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INFLUENCE OF CEMENT COMPOSITION ON CONCRETE DURABILITY IN CHLORIDE-SULFATE ENVIRONMENTS

By

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A Doctoral Thesis
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DEDICATED TO

MY BELOVED PARENTS, WIFE AND CHILDREN
ACKNOWLEDGEMENT

All praise, glory, thanks and gratitude be to almighty Allah, who bestowed me health, impetus, power and patience to accomplish this work, in addition to blessing me with the basic-tools for education and learning, i.e. hearing, sight and intelligence.

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The poor durability performance of reinforced concrete structures is a major problem facing the construction industry throughout the world. It is estimated that more than $200 billion will be required to repair and rehabilitate deteriorated concrete structures in the USA. Similarly, it is estimated that more than £2 billion will be needed to repair deteriorated concrete structures in the UK. Also, considerable resources have to be diverted towards the repair of deteriorated concrete structures in the countries along the Arabian Gulf. Concrete deterioration, worldwide, is mainly attributed to reinforcement corrosion that is caused by chloride ions. However, the effect of other ions, particularly sulfates, on reinforcement corrosion has not been adequately studied. Reinforced concrete structures in marine environments and those built in sabkha soils are exposed to both chloride and sulfate salts. The combined presence of these two ions may accelerate reinforcement corrosion. Cement chemistry may also significantly influence the mechanisms of reinforcement corrosion. The quantity of C₃A and the alkali content of cement affect its chloride-binding capacity. While considerable research has been conducted on the effect of C₃A content of cement on its chloride-binding and reinforcement corrosion, meagre data exist on the effect of cement alkalinity on chloride-binding, while no study has been conducted to evaluate the effect of cement alkalinity on reinforcement corrosion.

This study was conducted to investigate the effect of sulfate concentration and the cation type associated with sulfate ions, and cement alkalinity on pore solution chemistry, and reinforcement corrosion. The effect of sulfate cation type on morphological changes in concrete due to sulfate attack was also evaluated.

The effect of sulfate concentration (0, 1, 2.5 and 4% SO₄²⁻) and the cation type associated (Na⁺ and Mg²⁺) with the sulfate ions, and cement alkalinity on pore solution chemistry was evaluated by expressing the pore solution and analyzing it for OH⁻, Cl⁻, and SO₄²⁻ concentration. Reinforcement corrosion was evaluated by monitoring corrosion potentials and corrosion current density at regular intervals of up to 1200 days of exposure. The effect of sulfate concentration and the cation type on concrete deterioration, due to sulfate attack, was investigated by visual inspection and scanning electron microscopy.
Results of this study indicate that the quantity and the type of sulfate salts and cement composition affect the pore solution composition. The OH^-, Cl^- and SO_4^{2-} concentrations in plain and blended cements, contaminated with sodium chloride plus sodium sulfate, were more than those in similar cements contaminated with only sodium chloride or sodium chloride plus magnesium sulfate. These concentrations increased with increasing contamination of sodium sulfate and they were high in the plain cements compared to blended cements. The chloride-binding capacity decreased with increasing contamination of sodium sulfate.

The combined presence of chloride and sulfate ions did not affect the time-to-initiation of reinforcement corrosion. The corrosion current density, however, increased with increasing sodium sulfate concentration. However, in the case of magnesium sulfate, this increase was noted up to 2.5% SO_4^{2-}, beyond which a slight reduction in the corrosion current density was observed. The corrosion current density in the blended cement concretes was much less than that in the plain cement concretes. This may be attributed to the high electrical resistivity of blended cements compared to plain cements.

Cement alkalinity affected the pore solution chemistry, in that the OH^-, Cl^- and SO_4^{2-} concentrations increased with increasing alkalinity. The increase in the chloride and sulfate concentration with increasing cement alkalinity indicates that both calcium chloroaluminate and calcium sulphoaluminate hydrates become unstable at high alkalinity. The time-to-initiation of reinforcement corrosion increased and the corrosion current density decreased when the alkali content of cement increased up to 0.8% Na_2O equivalent. This suggests that the alkali content of cement can be increased to 0.8% (Na_2O equivalent) to increase the corrosion-resistance of concrete. However, the present limit of 0.6% should be implemented when it is expected that the aggregates are alkali-reactive.

The cation type associated with the sulfate ions significantly influenced the rate of concrete deterioration due to sulfate attack. No deterioration was noted on plain and blended cement concrete specimens exposed to sodium sulfate solution, even when the SO_4^{2-} concentration was as high as 4%. However, deterioration to varying degree was noted on both plain and blended cement concrete specimens exposed to magnesium sulfate solution. In the plain and fly ash cement concrete specimens, exposed to magnesium sulfate solution, deterioration was noted only when the SO_4^{2-} concentration was 2.5% and above. In the silica fume and blast furnace slag cement concrete specimens, exposed to magnesium sulfate solution, deterioration was noted when the SO_4^{2-} concentration was as low as 1%. Therefore, structures built using these cements and exposed to magnesium sulfate solution should be adequately protected, perhaps by the application of an epoxy-based coating.

Keywords: Alkalinity, Blended cements, Chloride, Chloride-sulfate environment, Cement morphology, Concrete deterioration, Reinforcement corrosion, Sulfates.
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CHAPTER 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 overall 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 CaCl₂ 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 C₃A phase of cement forming calcium sulfo-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 $C_3A$ 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.

Also no data are available on the threshold sulfate concentration which influences chloride-induced reinforcement corrosion. Such data will be helpful in formulating guidelines for limiting the sulfate concentration in the cement and other mix constituents, namely the aggregates, mineral and/or chemical admixtures, and mixing water. Furthermore, sodium sulfate was used to provide the sulfate ions in the studies conducted so far [5-8]. However, 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:

(i) effect of cation type associated with sulfate ions on chloride binding and reinforcement corrosion;

(ii) effect of sulfate concentration on chloride-induced reinforcement corrosion;
(iii) role of sulfate ions on the mechanisms of chloride-induced reinforcement corrosion; and

(iv) effect of cement alkalinity on reinforcement corrosion.

