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Corrosion performance of medium-strength and silica fume high-strength reinforced concrete in a chloride solution

O. Kayali *, B. Zhu

School of Aerospace, Civil and Mechanical Engineering, University of New South Wales at the Australian Defence Force Academy, Canberra, ACT 2600, Australia

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Abstract

High-strength reinforced silica fume–cement concrete slabs with a compressive strength of 70 MPa were tested for chloride diffusion and corrosion activity after partial immersion in a 2% chloride solution. Similar slabs with 32 MPa conventional concrete were tested in the same environment. Chloride diffusion in high-strength concrete was extremely low. In contrast, a high level of chloride concentration well beyond the depth of steel was noted in 32 MPa concrete. The corrosion potentials in 32 MPa concrete continued to gain larger negative values, far more than the threshold value of –350 mV (CSE). The potential values in high-strength concrete remained fairly stable and were in the vicinity of –200 mV (CSE). Corrosion current density in 32 MPa concrete acquired active values in relatively short time. In high-strength concrete, corrosion current density did not approach the threshold activation value. There is evidence that improvement in corrosion resisting property in high-strength concrete continues after the first 28 days of curing while such improvement does not occur in conventional concrete of 32 MPa. It is concluded that high-strength concrete containing 10% silica fume possesses exceedingly high corrosion resistance.

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1. Introduction

Concrete with compressive strength of more than 50 MPa has become one of the most important construction materials. However, it can be misleading to automatically assume that such concrete would also possess high performance qualities in different service situations. Ranking high among such situations is that of reinforcement corrosion. While the aspects of steel corrosion in reinforced concrete have been extensively studied and documented, the extent of such aspects in high-strength concrete is not evident. High-strength concrete almost invariably contains one or more workability enhancing admixtures. Usually a retarder and/or high range water reducing agent is used. Condensed silica fume and/or fly ash are also known to be widely used in high-strength concrete. The water to cement ratio is

E-mail address: o.kayali@adfa.edu.au (O. Kayali).

usually very low and the water to cementitious materials ratio is even lower. The supplementary cementitious materials are generally pozzolanic and therefore strength gain is expected to continue for a longer time than with conventional concrete. With very low water/ cement ratio, it is expected that the number of coarse pores will be less than in the case of conventional concrete. Pore sizes are also expected to be smaller. Perhaps more important is that many pores are expected to be isolated and the pore structure is expected to be discontinuous. Such development is of particular importance in the process of corrosion. Corrosion of steel in concrete occurs only if certain species are efficiently transported to the vicinity of the reinforcement. The presence of aggressive agents such as chlorides can cause depassivation of the reinforcing steel. Severe corrosion is known to be initiated by the ingress of chloride ions. This can happen in concrete even when the surrounding pH is as high as 12.5 [1]. This type of corrosion deterioration in concrete structures has proven to be the most disastrous and costly [2,3]. The property of diffusion of chloride ions in concrete appears to be the dominant

^{*}Corresponding author. Tel.: +61-2-626-88329; fax: +61-2-626-88337

factor in this type of corrosion. Again, this property depends to a large extent on the pore size distribution in the concrete matrix and whether the pore system is continuous [4,5].

Early in situ testing was suggested so as to alert the possibility of corrosion being active in a structure. Most popular of such testing is the determination of half-cell potential values as described by the ASTM C876 [6]. According to this standard, if the half-cell potential in a certain area is more negative than -350 mV coppercopper sulphate electrode (CSE), then there is a more than 90% probability that corrosion has initiated in that area. These guidelines were based on extensive research as that of Van Daveer [7]. The ASTM standard however, alerts the users that the test is only indicative of possible corrosion. Whether actual corrosion is taking place can only be confirmed by corrosion current measurement.

Research workers have endeavoured to establish a certain value of chloride ion concentration that would be considered as "threshold" value for corrosion initiation. Glass and Buenfeld [8] have reviewed threshold values suggested by many research workers and have shown total chloride values ranging from 0.17% to 2.2% by mass of cement. Kayyali and Hague [9] attached greater importance to the ratio of free chloride to hydroxyl ion concentrations in the pore solution. Concrete standards have suggested certain limits for chloride ion content in the vicinity of the reinforcement [10–12]. A value of 0.4% total chloride by mass of cement has been specified by the British Standard BS 8110 [10] as the maximum limit for total chloride content. ACI 318 [11] specifies a water-soluble chloride content of 0.15% while ACI 222 [13] specifies acid-soluble chloride content of 0.20%. The limit set by the Australian Standards is 0.8 kg/m³ of concrete. For a typical concrete this works out to be 0.235% by mass of cement.

