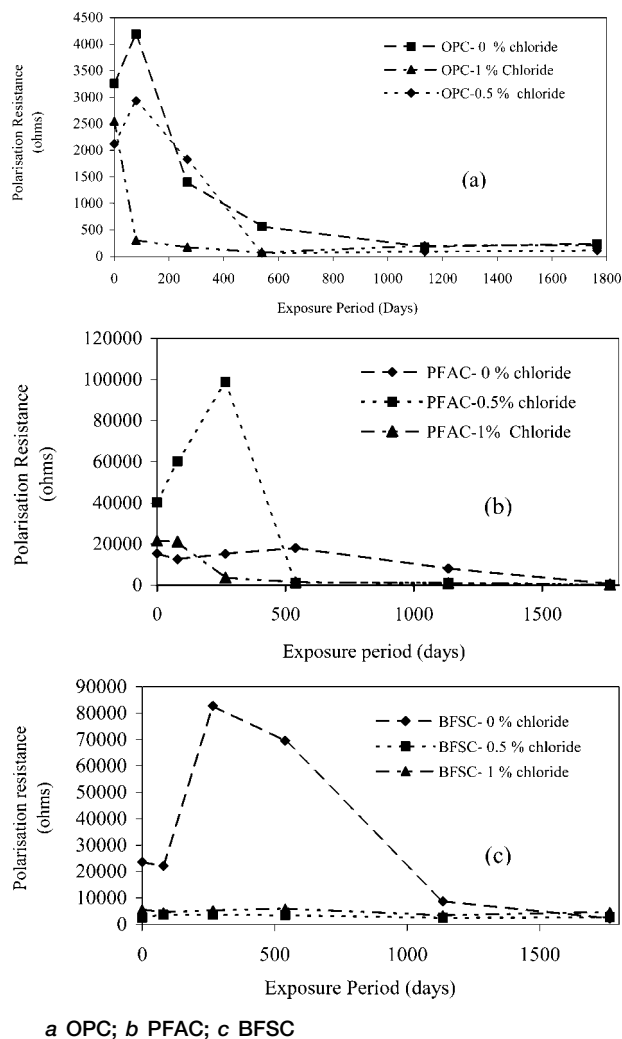
case of 1%  $\text{Cl}^-$  added concrete, the initial  $R_p$  value is 21 624  $\Omega$  which is 10 times higher than that of OPC concrete. After exposure to chloride, the value gets decreased after 80 days and attains a value of 181  $\Omega$  at the end of 1175 days.

In BFSC 0%  $\text{Cl}^-$  added concrete (Fig. 6c), the  $R_p$  value increased to 69 540  $\Omega$  at the end of 540 days from the initial value of 23 580  $\Omega$ . This indicated that up to the period of 540 days the passivity was maintained on the rebar. Then the value decreases with time and reaches to 2191  $\Omega$  at the end of 1765 days. In 0.5 and 1%  $\text{Cl}^-$  added concrete, the  $R_p$  values are lower than that of 0%  $\text{Cl}^-$  added concrete. The value is 2748 and 4666  $\Omega$  in 0.5 and 1%  $\text{Cl}^-$  added concrete at the end of 1765 days. Comparing the value at 1135 days, in blended cement concrete the  $R_p$  value is 47 times higher than that of OPC concrete in 0%  $\text{Cl}^-$  added concrete. In 0.5%  $\text{Cl}^-$  added concrete, the value of PFAC and BFSC concrete is 5 and 16 times higher than that of OPC concrete. The value is 10 and 35 times higher in 1%  $\text{Cl}^-$  added concrete.

##### Concrete of 30 MPa

From Fig. 7a, it can be seen that initially the  $R_p$  values are 13 020, 6428 and 4266  $\Omega$  in 0, 0.5 and 1%  $\text{Cl}^-$  OPC concrete. It is 4, 2.52 times higher than that of M20 OPC concrete. With time the permeation of chloride as well as added chloride increased the dissolution of rebar and decreased the  $R_p$  value. At the end of 1765 days, it is 356, 168 and 81  $\Omega$  in 0, 0.5 and 1%  $\text{Cl}^-$  added concrete respectively.

In PFAC 0%  $\text{Cl}^-$  added concrete, (Fig. 7b), the  $R_p$  value is maintained up to the period of 267 days. It varies from 107 204 to 181 200  $\Omega$  indicating that the passivity is maintained on the rebar. Compared to OPC concrete, the value is eight times higher. The  $R_p$  value decreases to 960  $\Omega$  at the end of 1765 days. In 0.5% added concrete, the  $R_p$  value varies from 1940 to 24 760, which is nine times higher than that of OPC concrete. Similarly in 1%  $\text{Cl}^-$  added concrete, it is between 17 986 and 9966  $\Omega$  which is also nine times higher than that of OPC concrete. Thereafter, the  $R_p$  value gets decreased to



a OPC; b PFAC; c BFSC  
6 Polarisation resistance time behaviour of rebar in 20 MPa concrete

8176 and 1579  $\Omega$  in 0.5 and 1%  $\text{Cl}^-$  added concrete after 540 days of exposure.

As shown in Fig. 7c, it can be seen that in BFSC 0 and 0.5%  $\text{Cl}^-$  added concrete, very high  $R_p$  value is observed up to the period of 1135 days and this indicates that the passivity is maintained. In 0%  $\text{Cl}^-$  added concrete, a maximum value of 221 460  $\Omega$  is obtained at the end of 80 days and a minimum value of 13 980  $\Omega$  at the end of 1135 days. The value is initially 21 times higher than that of OPC concrete. In 0.5%  $\text{Cl}^-$  added concrete, the maximum value is 177 800  $\Omega$  and minimum is 18,150  $\Omega$ . The initial value is seven times higher than that of OPC concrete. But in 1%  $\text{Cl}^-$  added concrete, up to the period of 267 days, the  $R_p$  value is higher then decreases with time and attains a value of 3518  $\Omega$  at the end of 1765 days. The value is initially  $\sim 19$  times higher than that of OPC concrete.