Cement chemistry also significantly influences the mechanisms of reinforcement corrosion. The two chemical properties of cements that effect its chloride binding capacity are the C₃A content and alkalinity. While considerable research has been conducted on the effect of C₃A phase of cement on its chloride binding capacity and reinforcement corrosion, meagre data exist on the effect of alkalinity of cement on chloride binding and pore solution chemistry. However, no data are available on the effect of cement alkalinity on reinforcement corrosion. It is worth stating that both chloride concentration and cement alkalinity control the time to initiation of reinforcement corrosion in the corrosion model suggested by Tutti [16] and Browne [17]. According to Hausman [18], the break down of the passive layer and initiation of reinforcement corrosion can occur when the \( \frac{Cl^-}{OH^-} \) ratio is more than 0.6. Gouda [19] indicated that this value could be as low as 0.3. High alkalinity also inhibits chloride binding by cement [7].

Few investigators [20-22] have reported a significant inhibiting effect of an alkaline pore solution environment on the chloride binding capacity of cement. Page and Vennesland [20] reported a substantial decrease in the chloride binding capacity of silica fume cements due to a resulting decrease in the alkalinity of the pore solution. A recent study by Talib [23] indicated a decrease in the pore solution alkalinity due to cement replacement with silica fume. The chloride binding capacity of silica fume cements, with up to 15% silica fume, was more than that of plain cements. However, further addition of silica fume resulted in a
slight decrease in the chloride binding capacity. The author [23] indicated that chloride binding capacity of silica fume cements is not totally related to the alkalinity of the pore solution. Gunkel [21] has shown that the alkali effect of weakening of the chloride binding of cement may be even greater than the sulfate effect. Tests conducted by Tritthart [22] also indicated that the uptake of chlorides is reduced to half, when the storage of specimens was changed from a 12.5 pH environment (saturated calcium hydroxide solution) to a pH environment of 13.7 (0.5 M NaOH solution).

Whilst the effect of cement alkalinity on its chloride binding has been evaluated to a certain extent, there is a need to investigate its effect on reinforcement corrosion.

1.3 RESEARCH OBJECTIVES

The purpose of this research was to investigate the effect of sulfate ions and cement alkalinity on pore solution chemistry and chloride-induced reinforcement corrosion. The specific objectives were:

Objective 1: to evaluate the effect of sulfate ions and associated cation type on pore solution chemistry, i.e., \( \text{OH}^- \), \( \text{Cl}^- \) and \( \text{SO}_4^{2-} \) concentrations;

Objective 2: to assess the effect of sulfate concentration and associated cation type on chloride-induced reinforcement corrosion;

Objective 3: to study the effect of cement alkalinity on reinforcement corrosion and pore solution chemistry, i.e., \( \text{OH}^- \), \( \text{Cl}^- \) and \( \text{SO}_4^{2-} \) concentrations; and
Objective 4: to investigate the effect of sulfate cation type on morphological changes of cement and concrete deterioration due to sulfate attack.

1.4 RESEARCH PROGRAMME

To fulfill the objectives of this research, the following experimental work was conducted (full details are provided in Chapter 3):

1.4.1 Effect of Sulfate Concentration on the Pore Solution Chemistry in Chloride-admixed Cements (Series I)

Specimens: 50 mm diameter by 75 mm high cement paste cylinders

Cements: SRPC (C₃A: 3.6%), OPC-A (C₃A: 8.5%), OPC-B (C₃A: 9.65%), blast furnace slag (BFS), silica fume (SF) and fly ash (FA)

Contamination: Fixed Cl⁻ : 0.8%
Variable SO₄²⁻ : 0, 1.0, 2.5, and 4.0% (Na₂SO₄)
Variable SO₄²⁻ : 0, 1.0, 2.5, and 4.0% (MgSO₄)

Techniques: Pore solution extraction
Pore solution analysis for OH⁻, Cl⁻ and SO₄²⁻

Cement paste specimens were made with fixed chloride contamination of 0.8%, by weight of cement, and the sulfate contamination was varied as shown above.

The data developed through the above experimental work were utilized to elucidate the role of sulfate concentration and the associated cation type on pore solution composition of plain and blended cements.
1.4.2 Influence of Sulfate Concentration and Associated Cation Type on Chloride-induced Reinforcement Corrosion and Concrete Deterioration (Series II)

Specimens: 75 mm diameter by 150 mm high reinforced concrete cylinders

Cements: SRPC (C₃A: 3.6%), OPC-A (C₃A: 8.5%), OPC-B (C₃A: 9.65%), blast furnace slag (BFS), fly ash (FA), and silica fume (SF)

Exposure Solutions:

Fixed Cl⁻ : 5% NaCl
Variable SO₄²⁻ : 0, 1.0, 2.5, and 4.0% (Na₂SO₄)
Variable SO₄²⁻ : 0, 1.0, 2.5, and 4.0% (MgSO₄)

Techniques: Corrosion potentials;
Corrosion current density (I_{corr}) using linear polarization resistance method (LPRM);
Visual inspection; and
Scanning electron microscopy (SEM)

The exposure solutions contained 5% NaCl and varying sulfate concentration as indicated above.

The data produced through the above experimental work were utilized to clarify the role of sulfate concentration and the associated cation type on reinforcement corrosion and concrete deterioration due to sulfate attack.

1.4.3 Effect of Cement Alkalinity on Pore Solution Chemistry in Chloride-admixed Cements (Series III)

Specimens: 50 mm diameter by 75 mm high cement paste cylinders

Cements: SRPC (C₃A: 3.6%), OPC-A (C₃A: 8.5%).

Contamination: Fixed Cl⁻ : 0.8%
Variable Na₂O : 0.4, 0.6, 0.8, 1.0, 1.2, and 1.4%.
Techniques: Pore solution extraction and analysis for OH⁻, Cl⁻ and SO₄²⁻.

Cement paste specimens were made with fixed chloride contamination of 0.8%, by weight of cement, and the alkalinity (Na₂O equivalent) was varied as shown above.