Nevertheless, the limits on chloride concentration and half-cell potential values have been concluded after studies conducted mainly on conventional concrete. That is concrete prepared with natural aggregates, ordinary portland cement and water. Such limits and indicative values might not be correct when the structure is prepared with concrete that has twice the strength and essentially different matrix. Much research is needed to establish such values. Nevertheless, relatively short term testing is important in order to establish bases of comparison.

This paper reports results of a study that has been conducted on reinforced concrete slabs exposed to chloride ion environment. There was no acceleration of testing neither was there an augmentation of chloride ions beyond what is expected in marine or coastal exposure. The testing lasted for nearly two years and the results are believed to show distinct superiority in the performance of high-strength reinforced concrete slabs when exposed to this type of aggressive environment.

2. Experimental program

The program reported here consisted of experiments conducted on two types of concrete: The first type was medium-strength concrete (referred to here as MS) and the second was high-strength concrete (referred to here as HS). In both types, the coarse aggregates were crushed granite and the fines were from river sand. HS concrete contained silica fume as 10% of the cement mass. A sodium polynaphthalene sulphonate superplasticiser was also added to produce the HS concrete. The chemical composition of cement and silica fume are shown in Table 1. Mix constituents, properties of fresh concrete, and the compressive strength are shown in Table 2. Three slabs whose dimensions are 470 mm×470 mm×150 mm, were cast from each mix. One of these

Table 1 Chemical composition of ordinary portland cement and silica fume

Chemical constituent	Cement mass (%)	Silica fume mass (%)
SiO ₂	19.9	94.0
Al_2O_3	6	0.4
Fe_2O_3	4.8	0.7
CaO	64.9	0.3
MgO	0.8	0.1
SO_3	2.7	0.15
Na_2O	0.05	0.2
K_2O	0.4	0.3
Loss on ignition	1.5	3.0
Insoluble residue	0.16	_

Table 2 Mixture proportions, fresh concrete properties and 28-day compressive strength

	Concrete	
	MS	HS
Cement (kg/m³)	295.2	450
Silica fume (kg/m³)	_	45
Total water (kg/m ³)	191.9	166.0
Superplasticiser (1)	_	9
Coarse aggregate (kg/m ³)		
Oven-dried	1210.2	1196.3
SSD condition	1219.9	1205.9
Sand (kg/m ³)		
Oven-dried	663.9	606.4
SSD condition	669.2	611.3
Water needed to arrive at SSD condition (kg/m³)	15.0	14.4
Water in excess of SSD condition (kg/m³)	176.9	151.6
Water/cement ratio	0.60	0.337
Water/cementitious materials ratio	0.60	0.306
Slump (mm)	60	100
Fresh density (kg/m ³)	2350	2390
Air content (%)	4.7	2.0
Compressive strength (MPa)	32.6	72.4

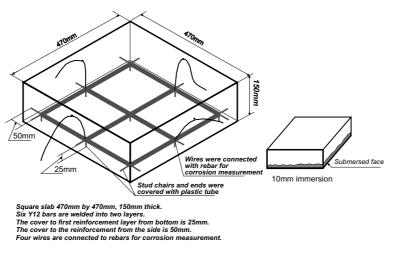


Fig. 1. Schematic details of reinforced concrete slab.

slabs was non-reinforced while the other two were reinforced. The non-reinforced slab served to periodically test for chloride ion penetration. The two reinforced concrete slabs were used to monitor reinforcement corrosion. Details of a typical slab and reinforcement are shown in Fig. 1.

All samples were initially cured for 28 days in a fog room at 21 °C. After the initial curing, one reinforced concrete slab was submerged to only a depth of 10 mm in a basin that contained potable water. The other reinforced slab was submerged to a depth of 10 mm in a basin that contained chloride ion solution. The submerged part was that nearer to the reinforcement. The concrete cover to the reinforcement was 25 mm from the bottom of slab and 50 mm from the side. The chloride solution was prepared by dissolving sodium chloride salt that was extracted and refined from natural seawater. NaCl solutions of 3.5% were prepared. The chloride ion concentration in these solutions was determined by potentiometry and found to be about 20,000 ppm. The salt solution was continuously agitated by means of an air pump and similar agitation was applied to the potable water regime. The concentration of chloride was periodically monitored and adjusted when necessary so as to keep the value of approximately 20,000 ppm relatively constant. The temperature in the containers was 20 ± 2 °C and the relative humidity in the laboratory was around 60%.