#### 40 MPa Concrete

From Fig. 8a, it can be inferred that the  $R_p$  value increases to 19 826  $\Omega$  at the end of 267 days from the initial value of 11 681  $\Omega$ . Thereafter it decreases to 1536  $\Omega$  at the end of 1765 days. Compared to 20 and 30 MPa concrete, the values are higher throughout the exposure period. In 0.5%  $\text{Cl}^-$  added concrete, though the initial value is less, the higher  $R_p$  value of 9423  $\Omega$  is observed at the end of 80 days. Then decreases with time

and attains a value of 242  $\Omega$  at the end of 1765 days. In the case of 1%  $\text{Cl}^-$  added concrete, the initial  $R_p$  value of 24 545  $\Omega$  gets decreased with time and attained 219  $\Omega$  at the end of 1765 days.

In PFAC 0%  $\text{Cl}^-$  added concrete (Fig. 8b), compared to OPC concrete, the  $R_p$  value is higher throughout the exposure period. It varies from 130 000 to 63 960  $\Omega$  which indicates that the passive condition of the rebar is maintained. At the end of 1765 days, it is 42 times higher than that of OPC concrete. Whereas in 0.5 and 1%  $\text{Cl}^-$  added concrete, higher  $R_p$  value is maintained up to the period of 1135 days. It varies from 138 740 to 82 420  $\Omega$  in 0.5%, and 29 965 to 42 960  $\Omega$  in 1%  $\text{Cl}^-$  added concrete respectively. Thereafter it decreases to 18 070 and 2064  $\Omega$  at the end of 1765 days.

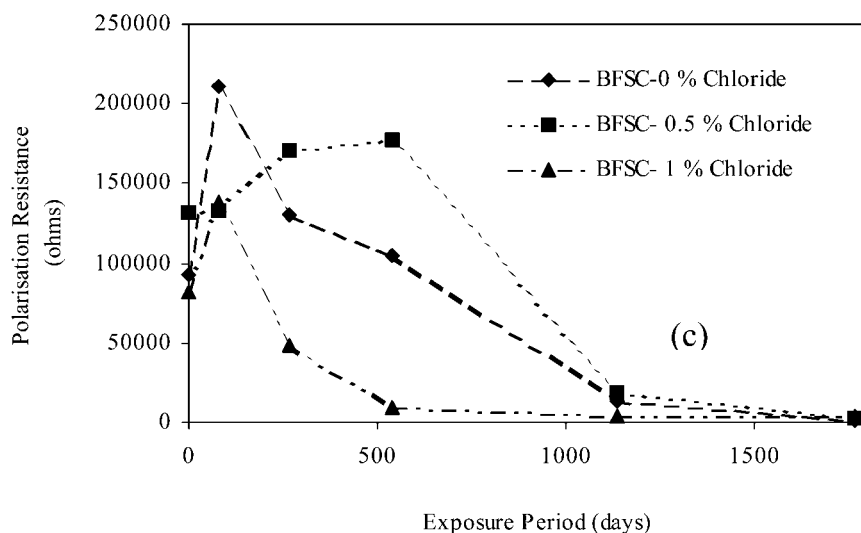
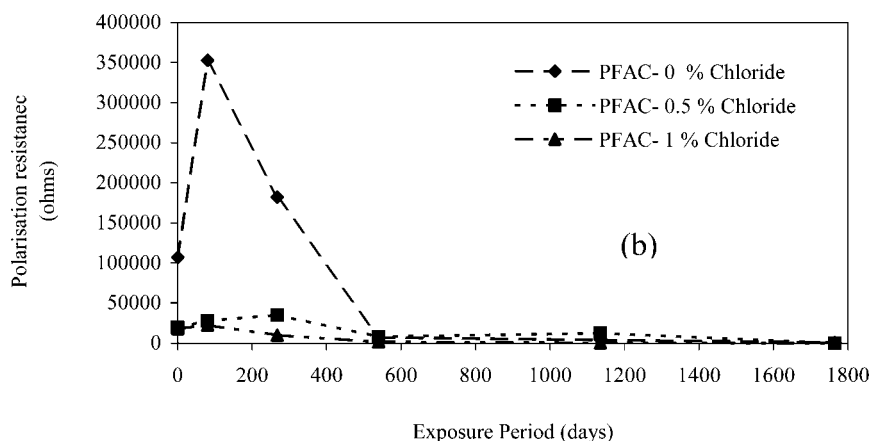
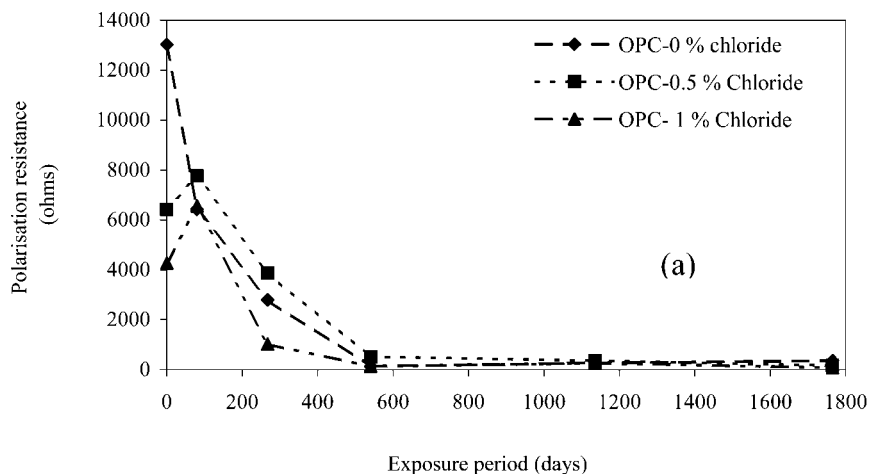
From Fig. 8c it is observed that in BFSC 0%  $\text{Cl}^-$  added concrete, the  $R_p$  value is 100 000  $\Omega$  which is 10 times higher than that of OPC concrete. The higher  $R_p$  value is maintained up to the period of 1135 days, which shows that the passivity of the rebar is maintained. The value is in the range between 101 440 and 199 779  $\Omega$ . Thereafter the  $R_p$  value decreases to 5568  $\Omega$  at the end of 1765 days. Similarly in 0.5 and 1%  $\text{Cl}^-$  added concrete, the value is 35 881 and 37 842  $\Omega$  at the end of 1135 days and gets decreased to 9233 and 2633  $\Omega$  at the end of exposure. Even in presence of 1% of chloride, the rebar in PFAC and BFSC concrete has a minimum of nine times higher  $R_p$  value than that of OPC concrete.