1.4.4 Effect of Cement Alkalinity on Chloride-induced Reinforcement Corrosion (Series IV)

Specimens: 75 mm diameter by 150 mm high reinforced concrete cylinders

Cements: SRPC (C₃A: 3.6%), OPC-A (C₃A: 8.5%)

Exposure: Fixed Cl⁻: 5% NaCl
Variable Na₂O: 0.4, 0.6, 0.8, 1.0, 1.2, and 1.4%

Techniques: Corrosion potentials
Corrosion current density (Icorr)

The experimental work associated with series III and IV has helped to explain the effect of cement alkalinity on the pore solution chemistry and reinforcement corrosion.

1.5 THESIS STRUCTURE

This thesis presents the results of the work conducted to achieve the research objectives as outlined in the previous section. Chapter 1 summarizes the causes of concrete deterioration, particularly reinforcement corrosion. The significance of this research and gaps in knowledge are highlighted with a view to elucidate the role of chloride and sulfate ions on pore solution composition and reinforcement corrosion. The details of objectives and experimental work are also included in this chapter.
Chapter 2 provides a review of literature pertaining to this research. The literature was reviewed and summarized to discuss the common causes of concrete deterioration, particularly those affecting reinforcement corrosion and sulfate attack. A review of literature on the effect of cement alkalinity on reinforcement corrosion is also included in this chapter.

In Chapter 3, the experimental methods, procedure and materials used to conduct the research are explained in detail. The results of tests conducted in Series I to evaluate the effect of chloride and sulfate concentration and the associated cation type on pore solution chemistry, i.e., OH⁻, Cl⁻ and SO₄²⁻ concentration in particular, are discussed in Chapter 4.

In Chapter 5, results of tests conducted in Series II to evaluate the effect of sulfate concentration and the associated cation type on chloride-induced reinforcement corrosion are discussed. The effect of cement alkalinity on pore solution composition, i.e., OH⁻, Cl⁻ and SO₄²⁻ concentration, and reinforcement corrosion (Series III and IV tests) are discussed in Chapter 6.

In Chapter 7, the morphological changes in concrete and its deterioration, when exposed to sodium chloride admixed with either sodium sulfate or magnesium sulfate (Series II tests) are presented. The conclusion and recommendations emanating from this study are presented in Chapter 8.
CHAPTER 2

LITERATURE REVIEW

2.1 DETERIORATION OF CONCRETE STRUCTURES

Deterioration of reinforced concrete structures is a major problem facing the construction industry, throughout the world. Many international conferences, sponsored by various concerned agencies, have been held to discuss the causes of this phenomenon and suggest remedial measures. Thousands of reports and research papers have been published on this subject. The causes of concrete deterioration can be classified as: (i) physical and (ii) chemical. The physical causes include surface wear or loss of mass due to abrasion, erosion and cavitation, and cracking due to temperature and humidity gradients, crystallization of salts in the pores, structural over-loading, impact and cyclic loading, and exposure to temperature extremes, such as freeze-thaw action or fire.

The chemical causes can be grouped into three categories. The first category is related to the reactions involving hydrolysis and leaching of the components of hardened cement paste. These type of reactions increase the porosity and permeability of concrete and lead to loss of alkalinity, loss of mass, increase the deterioration processes and loss of strength and rigidity. The second type of chemical deterioration is the exchange reactions between aggressive fluids and components of hardened cement paste. This type leads to the removal of calcium ions as soluble products that leads to loss of strength and rigidity of concrete. The third type is the reactions involving formation of expansive products which increase the internal stress and lead to deformation, loss of
strength and rigidity, cracking, spalling and pop out of concrete. There are four phenomena associated with the expansive chemical reactions which include, corrosion of reinforcement, sulfate attack, delayed hydration of free calcium oxide and magnesium oxide, and alkali-aggregate reaction [24]. However, some or all of these causes interact with each other to aggravate the deterioration processes. In the Arabian Gulf, the causes of deterioration of concrete structures in decreasing of order are: reinforcement corrosion, sulfate attack, salt weathering, and cracking due to shrinkage and thermal variations [25-28].

According to Skalny [1] in 1989, 253,000 bridges in the United States of America were in varying states of deterioration, and 3,500 were being added to this list every year. It has been estimated that more than $50 billion is required to repair and rehabilitate the highway structures in the United States, every year [2]. However, the overall cost of repairing or replacing all the deteriorated concrete structures in this country is about $200 billion [1,2]. Moavenzadeh [29] estimated that the cost of repairing the infrastructure would be between $1 to 3 trillion over the next 20 years. It has been estimated that more than £2 billion will be required to repair and rehabilitate deteriorated concrete structures in the United Kingdom [3,4].

The cost of repair and rehabilitation of deteriorated concrete structures in the countries along the Arabian Gulf is not very well documented, but undoubtedly considerable resources have to be diverted towards this effort. The Dubai tunnel [30] that was built in 1975 leaked so badly that the tunnel had to be completely repaired at a cost two times that of the initial investment. Similar difficulties were reported in the Suez tunnel and new dry dock at Abu Dhabi [30]. Studies conducted at
King Fahd University of Petroleum and Minerals (KFUPM) [25-28] have indicated that concrete structures along the Arabian Gulf show signs of distress within a short period of 10 to 15 years. Reports from other parts of the world are equally disturbing. Seabrook [31] reported that 400 concrete piles of the Rodney terminal on the eastern seaboard of Canada suffered cracking and spalling from freeze-thaw cycles and had to be repaired by epoxy injection.

However, it should be emphasized that concrete is a durable material, if it is manufactured and maintained properly. There are many concrete structures, 50-100 years old, which are still in a good condition [32]. The durability of concrete can be improved and deterioration can be minimized by using adequate mix design, selecting materials compatible with the service environment, and using appropriate placement and curing techniques. It is important to produce dense, impermeable and chloride-free concrete.

