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# **EFFECT OF SULFATE CONCENTRATION AND ASSOCIATED CATION TYPE ON CHLORIDE-INDUCED REINFORCEMENT CORROSION**

## **1. Introduction**

### **1.1 Concrete Durability**

The poor durability performance of reinforced concrete structures is a major problem facing the construction industry throughout the world. It has been estimated that more than \$ 200 billion [1,2] is required to repair and rehabilitate deteriorated concrete structures in the USA. Similarly, it has been estimated that more than £ 2 billion [3,4] will be needed to repair deteriorated concrete structures in the UK. The cost of repair and rehabilitation of deteriorated reinforced concrete structures in the countries along the Arabian Gulf is not well documented. However, considerable resources have to be diverted towards the repair of deteriorated concrete structures in this region.

The deterioration of concrete structures in temperate climatic conditions, as in Europe and North America, is mainly attributed to reinforcement corrosion that is caused by ingress of deicer salts or carbonation. Insufficient concrete cover over reinforcing steel and/or poor quality concrete accelerate the deterioration process. The environmental and geomorphical conditions in the coastal areas of the Arabian Gulf lead to a reduction in the useful service-life of concrete structures in this region. The environment, soil, and ground water, which are heavily admixed with chloride and sulfate salts, are conducive to the initiation of deterioration processes. The daily and seasonal variations in the temperature and the humidity accelerate the rate of deterioration. The ambient temperature in the Arabian Gulf is relatively high (40 to

45 °C) compared to USA or Europe (15 to 25 °C). The direct solar radiation effect raises the temperature to as high as 70 to 80 °C on the concrete surface. This thermal effect influences the over all mechanisms of the deterioration processes, namely reinforcement corrosion, sulfate attack, salt weathering, and shrinkage and thermal cracking. Further, the rate of reinforcement corrosion increases rapidly when the ambient temperature is in the range of 20 to 40 °C.

Concrete normally provides an ideal environment for the reinforcing steel. The high alkalinity of the pore solution aids the formation of a thin invisible protective film on the steel reinforcement, which prevents it from corrosion. However, reinforcement corrosion is initiated once this protective layer is destroyed by aggressive species, such as chloride and carbon dioxide. Chloride ions are considered to be the primary cause of reinforcement corrosion. Further, the rate of reinforcement corrosion is strongly influenced by the environmental factors and concrete properties, such as permeability, type of cement, intensity of cracks, and concrete cover. Moreover, deterioration of concrete structures due to chloride-induced reinforcement corrosion out-weighs that due to carbonation. Chlorides are introduced into the concrete through admixtures, admixed aggregates and/or mixing water. Alternatively, they may penetrate the hardened concrete from the external environment.

Also, several other factors such as temperature, humidity, carbonation and sulfate contamination may directly or indirectly influence the mechanisms of chloride-induced reinforcement corrosion. Temperature and humidity accelerate the rate of reinforcement corrosion, as does carbonation of chloride-admixed concrete. Similarly, the conjoint presence of chloride and sulfate ions may significantly affect

reinforcement corrosion. Such a situation is representative of the marine environments and substructures exposed to soil and groundwater admixed with chloride and sulfate salts. Studies, such as those conducted by Holden et al. [5], Maslehuddin et al. [6] and Hussain [7], have concentrated mainly on the effect of sulfate ions on the chloride binding of cement and reinforcement corrosion. Sodium sulfate was utilized either to contaminate concrete or was admixed in the exposure solution. This was done on the pretext that this is the predominant constituent of sea water, soil and ground water. However, sulfates can be associated with magnesium, calcium and sodium cations. Since the solubility of calcium sulfate is very low, it is expected that the other two salts, namely magnesium sulfate and sodium sulfate, dominate deterioration of concrete. As such, it is appropriate to study the effect of both sodium sulfate and magnesium sulfate on chloride binding and reinforcement corrosion.

## **1.2 Significance of This Research And Gaps In Knowledge**

As stated earlier, deterioration of concrete structures worldwide is mainly attributed to reinforcement corrosion. This could be caused by a reduction in the pH of concrete due to carbonation or the ingress of the chloride ions to the steel surface. Reinforcement corrosion due to carbonation is more common in old structures, particularly in industrial areas. Chloride-induced reinforcement corrosion is normally observed in highway structures (where  $\text{CaCl}_2$  has been used as a deicing salt) and marine structures. In the Arabian Gulf, reinforcement corrosion is mainly attributed to the chloride ions which are either contributed by the mix constituents or they diffuse hardened concrete from the service environment. However, reinforcement

corrosion may also be influenced by the concomitant presence of sulfate and chloride ions.

The earliest investigation to evaluate the effect of sulfate ions on the chloride binding of cements was conducted by Holden et al. [5], who reported a substantial increase in the chloride concentration in the specimens which were admixed with sodium chloride plus sodium sulfate compared to those in which only sodium chloride was admixed. They attributed the reduction in the chloride binding capacity of cements, in the presence of sulfate ions, to the preferential reaction of sulfate ions with C<sub>3</sub>A phase of cement forming calcium sulpho-aluminate hydrate. Maslehuddin et al. [6] evaluated the conjoint effect of chloride and sulfate contamination and temperature on the pore solution chemistry. In their study, cement mortar specimens were admixed with sodium chloride and sodium chloride plus sodium sulfate and exposed to temperatures in the range of 25 to 70 °C. It was reported that both temperature and sulfate contamination influence the chloride binding capacity of plain and blended cements. In the chloride-admixed specimens, the chloride binding was influenced by the exposure temperature. The sulfate contamination had a similar effect to that of temperature on chloride binding. In the presence of sulfate ions, the chloride binding capacity of cements was considerably reduced. This trend was observed at all the exposure temperatures. The sulfate concentration in the specimens admixed with sodium chloride plus sodium sulfate was more than that in the specimens admixed with only sodium sulfate. The authors [6] reported that the quantity of calcium sulpho-aluminate formed in the cements admixed with sodium chloride plus sodium sulfate was less than that formed in the sulfate-admixed specimens. This was attributed to the conjoint reaction of C<sub>3</sub>A with these two ions. The decrease in the

chloride binding capacity of cements, due to the concomitant presence of chloride and sulfate ions, at room temperature, has also been reported by Hussain [7] and Maslehuddin et al. [6] also reported that the sulfates have a more pronounced effect than the increase in temperature.

The increase in the chloride concentration in the concrete admixed with chloride plus sulfate, compared with those admixed with only chloride may increase the rate of reinforcement corrosion in the former concrete. Maslehuddin et al. [8] indicated increased reinforcement corrosion in the concrete specimens admixed with sodium chloride plus sodium sulfate compared to that in the concrete specimens admixed with only sodium chloride. They attributed such behaviour to: (i) decreased chloride binding, and (ii) reduced electrical resistivity, due to the incorporation of sulfate ions in the chloride-admixed concrete. Al-Tayyib et al. [9] reported seven fold increase in the corrosion of mild steel exposed to sulfate containing calcium hydroxide solution compared with similar solutions admixed with only chloride ions. While these two studies [8,9] have been conducted on admixed concrete or electrolyte, data are lacking on the concomitant effect of chloride and sulfate ions penetrating hardened concrete from the external environment. Limited data developed by Al-Amoudi et al. [10-15] indicated that sulfate ions significantly influence the mechanism of chloride-induced reinforcement corrosion. While the sulfate concentration did not affect the time to initiation of reinforcement corrosion, its rate was significantly enhanced. In these studies [10-15] two concentrations of sulfate ions (0.55 and 2.1%) were investigated. The required concentrations of sulfate ions were obtained by mixing equivalent quantities of sodium sulfate and magnesium sulfate salts. Due to this mixing, the effect of cation type associated with the sulfate ions on reinforcement

corrosion could not be appreciated. The present study was, therefore, planned to evaluate: (i) the effect of sulfate concentration and (ii) the cation type associated with the sulfate concentration on reinforcement corrosion. The precise role of sulfate ions on the mechanisms of reinforcement corrosion, however, is not known.