Based on the foregoing discussion it is inferred that in PFAC and BFSC concrete, the passivity is not affected in presence of added chloride. Furthermore, the higher  $R_p$  value indicates that the passive layer grows in thickness with time by the hydrated cement products such as calcium silicate hydrates and calcium aluminate hydrates. It was reported that these hydration products would maintain higher pH and also produce significant inhibitive effects at the steel concrete interface.<sup>33–35</sup> In addition to this, higher chloride binding capacity of blended cement concrete may reduce the availability of free  $\text{Cl}^-$  ions near the rebar thus able to maintain the passivity. The increase in  $R_p$  with an increase in strength of concrete indicates that the higher alkalinity due to increased cement content maintained the passivity of rebar very longer time in 30 and 40 MPa concrete compared to 20 MPa concrete.

#### Electrical resistance of 0% $\text{Cl}^-$ added concrete

Densification of pore structure in blended cement concretes is monitored by measuring the electrical resistance of the concrete with time. Decrease in resistance with time could be related to permeation of chloride through the cover concrete. In EIS technique, the resistance of the concrete is indicated distinctly by the high frequency arc in the frequency range between 100 kHz and 100 Hz. The diameter of the semicircle represents the resistance of the concrete. Figure 9 compares the resistance of the 0%  $\text{Cl}^-$  added concrete with the exposure period in 20, 30 and 40 MPa concrete respectively. From Fig. 9a, it can be seen that the resistance values are higher in PFAC and BFSC concrete than OPC concrete throughout the exposure period. In OPC and PFAC concrete, the value gets decreased with exposure to chloride solution whereas in BFSC concrete it increases up to a period of 1135 days. For example in 20 MPa OPC concrete, the initial value





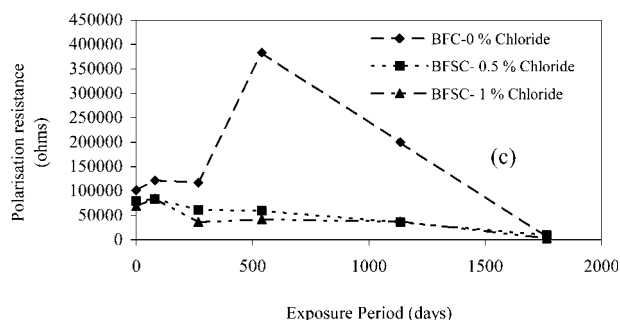
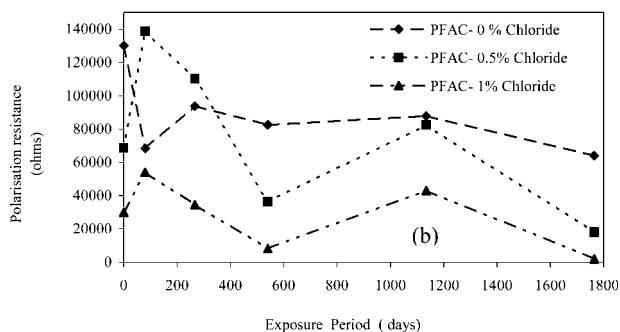
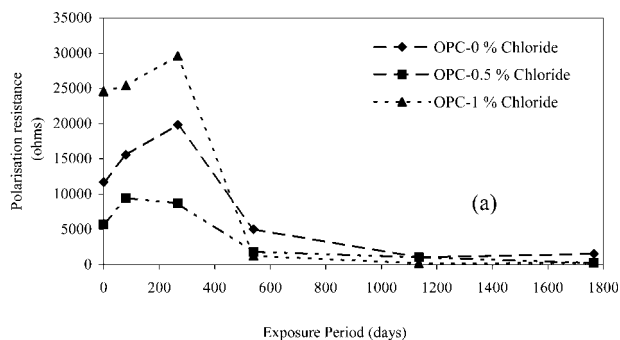
a OPC; b PFAC; c BFSC

#### 7 Polarisation resistance time behaviour of rebar in 30 MPa concrete

is 418  $\Omega$  and it gets decreased to 97  $\Omega$  at the end of 1785 days. In the case of BFSC concrete, the initial value is 648  $\Omega$  and it increases to 3298  $\Omega$  at the end of 1135 days. In PFAC concrete though the value decreases with time it is higher than that of OPC concrete. This may be attributed to the occurrence of pore refinement in PFAC and BFSC concrete by pozzolanic reaction. The pore refinement reduces the pore size which in turn reduces the diffusion of chloride. After 1135 days of exposure, the resistance values are 1925 and 3298  $\Omega$  in PFAC and BFSC concretes which are 25 and 50 times higher than that of OPC concrete.

Thereafter the value decreases to 619 and 2172  $\Omega$  in PFAC and BFSC concretes.