Extraction of representative samples from concrete was done using a grinder [14] that is capable of dry drilling, grinding and extracting sufficient quantity of sample at very small intervals of depth. The interval of 5 mm was chosen because it provided reasonably sufficient material for analysis. Determination of chloride ion concentration was performed according to ASTM standard methods C 1152 [15] and C 114 [15,16].

Copper/copper sulphate electrode half-cell potential values were determined as well as the corrosion current density. The corrosion current density was measured using the linear polarization resistance technique. An instrument had been specifically developed to overcome difficulties that were previously encountered when corrosion current density measurements in situ were attempted [17]. The main difficulty was the inability of other devices to accurately define the area of measurement [18]. Measurements of low corrosion rate were reported to have been erroneous by orders of magnitude [2]. The instrument that has been employed here uses a guard ring that was developed for the purpose of accurately defining the area of measurement [19,20] and follows the test method for on-site corrosion rate measurement as recommended by RILEM [21]. Assuming uniform corrosion across the bar surfaces within the confinement of the sensor ring, the measured corrosion current can be converted into corrosion rate. Measurements are taken by placing the sensor on the surface and making an electrical connection to the reinforcing steel. Corrosion current density, corrosion potential, E_{corr} , and electrical resistance of the concrete are measured over a defined area of the rebar by means of a sensor. The sensor, shown schematically in Fig. 2, comprises a central stainless steel counter-electrode, a stainless steel outer counter-electrode, a central reference half cell, an inner ring confinement half cell and an outer ring confinement half cell. The corrosion current density, I_{corr} , is calculated by means of the Stern and Geary [22] relationship:

$$I_{\rm corr} = B/R_p$$

where $B = (\beta_a \cdot \beta_c)/[2.3(\beta_a + \beta_c)]$, and β_a and β_c are the anodic and cathodic Tafel constants, respectively.

It is recommended that for reinforcing steel embedded in concrete, the value of *B* may be taken as 26 mV [23,24]. This technique has been reported to produce accurate results [25–27].

Measurements of $E_{\rm corr}$ and corrosion current density were taken from 20 locations on every slab at each specific testing time. The location of the 20 measurement

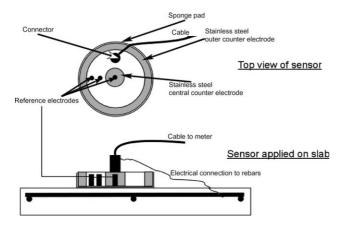


Fig. 2. Schematic details of the main sensor of the corrosion measurement instrument.

points were marked on the slabs parallel to, and directly above the locations of the bars. All measurement locations were on the surface that had been immersed in solution, that is the surface nearer to reinforcement, as schematically shown in Fig. 2. The electrical connection was established via an electrical wire whose end was welded to the rebar before casting. The wire was insulated from the point of weld and back to its socket on the instrument. Four wires were prepared this way on each slab and were welded to rebars at opposite locations as shown in Fig. 1. This was done in order to safeguard against the possibility of losing electrical connection of the cable. This also served to provide repetition of measurements using the different cables as connectors and thus confirm the recorded values. The average of the 20 measurements at each testing time was taken to represent the value of half-cell potential or corrosion current density at that particular duration.

3. Results and discussion

Profiles of chloride ion penetration for MS concrete slabs have been determined over a period of 390 days. These are shown in Fig. 3. After 28 days of exposure, the chloride level at the steel depth has exceeded the British Standards threshold value of 0.4% for corrosion initiation. At 90 days of exposure, the chloride concentration at the steel depth is more than 1%. If a conclusion is now based only on the chloride concentration value, one might conclude that the steel had been in highly active corrosion. However, results presented in Fig. 4 show that at 90 days, the value of half-cell potential has just exceeded -350 mV, CSE. That is it has only arrived to the value of threshold potential for high probability of corrosion activity, which is -350 mV, CSE with respect to copper/copper sulphate electrode [28,29]. The corresponding corrosion current density can be looked up in Fig. 5. From this figure it can be seen that for a 90-day

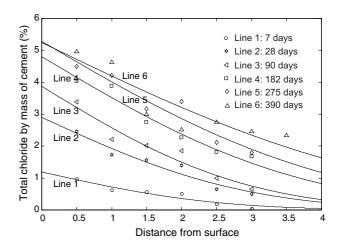


Fig. 3. Chloride concentration profile and regression curves for MS concrete at 7–390 days of exposure.