The deterioration of concrete structures in the temperate climatic conditions, as in Europe and North America, is partially attributed to reinforcement corrosion caused due to the use of deicer salts. The environmental and geomorphical conditions in the coastal areas of the Arabian Gulf are the primary causes for the reduction in the useful service-life of concrete structures in this region. The environment, soil and groundwater, which are heavily admixed with chloride and sulfate salts, are conducive to initiation of the deterioration processes. The diurnal and seasonal variations in temperature and humidity, in the Arabian Gulf, are relatively high. The summer temperature may be as high as 40 to 50 °C, compared to 20 to 30 °C recorded in USA or Europe. At this ambient temperature the concrete surface temperature may be as
high as 70 to 80 °C due to solar radiation [33]. This thermal affect influences the overall mechanisms of the deterioration processes, namely, reinforcement corrosion, sulfate attack, salt weathering, and cracking due to plastic and drying shrinkage, and thermal variations.

Another reason for the low durability of concrete in the Arabian Gulf is the poor quality of the local aggregate. Most of the aggregate available in this region is crushed limestone which is marginal, porous, absorptive, relatively soft and excessively dusty [34]. Dune or beach sand is used as fine aggregate. These sands are very fine and admixed with chloride and sulfate salts.

In the last two decades, particularly since 1972, the Arabian Gulf countries have experienced a rapid increase in the construction activity, more than any other area in the world, thus exerting a great strain on the ill-equipped and technically unqualified construction industry. Furthermore, the need for quick implementation of projects and the unprecedented rate of construction have not allowed development of design and construction specifications compatible with the local conditions. As a result, imported specifications and designs, unsuitable materials and equipment, and unskilled labour were used which lead to poor construction practices. The absence of close supervision, quality control and lack of awareness of the problem during the construction time are also other factors which have accelerated the deterioration process and magnified the problem in this region.

As stated earlier, the major forms of concrete deterioration are: reinforcement corrosion, sulfate attack, salt weathering, alkali-aggregate reaction and cracking due to shrinkage and thermal gradients. Since this study is related to the effect of chloride and sulfate and cement alkalinity
on pore solution chemistry and reinforcement corrosion, further discussion of concrete deterioration will be restricted to these topics.

2.2 CORROSION OF REINFORCING STEEL IN CONCRETE

Corrosion of reinforcing steel was first observed in marine structures and chemical manufacturing plants in the late fifties and early sixties [35]. In the seventies and eighties numerous reports of reinforcement corrosion in the bridge decks, parking and other structures exposed to chloride ions have highlighted a prominent problem. In recent years corrosion of reinforcing steel in concrete structures has received increasing attention and become an international topic and subject of discussion among concrete technologist and corrosion scientists.

The failure of concrete due to reinforcement corrosion occurs in the form of expansion, cracking and spalling of concrete cover. According to Cabrera [36], reinforcement corrosion in concrete leads to a reduction of bond strength and reduction of steel cross section and loss of serviceability. Further, the corrosion of reinforcing steel in concrete affects the aesthetic appearance of a structure and reduces its structural integrity.

Reinforcement corrosion in concrete structures is influenced by many factors such as cement content, cement type, admixtures, alkalinity of concrete, cracking, water cement ratio, quality of concrete, permeability, construction practices, electrical resistivity, concrete cover and environmental factors.

Concrete provides both physical and chemical protection to the reinforcing steel. The physical protection is provided by its dense structure, which retards the ingress of aggressive species, such as
oxygen, moisture, and chloride ions, to the steel-concrete interface. The chemical protection is provided by the high alkalinity of the pore solution (pH > 13.5) at which a submicroscopically thin protective film of $\gamma$-Fe$_2$O$_3$ is formed on the steel surface.

The breakdown of the passive layer is attributed to: (i) reduction in the pH of the surrounding concrete, mainly due to carbonation, and (ii) penetration of aggressive ions, like chlorides, to the steel surface. Reinforcement corrosion due to penetration of carbon dioxide may result in uniform corrosion and is commonly observed in industrial areas and in old structures. However, deterioration of concrete in many parts of the world is mostly attributed to chloride induced reinforcement corrosion. Also, this form of deterioration out-weighs that due to carbonation. Chlorides may be introduced into concrete at the time of mixing through admixtures, admixed aggregates, and mix water. Alternatively, they may penetrate the hardened concrete from the service environment.

The precise role that the chloride ion plays in the corrosion process, however, is not agreed upon. A number of mechanisms by which chlorides breakdown the passive layer have been proposed, the chemical dissolution of the film [37], build-up of the metal holes at the film/substrate interface [38], and local acidification and pitting due to high chloride concentrations at the iron oxide/pore solution interface [39]. Leek and Poole [40], based on SEM-EDS studies of the passive film break down on steel in mortar prisms, have shown that chloride ions initiate corrosion by breaking the bond between the passive film and the metal. However, almost all researchers agree that chloride ions act as an essential catalyst in the corrosion reaction. Chloride ions also cause a shift of potential of the steel. Non-uniform penetration of chloride ions
to the level of steel produces differences in potential and leads to the formation of "macro" corrosion cells. Non-uniform penetration is a general occurrence, and results from such factors as variations in concrete cover and local differences in concrete quality. On reaching the iron substrate, the chloride ions act as a catalyst for the oxidation of iron by taking an active part in the reaction.

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:

$$\text{Fe} \rightarrow \text{Fe}^{++} + 2e^- \quad (2.1)$$

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

$$\text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + 2e^- \rightarrow 2\text{OH}^- \quad (2.2)$$

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.

$$\text{Fe}^{++} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 \quad (2.3)$$

It is clear that for corrosion to occur, three conditions must be satisfied [32]:

i) Iron must be available in a metallic (Fe) state at the surface of reinforcing steel for anodic process.

ii) For cathodic process, oxygen and moisture must be present.

iii) The electrical resistivity of concrete must be low to facilitate the electron flow in the metal from anode to cathode.

If these three conditions are not satisfied, corrosion will not take place even in concrete structures that are continuously submerged in seawater.
The product of corrosion of steel \([\text{Fe(OH)}_2]\) 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.