In 30 and 40 MPa concrete, the values are higher compared to 20 MPa concrete. In 30 MPa concrete (Fig. 9b), initially the resistance value of PFAC and BFSC concrete is 1142 and 2328  $\Omega$ , which is 2.4 and five times higher than that of OPC concrete. The value increased up to the period of 1135 days and thereafter it gets decreased. In the case of OPC concrete, the value gets decreased after 267 days. As seen from Fig. 9c, in 40 MPa concrete, the initial resistance values of PFAC and BFSC concrete are 1813 and 2273  $\Omega$  which are 3.3



a OPC; b PFAC; c BFSC

**8 Polarisation resistance time behaviour of rebar in 40 MPa concrete**

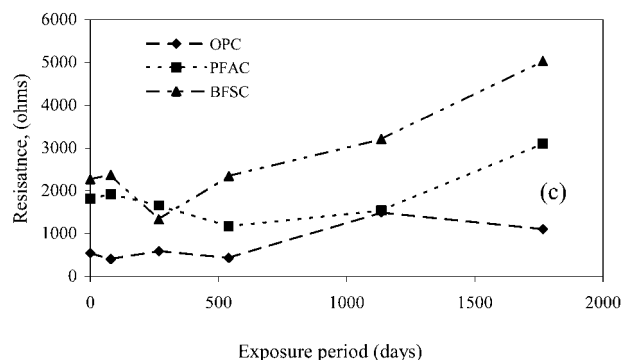
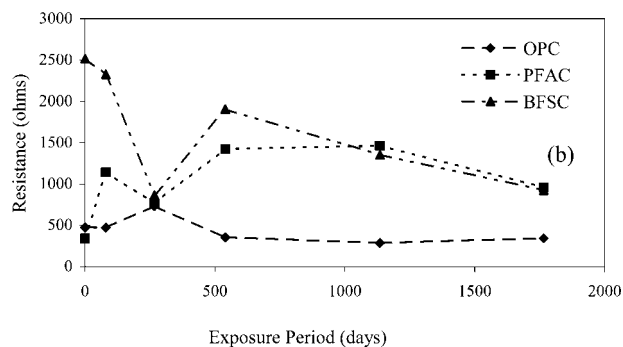
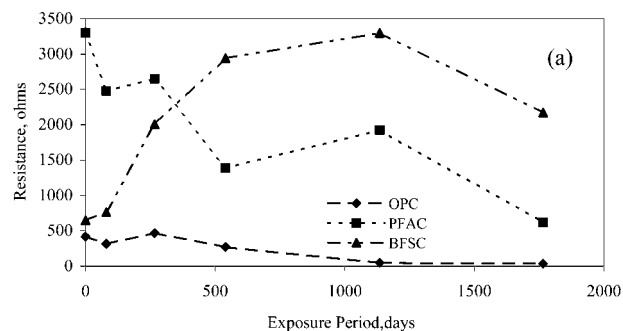
and four times higher than that of OPC concrete. The increase in resistance value throughout the exposure period in PFAC concrete and BFSC concrete indicates the reduction of permeation of chloride.

### Visual observation

Figure 10 compares the extent of rust at the end of 1135 days of exposure in 0, 0.5, 1%  $\text{Cl}^-$  added concretes. In 20 MPa PFAC and BFSC concrete (Fig. 10a–c), the rusted area increases with an increase of chloride, whereas in OPC concrete even in 0% chloride severe rusting is observed. Similarly in 30 MPa concrete (Fig. 10d–f) also rusting of rebar is more in OPC concrete than that in PFAC and BFSC concrete. In 40 MPa concrete (Fig. 10g–i), at 0%  $\text{Cl}^-$  added concrete, only negligible rusting is observed whereas in 0.5 and 1%  $\text{Cl}^-$  added concretes, the extent of rust is same in all the three cements.

### Gravimetric weightloss

Table 5 compares the corrosion rate with time. The rebar in PFAC and BFSC concrete is having very negligible corrosion rate up to the period of 1528 days, whereas OPC concrete has a higher corrosion rate of 0.0252 mm per year even at the end of 775 days. Permeation of chlorides has increased the corrosion rate with time and the value reached to 0.0544 mm per year