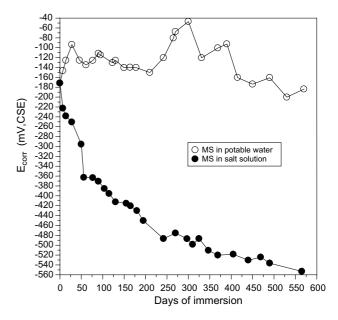


Fig. 4. $E_{\rm corr}$ vs. immersion period for MS concrete.

exposure the current density was around $0.25~\mu A/cm^2$. Several researchers have considered values of current density greater than $0.3~\mu A/cm^2$ to be indicative of active corrosion [30,31]. Andrade and Alonso [24] have provided a set of values for the levels of corrosion rates. They considered that corrosion current density of 0.1– $0.5~\mu A/cm^2$ is low and 0.5–1 $\mu A/cm^2$ is moderate. Values above 1 $\mu A/cm^2$ are considered high while values below $0.1~\mu A/cm^2$ are deemed negligible [3,24]. Gonzalez et al. [3] concluded that corrosion current density less than 0.1– $0.2~\mu A/cm^2$ would be acceptable with no durability risks. Other researchers have nominated the value of $0.3~\mu A/cm^2$ as the threshold for active reinforcement corrosion [31]. However, rates that are above the value of $1~\mu A/cm^2$ are considered hazardous [32]. Therefore,

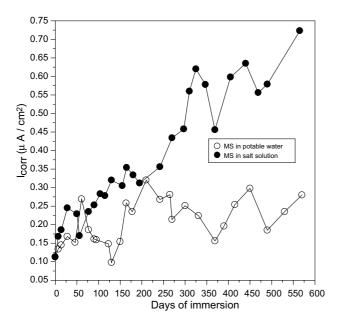


Fig. 5. I_{corr} vs. immersion period for MS concrete.

even if the more conservative value of 0.2 is adopted, when the chloride concentration profiles (Fig. 3) are examined in conjunction with the results obtained from corrosion measurements (Figs. 4 and 5), it can be seen that corrosion did not really pass the threshold of activity until after 90 days of continuous exposure. That is when the half-cell potential and the current density arrived to their threshold values. At that time the chloride ion concentration at the steel level is around 1%. Hence it could be argued that the concentration threshold of 0.4% by mass of cement may seem to be too conservative and that a value of 1% may probably be more realistic. This conclusion agrees very well with that of Lambert et al. for laboratory produced reinforced concrete [33]. It also agrees with the finding of Alonso et al. [34] despite their conservative definition of active corrosion rate being that higher than 0.1 µA/cm². Lambert et al. [33] have however, alerted to the difference in this respect between laboratory produced and field produced concrete. They observed that the limit of 0.4% has been based on surveys of real structures that exhibited chloride induced corrosion problems [35,36]. The difference in the threshold chloride ion concentration between the laboratory produced specimens and real structures may be related to the diffusivity of chlorides to the corrosion site [37]. Dhir et al. [37] showed that chloride concentration by itself cannot be the sufficient indicative of corrosion susceptibility and suggested that the diffusion coefficient of chloride in the particular concrete plays more of a defining role. Therefore, factors that reduce chloride diffusivity in concrete are also expected to reduce the risk of corrosion activity regardless of the chloride concentration at the steel level.

It is further observed that the half-cell potential values (Fig. 4) continued to decrease with the period of exposure. After 390 days, the concentration of chloride at the steel level was about 2.5% of the cement mass, the half-cell potential value was about -520 mV, CSE and the current density was about $0.55 \mu A/cm^2$. After 565 days, the E_{corr}-value was about 560 mV, CSE. Comparing the potential results with those of corrosion current density for the same slabs (Fig. 5), it can be seen that there is a clear correspondence between the value of potential and current density. Corrosion current density values increased from 0.1 μA/cm² at the beginning of exposure to 0.72 μA/cm² at the conclusion of testing. While 0.1 μA/cm² is considered extremely low, the value of 0.72 µA/cm² is considered still within the medium range [24]. This being the case despite the fact that the chloride concentration at the corrosion site level exceeded 2.5% by mass of cement.