Sulfate ions may be associated with other cations, namely magnesium and calcium. The solubility of calcium sulfate being very low, it is not uncommon to detect magnesium sulfate in seawater and soil and groundwater. The effect of cation type associated with sulfate ions needs also to be studied. Thus, areas requiring further research include:

## **2.4 EFFECT OF SULFATE IONS ON CHLORIDE-INDUCED REINFORCEMENT CORROSION**

As discussed earlier, reinforcement corrosion is caused by carbonation of concrete or by diffusion of chloride ions to the steel surface. The rate of corrosion may, however, be influenced by other factors, namely the presence of other cations, such as sulfates, temperature, availability of reactants, concrete quality etc.

Sulfates are contributed through the mix constituents or they may penetrate the hardened concrete from the service environment, such as seawater. Sulfate ions may influence the rate of reinforcement corrosion by reducing the chloride binding capacity of the cements and/or reducing the electrical resistivity of concrete.

Al-Tayyib et al. [9] reported a seven times increase in the corrosion activity in mild steel exposed to sulfate containing calcium hydroxide solutions over those containing chloride salts. Studies conducted by Al-Amoudi et al. [10-15] on the interactive effect of chloride and sulfate ions on corrosion of steel in cement paste and concrete specimens indicated that sulfate ions are hardly able to initiate

reinforcement corrosion. However, considerable reinforcement corrosion was observed in the cement paste specimens immersed in chloride-sulfate solutions. A free sulfate concentration of more than 0.55%, by weight of cement, associated with a chloride concentration of 15.7%, by weight of cement, was found to be necessary to accelerate reinforcement corrosion.

Similar results indicating higher reinforcement corrosion in specimens admixed with sodium chloride plus sodium sulfate compared to specimens admixed with only sodium chloride have been reported by Maslehuddin et al. [8]. The corrosion current density on steel in the concrete specimens admixed with sodium chloride plus sodium sulfate was 1.28 to 1.65 times that in the specimens admixed with only sodium chloride. Table 2.5 [42] shows some of these results. At room temperature (25 °C), the corrosion current density in Type I cement concrete specimens, admixed with only sodium chloride was  $0.39 \mu\text{A}/\text{cm}^2$  while it was  $0.50 \mu\text{A}/\text{cm}^2$  in the concrete specimens admixed with sodium chloride plus sodium sulfate.

The increase in corrosion current density due to sulfate contamination was 28 to 65%. Maslehuddin et al. [42] attributed the increase in reinforcement corrosion in the concrete specimens admixed with sodium chloride plus sodium sulfate compared to those admixed with only sodium chloride to the following causes. Firstly, the concomitant presence of chloride and sulfate salts increases the concentration of the free chloride ions in the pore solution compared to the specimens admixed with only sodium chloride. This increase in the free chlorides may be helpful in the early initiation of reinforcement corrosion. Secondly, the electrical resistivity of concrete admixed with sodium chloride plus sodium sulfate is lower than that in the specimens admixed with only sodium chloride [47]. Feliu et al. [48] and Lopez and Gonzalez



[49] have observed a direct relationship between the rate of metallic corrosion and the electrical conductivity of concrete.

**Table 2.5: Corrosion current density on steel in the concrete specimens admixed with sodium chloride or sodium chloride plus sodium sulfate [42].**

Exposure Temperature (°C )	Corrosion Current Density ( $\mu\text{A}/\text{cm}^2$ )		
	NaCl	NaCl + Na <sub>2</sub> SO <sub>4</sub>	Increase in I <sub>corr</sub> due to Na <sub>2</sub> SO <sub>4</sub> addition, %
25	0.39	0.50	28
40	0.52	1.27	44
55	1.29	2.14	65
70	1.8	2.45	36

Gouda and Halaka [50] investigated the influence of sulfate ions on reinforcement corrosion in the system Ca(OH)<sub>2</sub>-steel-chloride and reported that the presence of very small concentrations of Na<sub>2</sub>SO<sub>4</sub>, as low as 0.2 %, could cause steel depassivation. Morgan [51] indicated that addition of 50 ppm SO<sub>4</sub><sup>2-</sup> brought about pitting corrosion at chloride concentrations lower than when sulfate was absent. Investigations by Jarrah et al. [52] indicated an increase in the corrosion rate of steel with sulfate concentration in concrete specimens partially immersed in sulfate-chloride solutions. Stratfull [53] investigated the individual effect of sodium sulfate and sodium chloride on reinforcement corrosion. In that study, reinforcement corrosion was observed in the specimens placed in the sodium chloride solution, while it was not observed in specimens placed in the sodium sulfate solution. According to Gouda and Halaka

[50], even high dosages of sulfate ions do not appear to cause serious corrosion of reinforcing steel embedded in Portland cement concrete. Treadaway et al. [54], investigating the concomitant effect of chlorides and sulfates on reinforcement corrosion, reported higher weight loss in the specimens admixed with sodium chloride plus sodium sulfate than in the specimens admixed with only sodium chloride. Macmillan and Treadaway [55] also found higher reinforcement corrosion activity in the specimens admixed with sodium chloride plus sodium sulfate compared to the specimens admixed with only sodium chloride.

Al-Amoudi and Maslehuddin [13] investigated the effect of sodium chloride, mixed sodium and magnesium sulfate or sodium chloride plus mixed sodium and magnesium sulfate on reinforcement corrosion. The results indicated that the sulfate ions are hardly able to induce reinforcement corrosion. However, reinforcement corrosion was significant in the concrete specimens exposed to sodium chloride plus mixed sodium and magnesium sulfate solution and increased two times when the concentration of the mixed sulfate in the 15.7% chloride solution was increased from 0.55 to 2.1. Table 2.6 [13] shows some of these results. It is noticeable from this table that the concentration of water soluble chloride ions was 3.64, 3.58 and 3.56% by weight of cement in the specimens exposed to solutions containing 15.7%  $\text{Cl}^-$ , 15.7  $\text{Cl}^-+0.55\% \text{SO}_4^{2-}$  and 15.7  $\text{Cl}^-+2.1\% \text{SO}_4^{2-}$ , respectively. The concentration of water soluble sulfate ions, however, was influenced by both the chloride and sulfate concentration. It should be noted that the water-soluble chloride and sulfate ions in this table were obtained from solutions prepared by grinding concrete taken near the steel surface. This solution is highly diluted and completely different compared with pore solution that is highly concentrated. Thus the results of water-soluble chloride

and sulfate ions are expected to be different from those obtained by the pore solution analysis.

**Table 2.6: Concentrations (by weight of cement) of water Soluble Chloride and Sulfate Ions [13].**

Solution Composition	Chloride (%)	Sulfate (%)
15.7% Cl <sup>-</sup>	3.64	0.05
2.1% SO <sub>4</sub> <sup>2-</sup>	0.18	0.12
15.7% Cl <sup>-</sup> +0.55% SO <sub>4</sub> <sup>2-</sup>	3.58	0.18
15.7% Cl <sup>-</sup> +2.1% SO <sub>4</sub> <sup>2-</sup>	3.56	0.30

Figure 2.9 [13] shows the variation of corrosion current density with the sulfate concentration in the solution containing 3.6% Cl<sup>-</sup>. These data indicate that reinforcement corrosion due to chlorides is not influenced by water-soluble sulfate concentration below 0.18% by weight of cement. For sulfate concentration of more than 0.18%, the corrosion activity was significantly enhanced. An extension of this study [14] indicated that the effect of sulfate concentration was more pronounced on the corrosion current density, while no systematic effect was noticed on the time to initiation of reinforcement corrosion.