Reinforcement corrosion in concrete can be monitored using destructive and nondestructive techniques. In the destructive methods, a piece of steel bar is retrieved by coring out concrete and determining its loss in weight and hence the corrosion rate. However, these types of methods are not practical and destructive in nature, as a result they are rarely used. The nondestructive techniques that are used widely include: half-cell potential monitoring, double probe corrosion potential monitoring, electrical resistance, A.C. impedance, Tafel plot, electrochemical noise, and linear polarization resistance.

2.3 EFFECT OF CHLORIDE AND SULFATE IONS ON PORE SOLUTION CHEMISTRY

The effect of chloride and sulfate ions on the pore solution composition was studied by Holden et al. [5]. In that study [5], cement paste specimens prepared from different types of cements, OPC-A (C_3A: 7.7%), OPC-B (C_3A: 14.3%), SRPC (C_3A: 1.9%) with a W/C of 0.5 were admixed with fixed quantities of chloride and sulfate ions. The results indicated an increase in the OH\(^{-}\) concentration due to the inclusion of sulfates as compared to the alkalinity of pore solution of cement pastes admixed with only sodium chloride. The results also showed a substantial increase in the chloride concentration in the cements admixed with sodium chloride plus sodium sulfate compared to those admixed with only sodium chloride. These results reflect the tendency of
sulfate ions to react preferentially with the C₃A of cement, thus inhibiting the formation of Friedel's salt. Thus, corrosion risk is likely to be significantly increased in circumstances where concrete is admixed with both chloride and sulfate salts. Treadaway et al. [41] confirmed the results of the aforesaid laboratory studies by conducting long-term exposure trials.

Table 2.1 [5] shows some of the results reported by Holden et al. [5]. It is clear from this table that the addition of sodium chloride resulted in an increase in the Cl⁻ and OH⁻ concentrations of the pore solution in all types of cements used. However, the combined additions of sodium chloride and sodium sulfate resulted in a significant increase in the concentrations of these two ions in all types of cements. As it is apparent from the data in Table 2.1, the OH⁻ and Cl⁻ concentrations were highly effected by the C₃A content of the cement and alkalinity. The Cl⁻ concentration in the high C₃A cements was less than that in the low C₃A

<table>
<thead>
<tr>
<th>Cement</th>
<th>Series I (No contamination)</th>
<th>Series II (0.4% Cl⁻)</th>
<th>Series III (0.4% Cl⁻ +1.5% SO₄⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cl⁻ mM/L OH⁻ mM/L Cl/OH⁻</td>
<td>Cl⁻ mM/L OH⁻ mM/L Cl/OH⁻</td>
<td>Cl⁻ mM/L OH⁻ mM/L Cl/OH⁻</td>
</tr>
<tr>
<td>OPC-A</td>
<td>2 589 0.003</td>
<td>83 741 0.112</td>
<td>215 1318 0.163</td>
</tr>
<tr>
<td>OPC-B</td>
<td>3 479 0.006</td>
<td>41 661 0.062</td>
<td>153 1047 0.146</td>
</tr>
<tr>
<td>OPC-B + 30% PFA</td>
<td>2 339 0.006</td>
<td>39 457 0.085</td>
<td>145 851 0.170</td>
</tr>
<tr>
<td>OPC-B + 65% BFS</td>
<td>5 355 0.014</td>
<td>28 457 0.061</td>
<td>147 741 0.198</td>
</tr>
<tr>
<td>SRPC</td>
<td>2 347 0.006</td>
<td>110 501 0.220</td>
<td>257 1000 0.257</td>
</tr>
</tbody>
</table>
cements. In the case of pulverized fuel ash (PFA) and blast furnace slag (BFS) cements, an increase in Cl⁻ and OH⁻ concentrations was noticed. However, this increase was less than that in the same type of cement without PFA or BFS. Further, the Cl⁻/OH⁻ ratio in the PFA and BFS cements was higher than that in the same cement without PFA or BFS. Despite of the high Cl⁻/OH⁻ ratio in the PFA and BFS cement specimens, experience indicated that the performance of these cements in resisting reinforcement corrosion is better than plain cements.

Maslehuddin et al. [42,43] indicated that the addition of sodium chloride or sodium chloride plus sodium sulfate at the time of mixing increased the Cl⁻ and OH⁻ concentrations of the pore solution of mortar specimens. In those studies [42, 43], plain and blended cement mortar specimens were made with an effective W/C ratio of 0.50 and sand to cementitious materials ratio of 2.0. Figures 2.1 through 2.4 [43] show the OH⁻ concentrations of the pore solution in SRPC (C₃A: 3.5%), OPC-A (C₃A: 8.5%), OPC-B (C₃A: 14.5%) and silica fume cements, respectively, that were exposed to temperature from 25 to 70 °C. The Cl⁻ concentrations of the pore solution in these cements exposed to same temperatures are shown in Figures 2.5 through 2.8. The OH⁻ and Cl⁻ concentrations at room temperature (25 °C) are summarized in Table 2.2.

The data in Table 2.2 indicate that the OH⁻ concentrations in the OPC-B mortar specimens admixed with sodium chloride or sodium chloride plus sodium sulfate is more than that in the OPC-A mortar specimens which is more than that in the SRPC mortar specimens with similar contamination. The Cl⁻ concentration in the OPC-B mortar specimens admixed with sodium chloride or sodium chloride plus sodium sulfate is less than that in the OPC-A mortar specimens which
is less than that in the SRPC mortar specimens with similar contamination. The results indicated that the chloride concentration decreased with increasing C₃A content of cements. Also, it is noticeable that the chloride concentration in the specimens admixed with sodium chloride plus sodium sulfate is more than that in the specimens admixed with only sodium chloride.

Table 2.2: Pore solution composition of cement mortar specimens admixed with sodium chloride and sodium sulfate at room temperature (25 °C) [43].