Continuous exposure to normal potable water did not appear to adversely affect corrosion behaviour in these slabs. The value of half-cell potential did not drop below -200~mV and the value of corrosion current density remained, on the whole, below $0.3~\mu\text{A/cm}^2.$ Nevertheless, there is evidence of tendency towards more negative values of half-cell potential when this concrete is exposed to potable water for a long time. This may be due to leaching of calcium hydroxide, moisture saturation of the cover layer and a drop in its resistivity, and the availability to oxygen and moisture of a continuous porous system.

The behaviour of MS concrete slabs in potable water and salt solution has not been far from what the authors expected. However, establishing this behaviour in association with this work is necessary when the behaviour of similarly reinforced HS concrete slabs is examined. Diffusion of chloride ions into HS concrete was very shallow. During the nearly two years of exposure period, the value of chloride ion concentration detected beyond a depth of 5 mm was negligibly small. Samples gathered at depths of 10 mm and beyond had no detectable chloride ions. This made establishing reasonably accurate concentration profiles extremely difficult. Nevertheless, within the first 5 mm, the total value of chloride ion concentration in the gathered powder was bout 3% by mass of cementitious material. It is, however, important to note that this value is very much influenced by the concentration at the surface and indeed may be considered to represent the surface concentration [38].

Figs. 6–8 illustrate the values of corrosion measurements on slabs prepared from HS concrete. Fig. 6 shows the development of half-cell potential values throughout the exposure period. The potential values started from –90 mV, CSE for both cases of potable and salt solution submersion. Almost immediately, the slab that was subjected to salt solution displayed a sharp negative

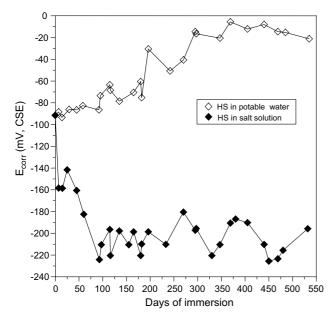


Fig. 6. E_{corr} vs. immersion period for HS concrete.

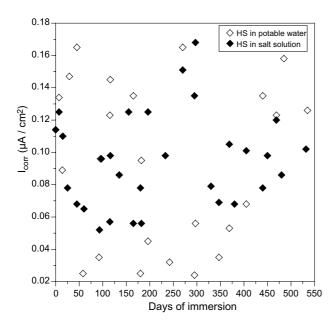


Fig. 7. I_{corr} vs. immersion period for HS concrete.

increase in $E_{\rm corr}$ -values. The descending trend continued until about 100 days of exposure, after which stability is observed to have occurred. $E_{\rm corr}$ -values appeared to fluctuate between -180 and -230 mV. This stable range of values indicates very low corrosion susceptibility. In contrast, the slab that was in contact with potable water showed a steady ascent in the recorded potential values. This trend has not been observed in the slabs of MS concrete. The corrosion potentials in HS concrete slab in potable water was about -20 mV after nearly 550 days while the corresponding E-value for MS concrete slab

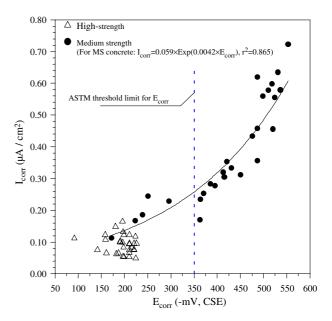


Fig. 8. I_{corr} vs. E_{corr} for MS and HS concretes.