Also, Al-Amoudi et al. [14] indicated that the corrosion potentials in the cement concrete specimens were low in the initial stage of exposure except in the blast

furnace slag cement concrete specimens, which were high from the first day of exposure. They [14] reported that corrosion initiation was noted after about 200 days of exposure in the plain cement concrete specimens while it was noted after about 500 days of exposure in the silica fume cement concrete specimens. High corrosion potentials on steel in the blast furnace slag cement concrete specimens were also reported by Other researchers [47, 11].

Several studies [56-59] indicated that the diffusion of chloride ions was faster than that of the sulfate ions. Oberholster [56] indicated that the diffusion of chloride ions is 10 to 100 times faster than that of sulfate ions. Maslehuddin et al. [60] reported that the high concentration of chloride ions is not only conducive for initiation of reinforcement corrosion, but also decreases the electrical resistivity of concrete which is helpful in sustaining the electrochemical reactions. Saleem et al. [61] indicated that when sulfate concentration was increased from 7.2 to 43.2 kg/m<sup>3</sup>, the electrical resistivity of concrete decreased from 40 to 8 kΩ.cm.

Though sulfate ions are known to accelerate reinforcement corrosion, the relationship between sulfate concentration associated with chloride ions diffusing from external environment and their influence on the rate of reinforcement corrosion needs to be studied. Similarly, there is a need to evaluate the effect of cation type i.e. sodium or magnesium, associated with sulfate ions on reinforcement corrosion.

Corrosion is an electrochemical process. For corrosion to take place a composite of anodes and cathodes, electrically connected through the body of steel itself, are required. At the anode, iron is oxidized to ferrous ions:



At the cathode, in the presence of moisture, oxygen is reduced:



To complete the electrical circuit, the hydroxyl ions produced at the cathode flow back to the anode, where they react with the ferrous ions to form ferrous hydroxide, as shown in Eq. 2.3.



The product of corrosion of steel [ $\text{Fe}(\text{OH})_2$ ] occupies a volume, which is 2 to 14 times the original volume of steel itself. The increased volume exerts tensile stresses on the surrounding concrete that are greater than its flexural strength. Since concrete is weak in tension, it cracks and leading to spalling of the concrete cover.

Objective: to assess the effect of sulfate concentration and associated cation type on chloride-induced reinforcement corrosion;

## 2 EXPERIMENTAL PROGRAM

### 2.1 *Materials and Specimen Preparation*

Five cements, namely sulfate-resisting Portland cement (SRPC;  $\text{C}_3\text{A}$ : 3.6%), ordinary Portland cement (OPC-A;  $\text{C}_3\text{A}$ : 8.5%), blast furnace slag (BFS), silica fume (SF) and fly ash (FA) cements were used to prepare reinforced concrete specimens. In the fly ash cement paste specimens, 20% fly ash was used as a replacement of ordinary Portland cement (OPC-A). In the silica fume cement paste specimens, 10% OPC-A cement was replaced with silica fume, while blast furnace slag cement contained 70% BFS and 30% OPC-A. The chemical composition of the cements and the supplementary cementing materials, as provided by the suppliers, is shown in Table 3.1. Reinforced concrete cylinders, 75 mm in diameter and 150 mm high, were

cast using concrete with an effective water to cementitious materials ratio of 0.45 and total cementitious materials content of  $350 \text{ kg/m}^3$ . Crushed dolomitic limestone with a specific gravity of 2.43 and absorption of 3%, and dune sand with a specific gravity of 2.53 and absorption of 0.57% was used as fine aggregate. The coarse and fine aggregates were clean and free from all types of salts, dust and other fine particles. Table 3.3 shows the grading of coarse aggregate. The quantities of material used in each mix are shown in Table 3.4. The volume of water in each mix was adjusted to compensate for the absorption of coarse and fine aggregate. All mixtures have the same water to cementitious materials ratio to be consistent, but this is not representative of practice where workability is affected. Therefore, in silica fume mixtures, a suitable dosage of Conplast 430, which is a high-range water reducer, was used and the time of mixing was longer than other cements.

**Table 3.1: Composition of cements and supplementary cementing materials.**

Constituent (Wt %)	SRPC <sup>1</sup>	OPC-A <sup>2</sup>	BFS <sup>4</sup>	SF <sup>3</sup>	FA <sup>0</sup>
SiO <sub>2</sub>	22.00	20.52	35.40	92.50	49.72
Al <sub>2</sub> O <sub>3</sub>	4.08	5.64	7.80	0.40	47.58
Fe <sub>2</sub> O <sub>3</sub>	4.24	3.80	0.52	0.40	1.28
CaO	64.07	64.35	43.7	0.50	0.48
MgO	2.21	2.11	8.50	0.90	0.30
SO <sub>3</sub>	1.96	2.10	1.13	0.50	0.20
Loss on ignition	0.80	0.70	-	-	-
K <sub>2</sub> O	0.31	0.36	-	-	-
Na <sub>2</sub> O	0.21	0.19	-	-	-
Na <sub>2</sub> O equivalent	0.41	0.43	-	-	-
C <sub>3</sub> S	54.57	56.70	-	-	-

C <sub>2</sub> S	21.91	16.05	-	-	-
C <sub>3</sub> A	3.64	8.52	-	-	-
C <sub>4</sub> AF	12.90	11.56	-	-	-

<sup>1</sup> Sulfate-resisting Portland cement (C<sub>3</sub>A: 3.6%)

<sup>2</sup> Ordinary Portland cement (C<sub>3</sub>A: 8.5%)

<sup>4</sup> Blast furnace slag

<sup>5</sup> Silica fume

<sup>6</sup> Fly ash

The steel bars were cleaned and coated with an epoxy coating at the concrete-air interface and bottom of the bar in order to avoid crevice corrosion at these locations. The steel bars were cleaned mechanically with a silicon carbide paper, wherever necessary, and degreased with acetone prior to casting in concrete. The concrete specimens were cast in steel moulds. Before casting, the moulds were cleaned and slightly oiled to facilitate the demolding process. The 12 mm diameter steel bar was then fixed centrally at the middle of the mould providing a 25 mm clear cover at the bottom.

The concrete ingredients were mixed in a mechanical mixer and placed in the moulds in two layers by consolidation on a vibrating table. After casting, the specimens were covered with polyethylene sheets and allowed to cure at the laboratory temperature for 24 hours. The specimens were then demolded and cured in potable water maintained at 25 °C for 28 days. After this curing period, the specimens were dried by keeping them at room temperature for one week and then placed in plastic containers containing the test solutions.

***Table 3.3: Grading of coarse aggregate.***

Sieve opening, mm	Percentage passing
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25.0	100
19.0	90
12.5	55
9.5	20
4.75	5
2.36	0

**Table 3.4: Quantities of materials used for casting reinforced concrete cylinders.**

Constituent	Weight per cubic metre, kg
Cementitious material	350
Coarse aggregate	1116
Fine aggregate	684
Water	158

## **2.1 Exposure Solutions**

Seven exposure conditions were investigated, as detailed in Table 3.5. All the test solutions contained 5% NaCl and varying concentrations of sodium or magnesium sulfate solutions. The 5% NaCl solution used in this study represents the chloride concentration of the seawater. The sulfate concentration was varied from 0 to 4% to systematically evaluate the effect of these ions on chloride-induced reinforcement corrosion. However, 4%  $\text{SO}_4^-$  represents the highest quantity of sulfate available in the sabkha soils. Three reinforced concrete specimens from each concrete mix were placed in each solution. The concentration of the solutions was monitored and adjusted every two weeks.