<table>
<thead>
<tr>
<th>Contamination</th>
<th>0.8% Cl⁻</th>
<th>0.8% Cl⁻ + 15% SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cl⁻ mM/L</td>
<td>OH⁻ mM/L</td>
</tr>
<tr>
<td>SRPC</td>
<td>350</td>
<td>324</td>
</tr>
<tr>
<td>OPC-A</td>
<td>302</td>
<td>401</td>
</tr>
<tr>
<td>OPC-B</td>
<td>179</td>
<td>536</td>
</tr>
<tr>
<td>OPC-A+10% SF</td>
<td>312</td>
<td>72</td>
</tr>
</tbody>
</table>

Rasheeduzzafar et al. [44] indicated that the addition of sodium chloride at the time of mixing increases the OH⁻ and Cl⁻ concentration in the pore solution of concrete. They tested four Portland cements with varying C₃A (2.04, 7.59, 8.52 and 14%) contents and different levels of sodium chloride concentrations (Cl⁻: 0.3, 0.6, 1.2, and 2.4%). The results indicated that as the sodium chloride contamination increases, the OH⁻ and Cl⁻ concentrations of the pore solution increase in all the cements. The increase in the Cl⁻ concentration of the pore solution was significant for Cl⁻ addition of 1.2% or more, while the OH⁻ concentration did not
vary significantly. However, the OH\textsuperscript{-} concentration of the pore solution increased while the Cl\textsuperscript{-} concentration decreased with increasing C\textsubscript{3}A content of cements. This indicates that high C\textsubscript{3}A content of cement is beneficial in binding chloride ions.

Hussain et al. [45] indicated that the addition of sodium chloride and sodium sulfate at the time of mixing increased the OH\textsuperscript{-} and Cl\textsuperscript{-} concentrations of the pore solution significantly. In that study [45], three ordinary Portland cements with varying C\textsubscript{3}A contents with two levels of sodium chloride contamination (Cl\textsuperscript{-}: 0.6 and 1.2\%) and two levels of sodium sulfate (the total SO\textsubscript{3} content of cement was raised to 4\% and 8\% on a weight basis) were tested. Table 2.3 [45] shows the results of the pore solution of the cement paste specimens admixed with 0.6 Cl\textsuperscript{-} and varying concentrations of sodium sulfate.

\textit{Table 2.3: Pore solution composition in cement paste specimens admixed with 0.6 Cl\textsuperscript{-} and varying levels of sodium sulfate concentration [45].}

<table>
<thead>
<tr>
<th>Cement</th>
<th>C\textsubscript{3}A</th>
<th>0.6 Cl\textsuperscript{-}</th>
<th>0.6 Cl\textsuperscript{-} + 2.5% SO\textsubscript{3}</th>
<th>0.6 Cl\textsuperscript{-} + 5.5% SO\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>\textsuperscript{C}l \text{mM/L}</td>
<td>\textsuperscript{OH} \text{mM/L}</td>
<td>\textsuperscript{Cl/\text{OH}}</td>
<td>\textsuperscript{C}l \text{mM/L}</td>
</tr>
<tr>
<td>1</td>
<td>2.04</td>
<td>210</td>
<td>265</td>
<td>0.79</td>
</tr>
<tr>
<td>2</td>
<td>7.59</td>
<td>109</td>
<td>391</td>
<td>0.28</td>
</tr>
<tr>
<td>3</td>
<td>8.52</td>
<td>51</td>
<td>503</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Table 2.4 [45] shows pore solution composition of cement paste specimens admixed with 1.2 Cl\textsuperscript{-} and varying concentrations of sodium sulfate reported by Hussain et al. [45]. These data indicated that the OH\textsuperscript{-} concentration of the pore solution increased significantly when the SO\textsubscript{3}
concentration was raised up to 4% and this increase was marginal when SO₃ concentration was raised from 4% to 8%. However, the Cl⁻ concentration of the pore solution increased significantly with both additions (4 and 8%).

Kayyali et al. [46] indicated that the addition of sodium chloride increased the OH⁻ concentration of the pore solution. Talib [23] also reported an increase in the OH⁻ concentration of the pore solution due to incorporation of sodium chloride.

Table 2.4: Concentrations of pore solution composition in cement paste specimens admixed with 1.2 Cl⁻ and varying levels of sodium sulfate concentration [45].

<table>
<thead>
<tr>
<th>Cement</th>
<th>C₃A</th>
<th>1.2 Cl⁻</th>
<th>1.2 Cl⁻ + 2.5% SO₃</th>
<th>1.2 Cl⁻ + 5.5% SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cl⁻ mM/L</td>
<td>OH⁻ mM/L</td>
<td>Cl/OH⁻</td>
<td>Cl⁻ mM/L</td>
</tr>
<tr>
<td>1</td>
<td>2.04</td>
<td>530</td>
<td>254</td>
<td>2.09</td>
</tr>
<tr>
<td>2</td>
<td>7.59</td>
<td>342</td>
<td>413</td>
<td>0.83</td>
</tr>
<tr>
<td>3</td>
<td>8.52</td>
<td>216</td>
<td>534</td>
<td>0.40</td>
</tr>
</tbody>
</table>

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 \( \mu \text{A/cm}^2 \) while it was 0.50 \( \mu \text{A/cm}^2 \) 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].

<table>
<thead>
<tr>
<th>Exposure Temperature (°C)</th>
<th>Corrosion Current Density (μA/cm²)</th>
<th>Increase in Icorr due to Na₂SO₄ addition, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaCl</td>
<td>NaCl + Na₂SO₄</td>
</tr>
<tr>
<td>25</td>
<td>0.39</td>
<td>0.50</td>
</tr>
<tr>
<td>40</td>
<td>0.52</td>
<td>1.27</td>
</tr>
<tr>
<td>55</td>
<td>1.29</td>
<td>2.14</td>
</tr>
<tr>
<td>70</td>
<td>1.8</td>
<td>2.45</td>
</tr>
</tbody>
</table>

Gouda and Halaka [50] investigated the influence of sulfate ions on reinforcement corrosion in the system Ca(OH)₂-steel-chloride and reported that the presence of very small concentrations of Na₂SO₄, as low as 0.2 %, could cause steel depassivation. Morgan [51] indicated that
addition of 50 ppm $\text{SO}_4^{2-}$ 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% Cl\(^-\), 15.7 Cl\(^-\)+0.55% SO\(_4\)^{2-} and 15.7 Cl\(^-\)+2.1% 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].**

<table>
<thead>
<tr>
<th>Solution Composition</th>
<th>Chloride (%)</th>
<th>Sulfate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.7% Cl(^-)</td>
<td>3.64</td>
<td>0.05</td>
</tr>
<tr>
<td>2.1% SO(_4)^{2-}</td>
<td>0.18</td>
<td>0.12</td>
</tr>
<tr>
<td>15.7% Cl(^-)+0.55% SO(_4)^{2-}</td>
<td>3.58</td>
<td>0.18</td>
</tr>
<tr>
<td>15.7% Cl(^-)+2.1% SO(_4)^{2-}</td>
<td>3.56</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Figure 2.9 [13] shows the variation of corrosion current density with the sulfate concentration in the solution containing 3.6% Cl\(^-\). 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/m³, 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.