was about -200 mV. The ascending trend in the E-value of high-strength concrete is likely to be the result of continuing chemical reactions due to silica fume. The presence of a pozzolanic additive such as fly ash or silica fume is expected to sharply raise the resistivity of concrete [39]. Silica fume is a highly pozzolanic material [40]. It has been assumed that pozzolanic activity shows significant effects only after 28 days [41]. Swamy and Laiw [42] reported a 23% increase in concrete strength between 28 and 556 days of age when the concrete contained 10% silica fume replacement (by mass of cement). In their study, the strength of the comparable concrete that did not contain silica fume increased by only 8%. Continuing hydration would result in the formation of large formation of C-S-H phase in the capillary pores [42]. This would lead to further pore blocking and constriction and hence a reduction in permeability to moisture and oxygen. Moreover, this result may be regarded as indication of minimal leaching that can occur in HS concrete exposed to potable water. In the HS slabs exposed to chloride, no chloride ions were detected at the depth of steel even after nearly two years of exposure. This points to the likelihood of the effect of a discontinuous pore system that is efficient in blocking the chloride ions from arriving to the surface of the reinforcement. This confirms previously reported results which showed that concrete containing silica fume provided very low permeability to chlorides [43]. Bentz et al. [44] have observed that the pozzolanic gel produced from silica fume has about 25 times less diffusivity than the gel produced from normal cement hydration. Bentz [45] also concluded that a silica fume addition of 10% may reduce the diffusivity of concrete to chloride ions by more than 15 times. Nevertheless, the corrosion potential values of HS concrete in potable water were different to the values in the chloride solution. This is believed to be due to the basic differences that develop in the saturated concrete cover in these two cases. Pastes containing silica fume had been found to result in significant reduction in the pH of the pore solution [46,47]. Gowripalan and Mohamed [48] have more recently confirmed that addition of silica fume resulted in reducing the pH value quite significantly. In contrast, research on the capacity of silica fume to bind chloride ions is still not conclusive. Page and Vennesland [46] observed that silica fume reduced the capacity of the cement to bind chloride ions, while Byfors et al. [49] found that silica fume enhances the chloride binding capacity. In the context of the present work however, it may be fair to say that the electrolyte in the case of potable water immersion is quite different to it when the exposure is to chloride solution.

It is interesting to observe that in spite of the clear difference in $E_{\rm corr}$ -values between the two environments, no such distinction was observed in current density measurements. Fig. 7 shows that the corrosion current density measurements in both environments were similar and extremely low in both conditions.

The relationship between corrosion current density and half-cell potential values during the time of exposure to salt solution is shown in Fig. 8. It is seen here that a current density of about $0.25 \,\mu\text{A/cm}^2$ is associated with the half-cell potential threshold value of 350 mV, CSE. From the results presented in Fig. 8 a relationship between half-cell potential (E_{corr}) and corrosion current density (I_{corr}) for MS concrete could be given by the equation:

$$I_{\text{corr}} = 0.059 \times \exp(0.004E_{\text{corr}}).$$

In less than two years of exposure, corrosion current density exceeding $0.5~\mu\text{A/cm}^2$ could be predicted from this relationship for MS concrete. In contrast, corrosion current density and half-cell potential values for HS concrete remained at a very low level throughout the testing period as can be seen in Fig. 8. At this instant it is important to note that the special ingredients of high-strength concrete such as silica fume, may result in particular effects on performance. Neville [50] pointed out to the special effect of silica fume in reducing corrosion risk by decreasing the penetrability of concrete and increasing its resistivity. It is interesting to note that this effect is observed in spite of the reported results that silica fume decreased the alkalinity of the matrix [46–48].

4. Conclusions

1. Reinforced concrete slabs, where the concrete was of conventional ingredients and medium strength, displayed a low to moderate tendency of reinforcement

- corrosion when partially submerged in chloride solution. This tendency was associated with a high chloride ion concentration occurring at the steel level.
- 2. The chloride concentration that has been recognised previously as the threshold value for initiating reinforcement corrosion appears to be conservative. A concentration value of about 1% by mass of cement seems to be more consistent with other corrosion measurements. Nevertheless, more research is needed to correlate field and laboratory results.
- 3. Reinforced concrete slabs whose concrete included silica fume as 10% by mass of cement and whose strength was around 70 MPa showed extremely low values of corrosion current density and half-cell potentials. These values remained very low even after long exposure to chloride ion solution.
- 4. The performance of high-strength concrete of the type similar to that reported here is believed to be excellent as far as resisting chloride-initiated corrosion is concerned. Nevertheless, the particular properties of the ingredients that are used to produce such concrete are believed to be essential.
- 5. A good correlation was noted between corrosion potential and corrosion current density values for medium-strength concrete. A steady decrease in $E_{\rm corr}$ -values from -170 mV, CSE was accompanied by a steady increase in the corrosion current density from 0.1 to 0.72 μ A/cm².

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