**Table 3.5: Composition of the test solutions.**

<b>GROUP</b>	Concentration of the test solution
1	5 % NaCl
2	5% NaCl + 1% SO <sub>4</sub> <sup>2-</sup> (Na <sub>2</sub> SO <sub>4</sub> was used)
3	5% NaCl + 2.5% SO <sub>4</sub> <sup>2-</sup> (Na <sub>2</sub> SO <sub>4</sub> was used)
4	5% NaCl + 4% SO <sub>4</sub> <sup>2-</sup> (Na <sub>2</sub> SO <sub>4</sub> was used)
5	5% NaCl + 1% SO <sub>4</sub> <sup>2-</sup> (MgSO <sub>4</sub> was used)
6	5% NaCl + 2.5% SO <sub>4</sub> <sup>2-</sup> (MgSO <sub>4</sub> was used)
7	5% NaCl + 4% SO <sub>4</sub> <sup>2-</sup> (MgSO <sub>4</sub> was used)

### **2.3 Monitoring of Reinforcement Corrosion**

Reinforcement corrosion was evaluated by measuring corrosion potentials and corrosion current density ( $I_{\text{corr}}$ ). These techniques are non-destructive in nature and provide both quantitative and qualitative indication of reinforcement corrosion. While corrosion potentials provide a qualitative indication of reinforcement corrosion, particularly its initiation, corrosion current density measurements provide a quantitative measurement of the rate of reinforcement corrosion

Reinforced concrete specimens were partially immersed in the test solution. The level of the solution was adjusted, so that only 85 to 90 mm of the bottom of the specimens was in the solution. Measurements were conducted on three specimens representing similar mix composition and average values were reported. Reinforcement corrosion was evaluated by measuring the corrosion potentials and corrosion current density at regular intervals. The corrosion potentials were measured using a saturated calomel reference electrode (SCE) and a high impedance voltmeter. The steel bar was connected to the positive terminal of the voltmeter

while the reference electrode was connected to its negative terminal. Figure 3.1 shows the schematic diagram of the experimental set up.

The corrosion current density was measured using the linear polarization resistance method (LPRM). In this technique, steel is polarized to  $\pm 20$  mV of the corrosion potential and resulting current is measured and the slope of the potential-current curve at the open circuit potential is obtained. Corrosion current density is then calculated using the Stern-Geary formula [101]:

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

Where

$$I_{\text{corr}} = \text{corrosion current density, } \mu\text{A/cm}^2$$

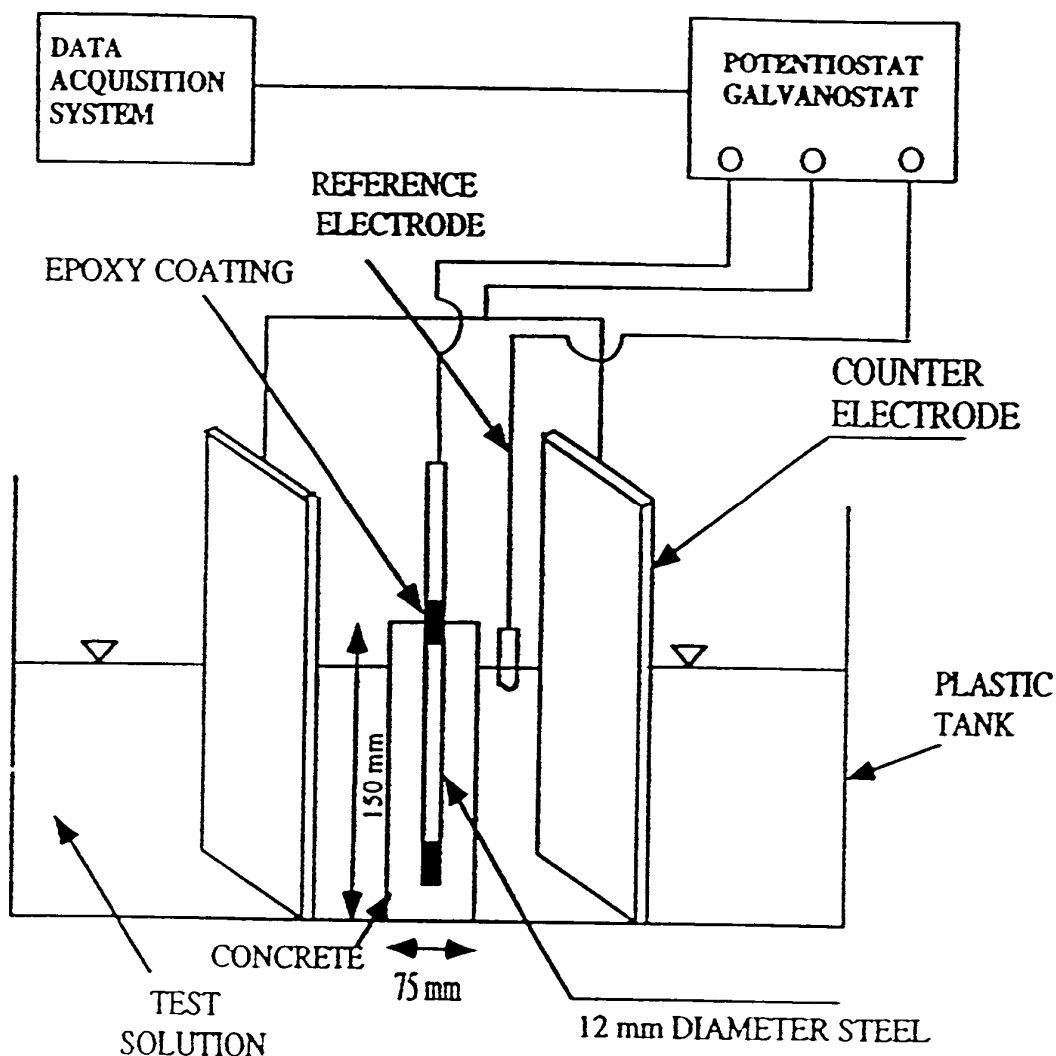
$$R_p = \text{polarization resistance, } \text{K}\Omega\cdot\text{cm}^2 \text{ (slope of the current-potential curve)}$$

$$B = \frac{\beta_a \cdot \beta_c}{2.3(\beta_a + \beta_c)}$$

Where  $\beta_a$  and  $\beta_c$  are the anodic and cathodic Tafel constants, mV/decade, respectively.

The Tafel constants are normally obtained by polarizing the steel to  $\pm 250$  mV of the corrosion potential (Tafel plot). However, in the absence of sufficient data on  $\beta_a$  and  $\beta_c$ , a value of B equal to 26 mV for steel in active condition and 52 mV for steel in passive condition is used [102]. In this investigation, Tafel constants of 120 mV/decade were used. In another study, Dehwah et al. [103] conducted Tafel plot experiments on concrete specimens and the results indicated that, the Tafel constants

are close 120 mV/decade. Lambert et al. [66] reported a good correlation between corrosion rate determined using these values and the gravimetric weight loss method.



**Figure 3.1: Schematic diagram of the experimental set up used to monitor corrosion potentials and corrosion current density.**

## ABSTRACT

The influence of sulfate concentration on chloride-induced reinforcement corrosion was evaluated using cylindrical reinforced concrete specimens, 75 mm

diameter and 150 mm high with a 12 mm diameter steel bar centered in the middle, that were prepared as described in Section 3.3.1. These specimens were exposed to sulfate-chloride solutions, as discussed in Section 3.3.2 and detailed in Table 3.4. The control specimens were placed in a 5% NaCl solution, while the other specimens were exposed to solutions containing both chloride and sulfate ions. The sulfate concentrations in the test solutions were varied as shown in Table 3.4. Also, the effect of cation type ( $\text{Na}^+$  or  $\text{Mg}^{++}$ ) associated with sulfate ions on reinforcement corrosion was investigated. Reinforcement corrosion was evaluated by measuring corrosion potentials and corrosion current density at regular intervals, as detailed in Section 3.3.3. The corrosion potentials and corrosion current density were measured on three replicate specimens. Statistical analysis indicated that the coefficient of variation between the three readings was within acceptable range. However, in limited instances where spurious readings were obtained, they were excluded while calculating the average value.