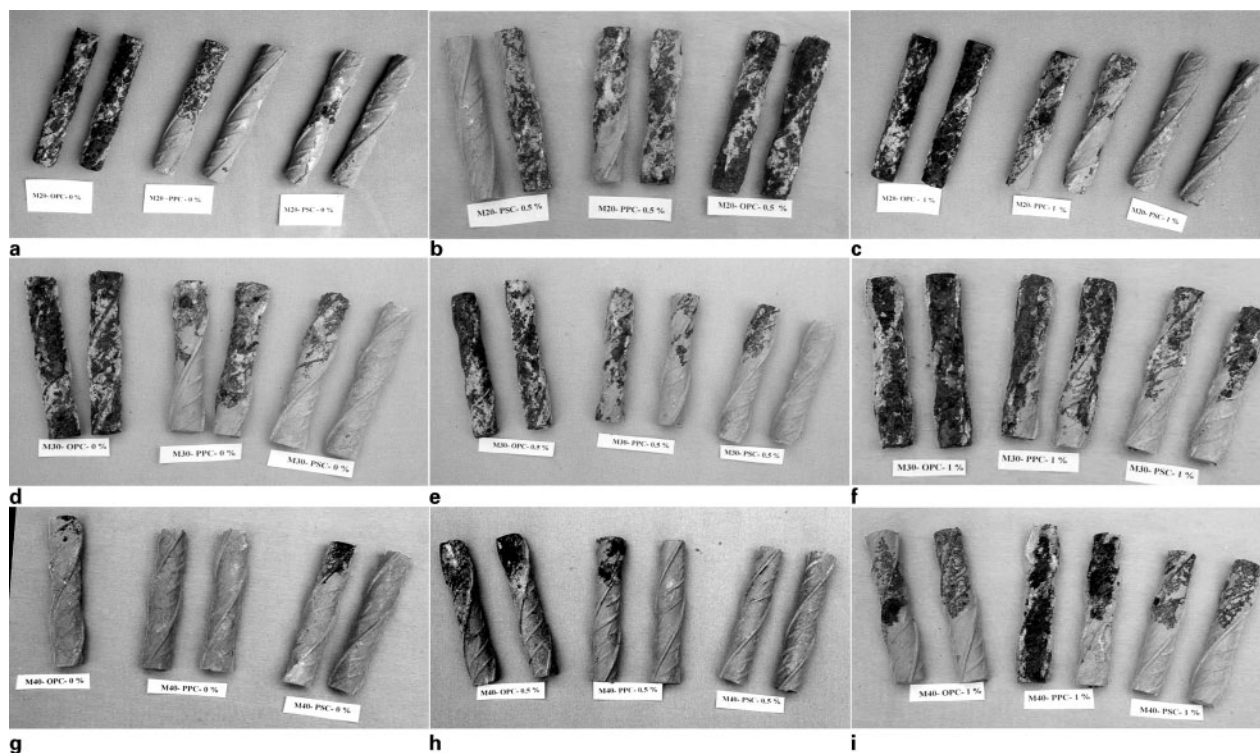


a 20 MPa; b 30 MPa; c 40 MPa

**9 Resistance versus time in 0% chloride added concrete**

at the end of 1765 days. In 0.5 and 1% chloride added concrete, the rate of corrosion is less in PFAC and BFSC concrete compared to that of OPC concrete throughout the exposure period. At the end of 1765 days, the rebar in PFAC and BFSC concrete has 41 and 72 times more corrosion resistance than that of OPC concrete.

Compared to 20 MPa concrete, in 30 MPa concrete the corrosion rate is less initially. After 775 days, the corrosion rate of rebar in 20 MPa concrete is 0.022 mm per year, which is two times higher than that of 30 MPa concrete. But thereafter it is the same in both the concretes. Hence it can be inferred that in 30 MPa concrete only the initiation of corrosion of rebar is delayed and if corrosion is initiated it behaves similar to 20 MPa concrete. The rate of corrosion is less in PFAC and BFSC concretes. At the end of 1765 days, the rebar has three and 73 times more corrosion resistance than that of OPC concrete. In the case of 0.5 and 1%  $\text{Cl}^-$  added concrete, the corrosion rate is less than in 20 MPa concrete. Because of high cement content, the  $\text{OH}^-$  ions concentration is more near the rebar causing a reduction in the rate of corrosion. The behaviour of rebar in PFAC and BFSC concrete is not changed in chloride added concrete. Both PFAC and BFSC bind more chlorides, which reduces the corrosion rate. In 0.5%



a M20-0% chloride; b M20-0.5% chloride; c M20-1% chloride; d M30-0% chloride; e M30-0.5% chloride; f M30-1% chloride; g M40-0% chloride; h M40-0.5% chloride; i M40-1% chloride

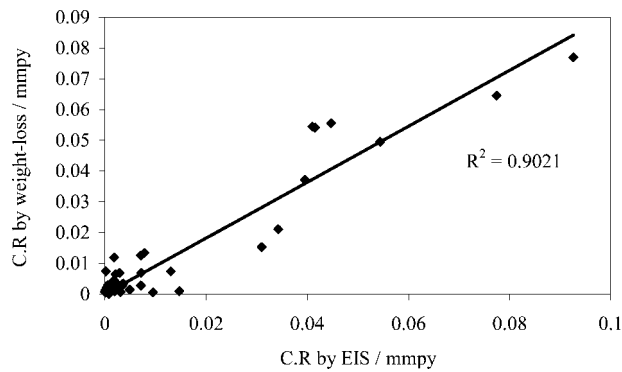
#### 10 Extent of rust on rebars after 1135 days of exposure

$\text{Cl}^-$  added concrete, the rebar has 12 and 50 times more resistant than that of OPC concrete and it reduces to nine and 12 times in 1%  $\text{Cl}^-$  added concrete.

In 40 MPa 0%  $\text{Cl}^-$  added concrete, the rate of corrosion is less throughout the exposure period and even at the end of 1765 days, only a very negligible

**Table 5** Corrosion rate with exposure period

		Corrosion rate, mm per year				
		Exposure period, days				
Grade/type of cement	Chloride added, %	775	1135	1528	1765	Durability factor
M20-OPC	0	0.0252	0.0544	0.0568	0.0544	–
M20-PFAC	0	0.0000	0.0000	0.0000	0.0074	7.4
M20-BFSC	0	0.0000	0.0010	0.0008	0.0027	20
M20-OPC	0.5	0.0337	0.0779	0.1397	0.0616	–
M20-PFAC	0.5	0.0001	0.0125	0.0460	0.0495	1.2
M20-BFSC	0.5	0.0000	0.0069	0.0008	0.0015	41
M20-OPC	1	0.0463	0.0645	0.1283	0.1514	–
M20-PFAC	1	0.0030	0.0030	0.0142	0.0541	3
M20-BFSC	1	0.0002	0.0007	0.0047	0.0021	72
M30-OPC	0	0.0124	0.0447	0.0690	0.0437	–
M30-PFAC	0	0.0092	0.0045	0.0052	0.0134	3
M30-BFSC	0	0.0000	0.0009	0.0006	0.0006	73
M30-OPC	0.5	0.0133	0.0542	0.0501	0.0555	–
M30-PFAC	0.5	0.0014	0.0030	0.0023	0.0047	12
M30-BFSC	0.5	0.0000	0.0010	0.0014	0.0011	50
M30-OPC	1	0.0302	0.0574	0.0662	0.0770	–
M30-PFAC	1	0.0082	0.0186	–	0.0085	9
M30-BFSC	1	0.0000	0.0119	–	0.0065	12
M40-OPC	0	0.0007	0.0007	0.0056	0.0014	–
M40-PFAC	0	0.0001	0.0006	0.0001	0.0007	2
M40-BFSC	0	0.0000	0.0007	0.0006	0.0015	1
M40-OPC	0.5	0.0062	0.0028	0.0213	0.0153	–
M40-PFAC	0.5	0.0000	0.0012	0.0010	0.0022	7
M40-BFSC	0.5	0.0000	0.0005	0.0020	0.0029	5
M40-OPC	1	0.0248	0.0371	0.0328	0.0211	–
M40-PFAC	1	0.0041	0.0074	0.0037	0.0034	6
M40-BFSC	1	0.0000	0.0023	0.0014	0.0026	8