2.5 INFLUENCE OF ALKALINITY ON REINFORCEMENT CORROSION

Since chloride is a unique destroyer of the passive film, there is thought to be a threshold concentration for such an activity. From this viewpoint, ACI 318 [62] limits the water-soluble chlorides to 0.15% by weight of cement. ACI Committee 224 [63] adopting a more conservative approach, suggested that the acid-soluble chloride concentration should not be more than 0.2% by weight of cement. The British Standard BS 8110 [64] allows a maximum chloride concentration of 0.4%. As reported by Rasheeduzzafar et al. [44], the Norwegian Code NS 3474 allows an acid soluble chloride content of 0.6%, RILEM permits 0.4% and the revised Australian Standards for Concrete Structures AS 3600 allows an acid-soluble chloride content of 0.80 kg/m$^3$ of concrete (0.22% by weight of cement for a typical concrete mix). Rasheeduzzafar et al. [44] indicated that the chloride threshold limits for cements with up to 8% C$_3$A agree very well with the ACI 318 limit of 0.15% water-soluble chlorides, as well as with the BS 8110 limit of 0.4% acid-soluble chlorides. Additionally, they reported that ACI, BS and Australian Code limits, appear to be conservative for concrete made with high C$_3$A cements. Lambert et al. [65] suggested that the critical level of chloride below which there was no significant probability of corrosion was around 1.5% by weight of cement. They attributed the increased chloride tolerance in their specimens compared with BS 8110 limit of 0.4% to the protective nature of concrete produced under well-controlled conditions of the laboratory.
Research findings, however, have shown that cement alkalinity also significantly influences chloride binding and hence the free chlorides [22]. Taking into account the concomitant effect of chloride and alkalinity, Hausmann [18] suggested the critical $\text{Cl}^-/\text{OH}^-$ to be around 0.6. Gouda [19], using pH values of the electrolyte representative of the concrete pore solution, indicated that the threshold $\text{Cl}^-/\text{OH}^-$ was 0.3. Lambert et al. [66] investigated the relationship between $\text{Cl}^-/\text{OH}^-$ and corrosion current density in various cements. Their investigation [66] indicated that the passive conditions of steel in concrete, characterized by corrosion current density ($I_{\text{corr}}$) substantially lower than 100 nA/cm$^2$, were maintained until a threshold $\text{Cl}^-/\text{OH}^-$ ratio of approximately 3 was exceeded. There was a considerable scatter in the values of $I_{\text{corr}}$ recorded at $\text{Cl}^-/\text{OH}^-$ ratios in excess of 3 and even at $\text{Cl}^-/\text{OH}^-$ ratios as high as 15 to 20, there were instances of bars suffering no significant corrosion.

Mangat and Molloy [67] indicated that a universal threshold $\text{Cl}^-/\text{OH}^-$ level is not applicable to all concrete. In their investigation, reinforcing steel corrosion was observed in the control matrix when the pore fluid $\text{Cl}^-/\text{OH}^-$ was 13, while at values of 17 and 18, in a silica fume cement concrete, reinforcement corrosion was insignificant. Similarly, minimal reinforcement corrosion was reported by Al-Amoudi et al. [12] in silica fume cement and blast furnace slag cement mortar specimens, placed in an aggressive sabkha environment, even at $\text{Cl}^-/\text{OH}^-$ of 3.3 and 6.5, respectively,

Further, the alkalinity of cement also significantly influences the $\text{OH}^-$ concentration, as well as the chloride binding capacity. Page and Vennesland [20] investigated the effect of 0, 10, 20, and 30% cement replacement by silica fume on the pore solution alkalinity and chloride
binding. Their results indicated that incorporation of an increasing percentage of silica fume in Portland cement paste would lead to a progressive reduction in the extent to which chloride ions, introduced during mixing, are excluded from the pore solution. Diamond [68] referring to the above hypothesis of Page and Vennesland [20], regarding the lowering of the chloride binding due to a reduction in the alkalinity, indicated that the reduced chloride binding capacity in the silica fume cements, among other phenomena, may be attributed to a reduction in the mix water due to the formation of hydration products. Rasheeduzzafar et al. [69] investigated the pore solution chemistry of silica fume cements admixed with 0.6 and 1.2% chloride ions and indicated that the chloride ion concentration in the 10 and 20% silica fume cement was more than double the free chloride ion concentration in the ordinary Portland cement. Several investigators [20-23,43,70] have reported a significant inhibiting effect of a strong alkaline pore solution environment on the chloride binding capacity of cement. Gunkel [21] has shown that the effect of alkali on the weakening of the chloride binding may be even greater than the sulfate effect. In a 0.5 w/c ratio hardened cement paste with 0 and 0.4% chloride, added as NaCl, the chloride concentration in the pore solution increased from 2900 ppm to 4100 ppm when 0.62% Na₂O was added to the cement through mix water. Chloride concentrations increased to only 3200 ppm when alkali-free and 1.36% CaSO₄ was added. However, the free-chloride concentration increased to 5700 ppm when both alkalis and sulfates were conjointly inducted through 1.42% Na₂SO₄ Tests conducted by Arya et al. [71] also indicated that the uptake of chlorides is reduced to half when the storage of specimens was changed from 12.5 pH environment (saturated calcium hydroxide solution) to a pH environment of 13.7 (0.5M NaOH solution).
The inhibiting effect of high alkali on chloride binding has also been reported by Hussain [7]. Recently, Talib [23] investigated the effect of alkali content of cement on the chloride concentration in the pore solution. The proportions of unbound chlorides, in both plain and silica fume cements, increased with the alkali content of cement.