## **3 RESULTS**

### **3.1 CORROSION POTENTIALS**

#### ***3.1.1 Corrosion Potentials in Plain Cement Concrete Specimens***

The variation of corrosion potentials with time on steel in the SRPC concrete specimens exposed to 5% NaCl solution, containing 0, 1, 2.5 and 4%  $\text{SO}_4^{--}$ , derived from sodium sulfate, is shown in Figures 5.1 through 5.4, respectively. Initially, the corrosion potentials were high (less negative) and decreased with the period of exposure. However, after 180 days of exposure, the corrosion potentials tended to be stable in all the specimens. Figures 5.5 through 5.7 depict the variation of corrosion potentials with time in the SRPC concrete specimens exposed to 5% sodium chloride

solution containing 1, 2.5 and 4%  $\text{SO}_4^{--}$ , derived from magnesium sulfate, respectively. In these specimens also the corrosion potentials were high in the initial stages but decreased almost linearly with the period of exposure.

The corrosion potentials on steel in the OPC-A ( $\text{C}_3\text{A}$ : 8.5%) concrete specimens exposed to 5% NaCl solution containing 0, 1, 2.5 and 4%  $\text{SO}_4^{--}$ , derived from sodium sulfate, are plotted against period of exposure in Figures A-1 through A-4 respectively. The trend of these data was similar to that indicated by steel in the SRPC concrete specimens exposed to similar solutions. The corrosion potentials in the OPC-A of concrete specimens exposed to sodium chloride plus magnesium sulfate solution are plotted in Figures A-5 through A-7, respectively. The corrosion potentials in these specimens were initially high but decreased with the period of exposure. However, these values were almost stable after 200 days. The corrosion potentials on steel in the concrete specimens exposed to 4% sulfate solution were high initially, but decreased linearly with the period of exposure.

Figures A-8 through A-11 show the variation of corrosion potentials with time on steel in the OPC-B ( $\text{C}_3\text{A}$ : 9.65%) concrete specimens exposed to 5% NaCl solution containing 0, 1, 2.5 and 4%  $\text{SO}_4^{--}$ , in the form of sodium sulfate, respectively. In these specimens also the corrosion potentials decreased with time and were stable after about 150 days. The variation of corrosion potentials with time on steel bars in these types of concrete specimens exposed to 5% NaCl solution mixed with 1, 2.5, and 4%  $\text{SO}_4^{--}$ , derived from magnesium sulfate, are plotted in Figures A-12 through A-14, respectively. The trend of these data was more or less similar to that noticed in the OPC-A concrete specimens exposed to similar solutions.

### ***3.1.2 Corrosion Potentials in Blended Cement Concrete Specimens***

The corrosion potentials on steel bars in the blast furnace slag (BFS) cement concrete specimens exposed to 5% NaCl solution admixed with 0, 1, 2.5 and 4%  $\text{SO}_4^-$ , derived from sodium sulfate, are plotted in Figures 5.8 through 5.11, respectively. The corrosion potentials in these specimens also decreased with time. Figures 5.12 through 5.14 depict the variation of corrosion potentials on steel in the blast furnace slag cement concrete specimens exposed to 5% NaCl solution admixed with 1, 2.5, and 4%  $\text{SO}_4^-$ , derived from magnesium sulfate, respectively. The corrosion potentials on steel in the blast furnace slag cement concrete specimens were either less than -270 mV SCE right from the initial stages of exposure, or a drastic reduction in the potentials were noted after one week of exposure.

Low corrosion potentials in the blast furnace slag cement concrete specimens were also reported by Maslehuddin et al. [111], Khan [47], and Al-Amoudi [78]. Macphee [112] attributed the low corrosion potentials on steel in the blast furnace slag cement concrete specimens to the reducing effect of sulfur species, namely  $\text{S}^-$ ,  $\text{S}_2\text{O}_3$ , etc, derived from the slag. These sulfur species create a reducing environment resulting in low corrosion potentials on steel in these cement concrete specimens. Also, the low corrosion potentials on reinforcing steel bars in the blast furnace slag cement concrete specimens may be attributed to the relatively excessive volume of free water available in this cement compared with other cements. Arup [113] attributed the high free water content to the lower water requirement for the pozzolanic reaction of slag compared to that required for hydration of ordinary Portland cement. The free water in the blast furnace slag cement present in the finer pores impedes the access of oxygen to steel-concrete interface. The limited access of

oxygen does not favor the formation of passive film that gives an impression that the steel is in an active state of corrosion. However, the corrosion current density is normally very low. This situation is similar to the state of reinforcing steel embedded in concrete structures located in the submerged zones of marine structures.

The corrosion potentials on steel in the silica fume (SF) cement concrete specimens exposed to 5% NaCl solution mixed with 0, 1, 2.5 and 4%  $\text{SO}_4^{--}$ , in the form of sodium sulfate, are plotted against period of exposure in Figures A-15 through A-18, respectively. The corrosion potentials were high during the initial stages of exposure. However, a sharp decrease was noted up to 210 days of exposure beyond which the potentials were more or less similar. Figures A-19 through A-21 show the time corrosion potentials curves for steel in the silica fume cement concrete specimens placed in 5% NaCl solutions admixed with 1, 2.5 and 4%  $\text{SO}_4^{--}$ , derived from magnesium sulfate, respectively. Initially, the corrosion potentials were high and thereafter decreased sharply up to an exposure period of 190 days and were stable at later times.

The corrosion potentials on steel in the fly ash (FA) cement concrete specimens exposed to 5% NaCl solutions containing 0, 1, 2.5 and 4%  $\text{SO}_4^{--}$ , derived from sodium sulfate, are plotted against time of exposure in Figures A-22 through A-25, respectively. The potentials decreased with time and were stable after about 150 days. Figures A-26 through A-28 show the corrosion potential-time curves for steel in the fly ash cement concrete specimens exposed to 5% NaCl solutions containing 1, 2.5 and 4%  $\text{SO}_4^{--}$ , derived from magnesium sulfate, respectively. The potentials decreased with time and were stable at later times.

### **3.2 TIME TO INITIATION OF REINFORCEMENT CORROSION**

The time-corrosion potential curves, discussed in Section 5.2, were used to evaluate the time to initiation of reinforcement corrosion, based on the ASTM C876 criterion. These values are summarized in Table 5.1 and plotted against sulfate concentration in Figures 5.15 and 5.16.

The time to initiation of reinforcement corrosion did not vary significantly with the type and concentration of the sulfate solution. However, corrosion initiation time was influenced by the type of cement. For example, reinforcement corrosion in plain cements occurred earlier than in blended cement concrete specimens. In the plain cements, reinforcement corrosion in SRPC ( $C_3A$ : 3.6%) occurred earlier than in OPC. In other words, the time to initiation of reinforcement corrosion increased with the  $C_3A$  content of cement. The delay in corrosion initiation in the plain cements, with increasing  $C_3A$  content, may be attributed to the chloride-binding capacity of cements with high  $C_3A$  content.

Among blended cements, corrosion initiation in the fly ash cement concrete specimens was noted earlier than that in the silica fume cement concrete specimens. The higher time to initiation of reinforcement corrosion in the blended cements may be attributed to their dense structure, which retards the diffusion of chloride ions to the steel surface. The delay in the initiation of reinforcement corrosion in the silica fume cement concrete is due to its dense structure compared to other plain and blended cements.