**11 Comparison of corrosion rate: EIS versus weight loss method**

corrosion rate of 0.001 mm per year is observed in all the three cements. Hence the protection of rebar is mainly attributed to the reduction of total porosity of concrete and pore refinement by pozzolanic reaction does not contribute much to 40 MPa concrete. In the case of 0.5 and 1%  $\text{Cl}^-$  added concrete, the corrosion rate of OPC concrete is 0.0153 and 0.0211 mm per year. But in PFAC and BFSC concrete even at the end of 1765 days, the rebar shows very negligible corrosion rate which is 5–8 times less than that of OPC concrete.

### Comparison of corrosion rate: EIS versus weight loss measurement

Figure 11 compares the corrosion rate measured by weight loss method with EIS method. It is clearly evident from the figure that correlation coefficient  $R$  between them was 0.95 and indicates that the corrosion rate values arrived by both methods are very close to

each other. When the rebar is under severely corroding condition, the corrosion rate measured by EIS is less than that by weight loss method.

### Chloride content

Table 6 compares the free chloride content available near the rebar level at the end of 775 and 1135 days. From the table it is seen that the free chloride available in OPC 0%  $\text{Cl}^-$  concrete is more than in PFAC and BFSC concrete and it is not changed in presence of added chloride. It is five and four times higher than that of PFAC and BFSC concrete respectively. The chloride is increased with exposure period. In addition to reduced diffusion of chloride, the higher binding capacity of PFAC and BFSC than OPC has contributed to the reduced chloride content in chloride admixed concrete. The chloride content decreases with an increase in strength of concrete. For example, in 0%  $\text{Cl}^-$  OPC concrete, it is 3.212, 2.466 and 1.813% by weight of cement in 20, 30 and 40 MPa concretes. Compared to PFAC concrete, in BFSC the chloride content is less at both the exposure periods. It is due to

- (i) the formation of additional calcium hydrates are more in BFSC than PFAC (Ref. 36) and this hydrates fill the pores in the pore structures reduces the diffusion of chloride
- (ii) replacement of slag in BFSC is more than (50%) the fly ash in PFAC (20%) and the presence of more alumina in slag bounds more chloride and thus reduces the availability of free chloride ions.

It can be also observed from Table 6, in blended cement concrete at 0 and 0.5%  $\text{Cl}^-$  levels, the  $\text{OH}^-$  ion concentration is one-fourth to that of OPC concrete. Reduction is more in BFSC concrete than in OPC

**Table 6 Comparison of  $\text{Cl}^-$  and  $\text{OH}^-$  ions content**

			Free chloride (% by weight of cement)	OH <sup>-</sup> ion concentration, mM <sup>-1</sup>	
			Exposure period, days		
Concrete	Type of cement	Chloride added, %	775	1135	At the end of 1135 days
M20	OPC	0	3.212	4.226	120
	PFAC	0	0.676	2.536	42
	BFSC	0	0.779	2.029	30
M20	OPC	0.5	3.381	4.649	111
	PFAC	0.5	1.352	4.902	36
	BFSC	0.5	1.183	3.719	30
M20	OPC	1	3.888	3.043	96
	PFAC	1	2.367	4.246	54
	BFSC	1	2.029	3.888	30
M30	OPC	0	1.781	2.397	120
	PFAC	0	1.781	3.356	45
	BFSC	0	0.137	0.411	54
M30	OPC	0.5	2.466	3.287	114
	PFAC	0.5	1.918	3.630	48
	BFSC	0.5	0.685	2.603	30
M30	OPC	1	2.466	4.315	132
	PFAC	1	2.466	2.192	66
	BFSC	1	1.233	2.329	54
M40	OPC	0	1.813	1.440	108
	PFAC	0	1.173	3.200	57
	BFSC	0	0.213	0.107	60
M40	OPC	0.5	1.280	2.080	132
	PFAC	0.5	1.387	1.813	90
	BFSC	0.5	1.280	1.600	72
M40	OPC	1	1.600	3.211	138
	PFAC	1	2.453	2.560	72
	BFSC	1	2.453	2.560	66

concrete. The replacement of slag in BFSC is 50%, causes more reduction of  $\text{OH}^-$  ions in BFSC than OPC and PFAC. With an increase in strength, the  $\text{OH}^-$  concentration increases considerably and it is around half of that of OPC concrete. Compared to 20 MPa concrete, the increase in cement content might be increases the  $\text{OH}^-$  ions concentration in 30 and 40 MPa concrete. From the table it is obviously seen that in presence of higher amount of chloride, the lower corrosion rate of rebar in blended cements than in OPC cement confirms the reduction of  $\text{OH}^-$  ion concentration did not accelerate the corrosion of rebars.