*Table 1: Time to initiation of reinforcement corrosion in the concrete specimens exposed to sodium chloride plus sodium sulfate or magnesium sulfate solutions.*

Exposure Solution	Time to initiation of reinforcement corrosion, days				
	SRPC	OPC-A	OPC-B	SF	FA
5% NaCl	118	132	139	201	159
5% NaCl + 1% SO <sub>4</sub> <sup>2-</sup> (Na <sub>2</sub> SO <sub>4</sub> )	113	117	119	205	155
5% NaCl + 2.5% SO <sub>4</sub> <sup>2-</sup> (Na <sub>2</sub> SO <sub>4</sub> )	137	146	148	158	153
5% NaCl + 4% SO <sub>4</sub> <sup>2-</sup> (Na <sub>2</sub> SO <sub>4</sub> )	119	133	131	158	168
5% NaCl + 1% SO <sub>4</sub> <sup>2-</sup> (MgSO <sub>4</sub> )	111	115	114	134	160
5% NaCl + 2.5% SO <sub>4</sub> <sup>2-</sup> (MgSO <sub>4</sub> )	116	126	131	152	151
5% NaCl + 4% SO <sub>4</sub> <sup>2-</sup> (MgSO <sub>4</sub> )	127	137	141	88	157

The time to initiation of reinforcement corrosion in the blast furnace slag cement concrete specimens was not evaluated using the ASTM C 876 criterion as the corrosion potentials in most of the specimens were less than -270 mV SCE from the initial stages of exposure. Several researchers [47,78,111] have reported similar results and the probable reasons for such a behavior have been discussed in Section 5.2.2.

### **3.3 CORROSION CURRENT DENSITY**

#### ***3.3.1 Corrosion Current Density in Plain Cement Concrete Specimens***

The variation of corrosion current density ( $I_{\text{corr}}$ ) with time on steel in the SRPC concrete specimens exposed to 5% NaCl solutions containing 0, 1, 2.5 and 4% SO<sub>4</sub><sup>2-</sup>, derived from sodium sulfate, is plotted against period of exposure in Figure 5.17. The  $I_{\text{corr}}$  increased almost linearly with the period of exposure. These values were very low and similar in all the specimens in the initial stages of exposure of up to 90

days. However, after this time, the  $I_{\text{corr}}$  on steel in the concrete specimens exposed to sodium chloride plus sodium sulfate solutions was more than that in the specimens exposed to sodium chloride solution.

Figure 5.18 shows the variation of  $I_{\text{corr}}$  with time in the SRPC concrete specimens exposed to 5% NaCl solutions admixed with 0, 1, 2.5, and 4%  $\text{SO}_4^{--}$ , derived from magnesium sulfate. Almost a linear increase in the  $I_{\text{corr}}$  values, with the period of exposure, was observed in all the specimens. Initially, these values were low and approximately the same in all the specimens. However, they increased with time and after 160 days of exposure, the  $I_{\text{corr}}$  on steel in the concrete specimens exposed to sodium chloride plus magnesium sulfate solution was more than that in the specimens exposed to only sodium chloride solution. Further, the  $I_{\text{corr}}$  values increased with increasing magnesium sulfate concentration of up to 2.5%, beyond which, the  $I_{\text{corr}}$  decreased slightly. The decrease in the  $I_{\text{corr}}$  due to excess of magnesium sulfate (4%  $\text{SO}_4^{--}$ ) may be attributed to the formation of magnesium hydroxide which blocks the pores in the concrete specimens exposed to these solutions and retards the ingress of oxygen and aggressive species to the reinforcing steel.

Figures 5.19 and 5.20 show the variation of  $I_{\text{corr}}$  with time of exposure on steel in the OPC-A ( $\text{C}_3\text{A}$ : 8.5%) and OPC-B ( $\text{C}_3\text{A}$ : 9.65%) concrete specimens exposed to 5% NaCl plus 0, 1, 2.5, and 4%  $\text{SO}_4^{--}$  sodium sulfate solutions, respectively. The trend of these data was similar to that exhibited by the SRPC concrete specimens exposed to similar solutions.

Figures 5.21 and 5.22 depict the  $I_{\text{corr}}$  on steel in the OPC-A and OPC-B concrete specimens exposed to 5% NaCl solution, admixed with 0, 1, 2.5, and 4%  $\text{SO}_4^{--}$ ,

derived from magnesium sulfate, respectively. The trend of these data was similar to that exhibited by the SRPC concrete specimens exposed to similar solutions.

### ***3.3.2 Corrosion Current Density in Blended Cement Concrete Specimens***

The  $I_{\text{corr}}$  on steel in the blast furnace slag cement concrete specimens exposed to 5% NaCl solution containing 0, 1, 2.5 and 4%  $\text{SO}_4^-$ , in the form of sodium sulfate, is plotted against period of exposure in Figure 5.23. These values were very low and similar in all the specimens in the initial stages of exposure of up to 125 days. After this period, the  $I_{\text{corr}}$  started to deviate and increase with time of exposure. The  $I_{\text{corr}}$  on steel in the concrete specimens exposed to sodium chloride plus sodium sulfate was more than that in the specimens exposed to sodium chloride only. Further, the  $I_{\text{corr}}$  increased with increasing sodium sulfate concentration.

Figure 5.24 depicts the  $I_{\text{corr}}$  on steel in the blast furnace slag cement concrete specimens exposed to 5% NaCl solutions containing 0, 1, 2.5 and 4%  $\text{SO}_4^-$ , derived from magnesium sulfate. The  $I_{\text{corr}}$  increased with period of exposure. Initially, the  $I_{\text{corr}}$  was very low and similar in all the specimens up to 150 days of exposure beyond which the  $I_{\text{corr}}$  started to increase. The  $I_{\text{corr}}$  in the concrete specimens exposed to sodium chloride plus magnesium sulfate was more than that in the specimens exposed to only sodium chloride. Further, the  $I_{\text{corr}}$  increased with increasing concentration of magnesium sulfate up to 2.5%  $\text{SO}_4^-$ , beyond which the  $I_{\text{corr}}$  decreased slightly. This trend is similar to that noted in the plain cement concrete specimens exposed to sodium chloride plus magnesium sulfate solution.

The  $I_{\text{corr}}$  values on steel in the silica fume and fly ash cement concrete specimens exposed to 5% NaCl solutions containing 0, 1, 2.5 and 4%  $\text{SO}_4^-$ , derived from

sodium sulfate, are shown in Figures 5.25 and 5.26, respectively. The trend of these data was similar to that exhibited by BFS cement specimens exposed to similar solutions.

Figures 5.27 and 5.28 show the  $I_{\text{corr}}$  on steel in the silica fume and fly ash cement concrete specimens exposed to 5% NaCl solution containing 0, 1, 2.5 and 4%  $\text{SO}_4^-$ , derived from magnesium sulfate, respectively. The trend of these data was similar to that exhibited by the blast furnace slag cement concrete specimens exposed to similar solutions.

### ***3.3.3 Corrosion Current Density in Plain and Blended Cement Concrete Specimens***

The  $I_{\text{corr}}$  on steel in the plain and blended cement concrete specimens after 1200 days of exposure to chloride-sulfate solution is summarized in Table 5.2. The  $I_{\text{corr}}$  in the plain cement concrete specimens was much higher than that in the blended cement specimens. Further, the  $I_{\text{corr}}$  on steel in the concrete specimens exposed to chloride plus sulfate solution was more than that in the specimens exposed to chloride solution.

The  $I_{\text{corr}}$  on steel in plain and blended cement concrete specimens exposed to sodium chloride plus sodium sulfate solution is plotted against sulfate concentration in Figures 5.29 and 5.30. The  $I_{\text{corr}}$  increased almost linearly with increasing concentration of sodium sulfate. The  $I_{\text{corr}}$  on steel in the plain and blended cement concrete specimens exposed to sodium chloride plus magnesium sulfate is plotted against sulfate concentration in Figures 5.31 and 5.32. In these specimens, the  $I_{\text{corr}}$  increased with increasing concentration of magnesium sulfate up to 2.5%  $\text{SO}_4^-$ .

However, it decreased slightly when the magnesium sulfate concentration was increased from 2.5 to 4%.

The  $I_{\text{corr}}$  on steel in the concrete specimens exposed to sodium chloride plus sodium sulfate is plotted against  $C_3A$  in Figure 5.33. The  $I_{\text{corr}}$  decreased significantly with increasing  $C_3A$  content. Figure 5.34 shows the relationship between  $I_{\text{corr}}$  and  $C_3A$  in the concrete specimens exposed to sodium chloride plus magnesium sulfate. The trend of these data is similar to that exhibited by concrete specimens exposed to sodium chloride plus sodium sulfate as shown in Figure 5.33.

Table.2: Corrosion Current Density after 1200 days of exposure.

Exposure solution	Corrosion current density, $\mu\text{A}/\text{cm}^2$					
	SRPC	OPC-A	OPC-B	BFS	SF	FA
5% NaCl	1.83	1.49	1.13	0.23	0.25	0.42
5% NaCl + 1% $\text{SO}_4^{--}$ ( $\text{Na}_2\text{SO}_4$ )	2.13	1.86	1.37	0.40	0.3	0.48
5% NaCl + 2.5% $\text{SO}_4^{--}$ ( $\text{Na}_2\text{SO}_4$ )	2.48	2.17	1.93	0.46	0.42	0.55
5% NaCl + 4% $\text{SO}_4^{--}$ ( $\text{Na}_2\text{SO}_4$ )	2.6	2.36	2.26	0.49	0.43	0.67
5% NaCl + 1% $\text{SO}_4^{--}$ ( $\text{MgSO}_4$ )	2.89	2.08	1.95	0.25	0.33	0.47
5% NaCl + 2.5% $\text{SO}_4^{--}$ ( $\text{MgSO}_4$ )	3.25	2.74	2.52	0.3	0.39	0.58
5% NaCl + 4% $\text{SO}_4^{--}$ ( $\text{MgSO}_4$ )	3.06	2.36	2.1	0.27	0.35	0.51

#### **4 DISCUSSION ON THE EFFECT OF SULFATE CONCENTRATION ON REINFORCEMENT CORROSION**

The role of sulfate ions on chloride-induced reinforcement corrosion is not very well investigated, particularly the effect of the associated cation. However, most of the data on this aspect have indicated an increase in the corrosion activity in the concrete specimens exposed to chloride and sulfate solutions. Stratfull [53] studied the individual effect of sodium chloride and sodium sulfate on reinforcement corrosion. In his investigation [53], reinforcement corrosion was observed in the concrete specimens exposed to sodium chloride solution while it was not noted in the specimens exposed to sodium sulfate solution. Gouda and Halaka [50] reported that, even high dosages of sulfate ions do not cause serious corrosion of reinforcing steel embedded in Portland cement concrete. Treadaway et al. [54] investigated the concomitant effect of chloride and sulfate ions on reinforcement corrosion in SRPC specimens. The results indicated higher weight loss in the specimens admixed with sodium chloride plus sodium sulfate compared to those specimens admixed with only sodium chloride.

Al-Amoudi and Maslehuddin [13] investigated the influence of sulfate and sulfate plus chloride ions on reinforcement corrosion in OPC concrete specimens and the results indicated that while the sulfate ions are hardly able to induce reinforcement corrosion, it was significant in the concrete specimens exposed to sodium chloride plus sodium sulfate solution. Reinforcement corrosion increased two times when the sulfate concentration in the 15.7% chloride solution has increased from 0.55 to 2.1%. An extension of this study [14] indicated a similar trend. The effect of sulfate concentration was observed to be more pronounced on the  $I_{\text{corr}}$  while no systematic

effect was observed on the time to initiation of reinforcement corrosion. Macmillan and Treadaway [55] indicated higher reinforcement corrosion in the concrete specimens admixed with chloride and sulfate salts than in the specimens admixed with only sodium chloride. The corrosion rate of steel in the concrete specimens admixed with 0.4%  $\text{Cl}^- + \text{SO}_4^{2-}$  was higher than that in the concrete specimens admixed with only 0.4%  $\text{Cl}^-$ , and was similar to those admixed with 1%  $\text{Cl}^-$ . Maslehuddin [43] indicated that the increase in reinforcement corrosion due to the concomitant presence of sulfate and chloride salts was 1.1 to 2.4 times that measured in the concrete specimens admixed with only sodium chloride. The increase in reinforcement corrosion due to the presence of sulfate ions was attributed to a decrease in the chloride binding and the electrical resistivity of concrete.

Few studies [9,50-51] were also conducted to investigate the influence of sulfate ions on corrosion of steel exposed to saturated  $\text{Ca}(\text{OH})_2$  solution. Morgan [51] found that addition of 50 ppm of  $\text{SO}_4^{2-}$  brought about pitting at lower chloride concentrations than when sulfate was absent. Gouda and Halaka [50] reported that small concentrations of  $\text{Na}_2\text{SO}_4$ , as low as 0.2%, could cause steel depassivation. Al-Tayyib et al. [9] indicated that corrosion of mild steel immersed in the sulfate solution, at elevated temperature ( $50^\circ\text{C}$ ) was seven times that immersed in the pure chloride solution. The increase in reinforcement corrosion was attributed to the modification of the protective ferric oxide film to a sulfate film, which may be less protective than the former.

As shown in Table 5.1, the data produced in the present study shows that sulfate ions have little effect on time to initiation of reinforcement corrosion. This may be attributed to the fact that initiation of reinforcement corrosion, when exposed to

mixed chloride and sulfate solution is predominantly governed by the relative diffusivity of these two ions. Several studies [52,56-59] have indicated that chloride ions diffuse faster than sulfate ions into hardened cement paste. Oberholster [56] reported that the diffusion of chloride ions is generally 10 to 100 times faster than that of sulfates. Rio and Turriziani [57] indicated that the diffusion of  $\text{Cl}^-$  ions in plain and blended cements was twice that of  $\text{SO}_4^{2-}$  ions. Stratfull [53] reported that concrete retained 14 times more chloride ions than sulfate ions. Barnes and Roy [58] reported that the diffusion rates of  $\text{SO}_4^{2-}$  ions is 2 to 5 times that of  $\text{Na}^+$  ions. Bakker [59] indicated that the diffusion of chloride anions is considerably faster than  $\text{SO}_4^{2-}$  and other cations. Oberholster [56] reported that the diffusion coefficient of chloride ions in hardened cement pastes increases when they are associated with divalent ions compared to monovalent ions.

The corrosion current density on steel in the concrete specimens exposed to chloride-sulfate solution was more than that in the specimens exposed to chloride solution. Further, the  $I_{\text{corr}}$  increased with increasing sulfate concentration.

The increase in the  $I_{\text{corr}}$  in the concrete specimens exposed to chloride and sulfate solutions may be attributed to the following two factors.

1. Increase in the concentration of free chloride ions in the pore solution due to the concurrent presence of sulfate and chloride ions.
2. Decrease in the electrical resistivity of concrete due to the concomitant presence of sulfate and chloride ions.

As discussed in Chapter 4, the concomitant presence of chloride and sulfate ions increases the concentration of free chloride ions in the pore solution. This increase in



the free-chloride ion concentration is ascribed to the simultaneous reaction of  $C_3A$  with both chloride and sulfate ions. Chloride ions normally react with  $C_3A$  in cement to form an insoluble compound known as calcium chloro-aluminate hydrate ( $C_3A \cdot CaCl_2 \cdot 10H_2O$ ), also known as Friedel's salt. This chemical reaction reduces the quantity of free chloride ions in the pore solution thereby decreasing the chances of steel depassivation. When chloride and sulfate ions are present,  $C_3A$  reacts with both sulfate and chloride ions as a result the proportion of chlorides bound is less than that when only chlorides are present. Holden et al. [5] evaluated the effect of sulfate ions on the chloride-binding capacity of cement, and reported a substantial increase in the chloride concentration in the specimens that were admixed with sodium chloride plus sodium sulfate compared to those admixed with only sodium chloride. The reduction in the chloride-binding capacity of cements, in the presence of sulfate ions, was attributed to the preferential reaction of the sulfate ions with  $C_3A$  forming calcium sulpho-aluminate hydrate. Maslehuddin et al. [6] indicated that  $C_3A$  reacts simultaneously with chloride and sulfate ions.