## Discussion

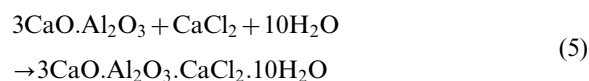
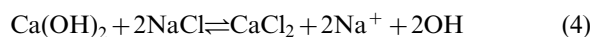
### Corrosion initiation time

As reported in ASTM C876,  $-270$  mV has been taken as threshold potential and time to reach this potential is taken as corrosion initiation time. The European Concrete Committee<sup>37</sup> has proposed another criterion based on  $R_p$  values; if the  $R_p$  value is more than  $130 \text{ k}\Omega \text{ cm}^2$  then the rebar is in passive condition and less than  $25 \text{ k}\Omega \text{ cm}^2$  indicates active condition. As per this, if the  $R_p$  value is  $>3300 \Omega$  (for the exposed area of the rebar) has been taken as perfect passivity and below this value as breakdown of passivity. The time to reach the  $R_p$  value of  $3300 \Omega$  has been taken as corrosion initiation time. The time taken to reach corrosion initiation of rebar in 0% chloride added concrete based on potential and  $R_p$  value is compared in Table 7. From the table it is evident that the values obtained from both are very close to each other. The  $R_p$  value is higher in PFAC and BFSC by 3.4 and 7.7 times than that of OPC concrete in 20 MPa; four and three times in 30 MPa; 3.5 and 2.3 times in 40 MPa concretes respectively. It is also observed that the time to reach the threshold potential value increases with the strength of concrete. It is 151 days in 20 MPa; 271 days in 30 MPa; 508 days in 40 MPa concrete. PFAC and BFSC concrete delay the time taken to reach threshold potential by 2.3–7.7 times compared with the OPC concrete. In chloride added concrete, though the rebar in PFAC and BFSC concrete showed active potential initially but with time the potential value decreased and indicated that even in the presence of 1% of chloride the passivity of rebar is maintained. The reduced permeation of chloride ions by pore structure refinement in PFAC and BFSC concrete by pozzolanic reaction delayed the initiation of corrosion in 0%  $\text{Cl}^-$  added concrete.

### Passivation of rebar in chloride admixed blended cement concrete

Initially, in the presence of 0.5 and 1%  $\text{Cl}^-$  added concrete, up to 80 days, the increase in  $R_p$  value is observed. When the chloride was added during the

mixing of concrete, the Friedel's salt formation by anion exchange mechanism which involves the ordered replacement of  $\text{OH}^-$  ions from aluminate ferrite hydrates by the  $\text{Cl}^-$  ions into the pore solution increases the pH.<sup>38–40</sup> This can be explained by the following equation



The increase in  $\text{OH}^-$  ions in the pore solution, maintained the passivity up to the period of 80 days in the presence of 0.5 and 1% chloride level. From Table 6, it can be seen in 30 MPa 1%  $\text{Cl}^-$  added concrete, the  $\text{OH}^-$  ions concentration is 132, 66 and 54 mM in OPC, PFAC and BFSC concrete whereas at 0%  $\text{Cl}^-$  level it is 120, 45 and 54 mM. Similarly in 40 MPa 0%  $\text{Cl}^-$  concrete, the  $\text{OH}^-$  ions in OPC, PFAC and BFSC is 108, 57, 60 mM whereas in 1%  $\text{Cl}^-$  added concrete it is 138, 72, 66 mM respectively. Because of reduced cement content, the Friedel's salt formation is less and release of  $\text{OH}^-$  ions also less in 20 MPa concrete. The increase in  $\text{OH}^-$  ion concentration increases the  $R_p$  value at 80 days and it is invariably observed at all the chloride levels.

The reduction of pore size by the formation of additional calcium hydrates and the higher chloride binding capacity increased the corrosion resistance of rebar in BFSC and PFAC than that of OPC concrete.