Maslehuddin et al. [60] also indicated that the effect of sulfate ions on chloride binding is similar to the effect of temperature. The elevated concentration of chloride ions, due to the concomitant presence of chloride and sulfate ions is not only conducive for initiation of reinforcement corrosion, but also decreases the electrical resistivity of concrete which is helpful in sustaining the electrochemical reactions.

The other factor that may contribute to an increase in the  $I_{corr}$  due to the concomitant presence of chloride and sulfate ions is the reduction in the electrical resistivity of concrete. The electrical resistivity of concrete specimens admixed with chloride plus sulfate salts is generally lower than that of specimens admixed with

only chloride ions. Khan [47] indicated that the electrical resistivity of concrete specimens admixed with sodium chloride was 1.4 to 7 times that of specimens admixed with sodium chloride plus sodium sulfate. Saleem et al. [61] reported that electrical resistivity of concrete decreased from 40 to 8 k $\Omega$ .cm when sulfate contamination was increased from 7.2 to 43.2 kg/m<sup>3</sup>. Further, the results [61] indicated that in the presence of sulfate, the tolerable level of chloride concentration, for reinforcement corrosion, decreased from 19.28 to 4.8 kg/m<sup>3</sup>. Several studies [17,47-48,58] have related the rate of reinforcement corrosion to electrical resistivity of concrete. Browne [17] investigated offshore structures and concluded that the concrete resistivity must fall below the range of 5,000 to 10,000  $\Omega$ .cm in order to support corrosion of reinforcement. An investigation of corrosion damage in a highway bridge conducted by Cavalier and Vassi [115] showed that reinforcement corrosion was almost certain when the electrical resistivity of concrete was below 5000  $\Omega$ .cm. Felliu et al. [48] and Lopez and Gonzalez [49] have observed a direct proportionality between the rate of metallic corrosion and the electrical conductivity of concrete.

The data produced in the present study suggest that the concomitant presence of chloride and sulfate ions does not influence the time to initiation of reinforcement corrosion. This trend was noted in both plain and blended cements when exposed to either sodium sulfate or magnesium sulfate solution admixed with sodium chloride. Such a behavior has also been reported by Al-Amoudi et al. [13-14], who exposed hardened concrete specimens to mixed solutions of sodium chloride, sodium sulfate and magnesium sulfate. In those studies [13-14] two concentrations of sulfate ions (0.55 and 2.1%) were investigated. The required concentration of sulfate ions was

obtained by mixing equal quantities of sodium sulfate and magnesium sulfate salts. Due to this mixing, the effect of cation type associated with the sulfate ions on reinforcement corrosion could not be appreciated. Maslehuddin et al. [42] reported that  $I_{\text{corr}}$  on steel in the concrete specimens admixed with sodium chloride plus sodium sulfate and exposed to temperature in the range of 25 to 70 °C increased 1.28 to 1.65 times that in specimens admixed with only sodium chloride.

The data developed in this study have also indicated that  $I_{\text{corr}}$  is influenced by the cation type associated with the sulfate ions. The  $I_{\text{corr}}$  increased with increasing concentration of sodium sulfate. Similarly, the  $I_{\text{corr}}$  increased as the concentration of magnesium sulfate increased. However, the  $I_{\text{corr}}$  decreased slightly when the concentration of magnesium sulfate was increased from 2.5 to 4.0%. The decrease in the  $I_{\text{corr}}$  due to excess of magnesium sulfate may be attributed to the formation of  $\text{Mg}(\text{OH})_2$  [76-77] which blocks the pores in the concrete specimens exposed to these solutions and retards the ingress of oxygen and aggressive species to the steel surface. In general, the data developed in the present study indicate that the chances of reinforcement corrosion, particularly the corrosion rate, increases when sulfate and chloride ions are concurrently present.

## 5. Conclusions

1. The combined presence of sulfate and chloride ions did not affect the time-to-initiation of reinforcement corrosion. However, the presence of sulfate ions in the chloride solution increased the rate of reinforcement corrosion. The  $I_{\text{corr}}$  increased with increasing sodium sulfate or magnesium sulfate. In the specimens exposed to magnesium sulfate solution, the increase continued up to 2.5%  $\text{SO}_4^{--}$ , beyond which, the  $I_{\text{corr}}$  decreased slightly.

2. The combined presence of sulfate and chloride ions did not affect the time-to-initiation of reinforcement corrosion. This is understandable since the chloride ions diffuse much faster than the sulfate ions.
3. The concurrent presence of chloride and sulfate ions, however, increased the rate of reinforcement corrosion.
4. The corrosion current density ( $I_{\text{corr}}$ ) on steel in plain and blended cement concrete specimens was very low and similar at the initial stages of exposure. However, it increased with the period of exposure.
5. The  $I_{\text{corr}}$  on steel in plain and blended cement concrete specimens exposed to sodium chloride plus sodium sulfate or sodium chloride plus magnesium sulfate solutions was more than the  $I_{\text{corr}}$  on steel in the concrete specimens exposed to only sodium chloride solution.
6. The  $I_{\text{corr}}$  on steel in plain and blended cement concrete specimens exposed to sodium chloride plus sodium sulfate solution increased with increasing sodium sulfate concentration. This increase was 1.1 to 2.0 times that in the concrete specimens exposed to only sodium chloride solution.
7. In plain and blended cement concrete specimens, exposed to sodium chloride plus magnesium sulfate solution, the  $I_{\text{corr}}$  increased with increasing magnesium sulfate concentration of up to 2.5%  $\text{SO}_4^{--}$ , beyond this concentration, the  $I_{\text{corr}}$  decreased slightly.
8. The increase in the  $I_{\text{corr}}$  in the plain and blended cement concrete specimens, exposed to sodium chloride plus magnesium sulfate solution, was 1.1 to 2.2

times that in the specimens exposed to only sodium chloride.

9. The increase in the  $I_{\text{corr}}$  on steel in the concrete specimens exposed to sodium chloride plus sodium sulfate or sodium chloride plus magnesium sulfate solution may be attributed to a decrease in the electrical resistivity of concrete due to the presence of chloride and sulfate ions.
10. The  $I_{\text{corr}}$  on steel in the concrete specimens exposed to sodium chloride plus magnesium sulfate solution was more than the  $I_{\text{corr}}$  on steel in the concrete specimens exposed to sodium chloride plus sodium sulfate solution.
11. The  $I_{\text{corr}}$  on steel in the OPC-B ( $C_3A$ : 9.65%) concrete specimens was less than that in the OPC-A ( $C_3A$ : 8.5%) concrete specimens which was less than that in the SRPC ( $C_3A$ : 3.6%) concrete specimens. This indicates that Type I cement performs better than Type V cement in resisting reinforcement corrosion. This behaviour may be attributed to increased chloride-binding of high  $C_3A$  cements which results in increased electrical resistivity. This trend was noted in all the concrete specimens exposed to sodium chloride or sodium chloride plus sodium or magnesium sulfate solutions.
12. The  $I_{\text{corr}}$  on steel in the blended cement concrete specimens, particularly, silica fume cement concrete specimens was less than that in plain cement concrete specimens. This may be attributed to the high electrical resistivity of the blended cement concrete