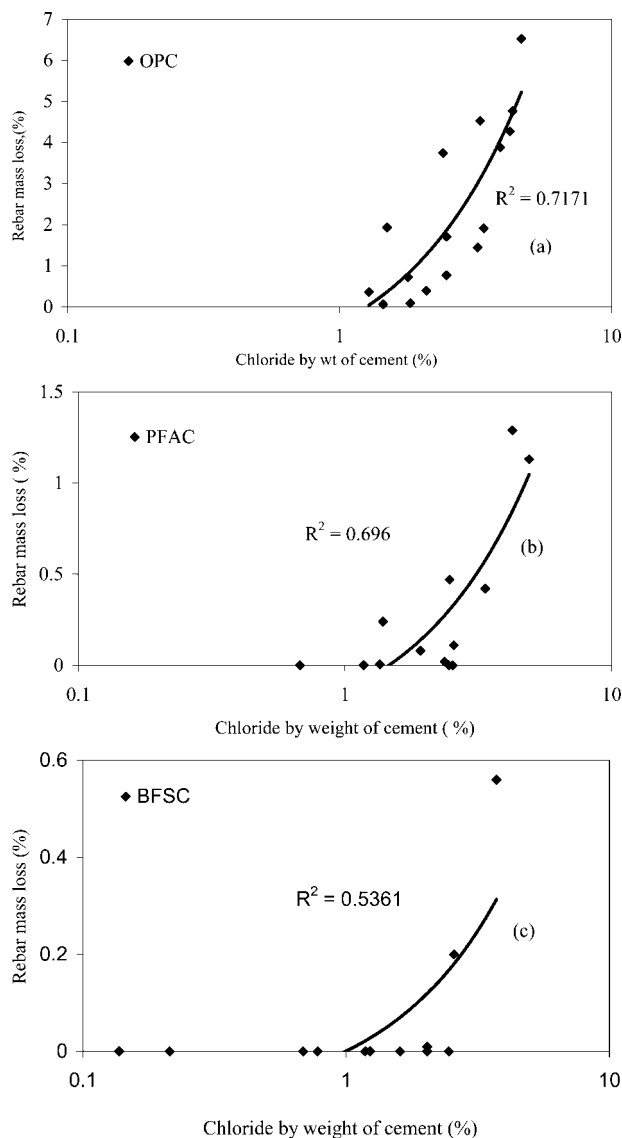
### Threshold chloride concentration

Figure 12 correlates the rebar mass loss with chloride content of all the three cements. The rebar mass loss increased linearly with the chloride content. It can be seen that for the negligible mass loss of  $<0.09\%$ , OPC, PFAC and BFSC can tolerate up to 1.813, 2.536 and 2.453% chloride by weight of cement respectively. In blended cement concrete it is 1.4 times higher than that of OPC concrete. It was reported that the chloride content for initiating corrosion in OPC concrete is in the range between 0.48 and 2.02% by weight of cement.<sup>41</sup> The threshold value found in the OPC concrete lies within the range reported by the earlier researchers. Because of higher chloride tolerable limit of rebar in PFAC and BFSC concrete, the corrosion resistance is more than that of OPC concrete. It is obvious that the rate of corrosion is mainly governed by the chloride ions near the rebar than  $\text{OH}^-$  ions.

Table 8 compares the rebar mass loss with  $E_{\text{corr}}$  and  $R_p$  of rebar in concretes containing three cements. In OPC, the  $R_p$  value is  $1570 \Omega$  at the threshold chloride concentration of 1.813% by weight of cement. In the case of PFAC, the  $R_p$  value is  $8030 \Omega$  at 2.536% of chloride whereas in BFSC it is  $41395 \Omega$  at 2.453% of chloride. At the threshold chloride concentration, the  $E_{\text{corr}}$  values are  $-351$ ,  $-297$  and  $-166$  mV in OPC, PFAC and BFSC concrete respectively. Higher the  $R_p$  values and less negative  $E_{\text{corr}}$  values in PFAC and BFSC than that of OPC concrete indicates that the additional calcium hydrates formed in the blended cement concretes provides inhibitive effect at the steel concrete interface and able to tolerate up to 2.4% of chloride near the rebar. The higher the concrete resistance observed in PFAC and BFSC concrete at the threshold chloride concentration confirms the lesser availability of free chloride ions in them.

**Table 7 Corrosion initiation time in 0%  $\text{Cl}^-$  added concrete: from OCP and  $R_p$**

Grade	From potential values			From $R_p$ values		
	OPC	PFAC	BFSC	OPC	PFAC	BFSC
M20	151	508	1158	80	1135	1135
M30	271	1158	1158	267	1135	1135
M40	508	>1765	1158	540	>1765	1135



12 Rebar mass loss versus chloride content

## Conclusions

1. The time taken for initiation of corrosion of rebar in 20 MPa concrete is delayed by 3.4 times in PFAC

than that of OPC concrete. In BFSC concrete it is delayed by eight times. In 30 and 40 MPa concrete it is delayed by four and three times in PFAC and BFSC concretes respectively.

2. After 1765 days of exposure, at 0%  $\text{Cl}^-$  chloride level, the durability factor of PFAC concrete is 7.4 times that of OPC in 20 MPa concrete and reduces to three and two in 30 and 40 MPa concretes. The durability factor of BFSC concrete is more than that of PFAC; it is 20 times more in 20 MPa concrete and 73 times in 30 MPa concrete respectively. As compared to OPC concrete, the increase in durability factor in blended cements is not significant in 40 MPa concrete. By comparing the durability factor obtained in all the three concretes at 0.5 and 1% chloride level, a minimum factor of 3 is obtained in PFAC and BFSC concrete.

3. In 0% chloride concrete, the reduction of diffusion of chloride by pore structure refinement as well as binding of more chlorides reduces the corrosion rate of rebar in blended cement concrete compared to that of OPC concrete.

4. In 0.5 and 1%  $\text{Cl}^-$  contaminated concrete, the reduction of free chloride ions by binding more chlorides in PFAC and BFSC concrete enhances the corrosion resistance of rebar. Higher  $\text{Al}_2\text{O}_3$  content of BFSC concrete increases its binding ability and reduces the rate of corrosion compared to that of PFAC concrete.

5. Reduction of  $\text{OH}^-$  ion concentration at the steel/concrete interface did not release the bound chloride as well as did not accelerate the corrosion of rebar. This is confirmed by observing a minimum factor of 10 times reduction of corrosion rate in PFAC and BFSC concrete than in OPC concrete at each interval of exposure period.

6. For the negligible mass loss of 0.09%, the chloride tolerable limit of rebar in blended cement concrete is 1.4 times higher than that of OPC concrete. Higher chloride tolerable limit may be contributed by the higher chloride ion binding capacity of blended cements as well as adsorption of chlorides into the interlayer of calcium silicates hydrates and calcium aluminate hydrates additionally formed by the pozzolanic reaction in blended cements. In addition to this, it appears that the additional calcium hydrates provide certain inhibitive

Table 8 Comparison of rebar mass loss versus  $E_{\text{corr}}$  and  $R_p$

Rebar mass loss, %	Chloride content, %	$E_{\text{corr}}$ , mV (versus SCE)	$R_p$ , $\Omega$	$R_{ct}$ , $\Omega$
OPC				
0.09	1.813	-351	1570	287
1.71	2.466	-422	516	211
4.76	4.315	-472	262	188
6.52	4.649	-459	201	51
PFAC				
0	0.676	-175	17 998	3155
0	1.173	-164	82 420	1173
0	2.453	-296	42 960	4785
0	2.536	-297	8030	2141
1.13	4.902	-352	1053	561
BFSC				
0	0.687	-320	177 800	2270
0	0.779	-115	69 540	2942
0	1.235	-202	8876	2814
0	2.029	-280	5952	1490
0	2.453	-166	41 395	2577
0.56	3.719	-352	2414	1827

effect at the steel concrete interface and increase the chloride tolerable limit near the rebar.

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