Roberts [72] studied the solubility of Friedel’s salt using different solutions at various temperatures and alkalinity. The results indicated that the solubility of calcium chloro-aluminate increased with alkali hydroxide. Way and Shayan [73] investigated the influence of adding NaOH on sulfate concentration and indicated that the early sulfate concentrations increased significantly with the cement alkalinity. Ong and Diamond [74] indicated that the addition of a high alkali cement (1.14 Na2O equivalent) to the mix water containing pre dissolved NaOH reduced the OH concentration that already present in the mix water. Diamond and Ong [75] indicated that the addition of alkali hydroxide to the mix water results in high concentration of sulfate ions in the pore solution.

The high alkali content of cement while inhibiting the chloride binding may also accelerate alkali-aggregate reaction, thereby enhancing reinforcement corrosion in the environments charged with chloride ions. However, one major contribution of the high alkalinity of cement is a reduction in the Cl-/OH⁻ ratio that controls the kinetics of reinforcement corrosion.

In the studies conducted so far, steel bars were placed in alkaline media or these salts were inducted as a contamination in concrete. The buffering action of an alkaline environment when chloride ions, diffuse from the external environment, needs to be investigated.
2.6 INFLUENCE OF SULFATE CATION TYPE ON DETERIORATION OF CONCRETE IN CHLORIDE-SULFATE ENVIRONMENT

The cation type associated with sulfate ions (Na\(^+\) or Mg\(^{++}\)) plays a significant role on the degree of deterioration of concrete. Several researchers [76-86] reported that magnesium sulfate is more severe on concrete than sodium sulfate, particularly silica fume and blast furnace slag cement concretes. Magnesium sulfate chemically reacts with calcium hydroxide in the presence of water to form gypsum and magnesium hydroxide. Magnesium hydroxide is relatively insoluble and poorly alkaline (pH<10.4). At this low pH, the stability of calcium silicate hydrate (C-S-H) is reduced. The decomposition of C-S-H may proceed to completion and all the calcium content of the binder may be replaced by magnesium.

The concomitant presence of sulfate and chloride ions in soils and marine environments causes deterioration of reinforced concrete structures due to reinforcement corrosion and sulfate attack. In the hardened cement paste it is the C\(_3\)A that locks chloride ions into insoluble compound of calcium chloro-aluminate hydrate (Friedel's salt), thereby causing its removal from its hazardous role of corrosion promotion. This is the same phase of cement, which in excess of a certain critical level, reacts with sulfate ions to form ettringite and gypsum thereby leading to degradation of concrete into a non-cohesive granular mass and to disruptive expansion [87]. It is obvious that whereas a higher proportion of C\(_3\)A would reduce the level of reinforcement corrosion by removing or lowering free chlorides from the pore electrolyte solution, it would pose a serious concrete durability
problem in terms of sulfate attack. When chlorides and sulfates exist concomitantly, such as in seawaters, sulfate bearing soils and ground water, both of them would react with C$_3$A to form insoluble compounds. Hjorth [88] reported, based on the work of Schwietz et al., that sulfate ions react preferentially with C$_3$A to form two insoluble compounds of calcium sulfo-aluminate hydrates, namely trisulfo-aluminate hydrate (C$_3$A.3CaSO$_4$ aqueous) and monosulfo-aluminate hydrate (C$_3$A.CaSO$_4$ • aqueous). The preferential reaction of sulfate ions with C$_3$A phase has also been reported by Holden et al. [5]. Their results showed a substantial decrease in the chloride binding capacity of cements due to the concomitant presence of sulfate and chloride salts compared to chlorides alone.

Chloride ions inducted at the mixing stage through chloride-accelerating admixtures, admixed aggregates and mix water were reported to enhance the sulfate resistance by Miller [89] and Yeginobali [90]. Harrison [91] studied the effect of sodium and calcium chloride additions in the range of 0 to 4.5% in mortar and concrete cubes on sulfate-resistance of cement using Type I and Type V cements over a period of one year for mortar and over seven years for concrete. The results of the mortar cubes have indicated that the chloride has either a negligible or generally beneficial effect on the sulfate resistance in both Type I and Type V cement mortars. A similar overall trend has been observed in the concrete cubes, with the apparent exception of some concrete containing calcium chloride, particularly those containing below 0.5% chloride by weight of cement.

Kind [92], through his extensive research on chloride-sulfate interaction in water retaining structures, reported increased
sulfate-resistance in some cements in sulfate solutions admixed with high chloride concentrations. He attributed this increase to:

i) the increased solubility of calcium hydro-aluminate phase leading to calcium sulfo-aluminate crystallization, i.e., ettringite is formed in the non-expansive form,

ii) decrease in the lime concentration in the pore solution leading to the conversion of the insoluble highly basic hydro-aluminate phases to soluble, low-basic forms; forming ettringite in the liquid phase in the non-expansive form, and

iii) the transformation of hydro-aluminate phases into chloro-aluminates, thereby reducing the quantity of ettringite formed.

Based on microscopic examination, Kind [93] further reported that the calcium sulfo-aluminate occurred in smaller quantities and was formed as weakly developed crystals in the presence of sodium and magnesium chlorides. This finding forms the basis for specifying higher sulfate limits in the presence of higher chloride concentrations in the Russian Standards. Both Biczok [84] and Lea [94], based on the work of Batta, confirmed that the expansion of concrete by sulfate attack in seawater is definitely retarded due to the concomitant presence of chloride and sulfates. They attributed this retardation to the increased solubility of sulfate phases in sodium and calcium chloride solutions. Connor and Rippstain, quoted by Harrison [91], found that the solubility of ettringite was three times greater in chloride solutions than in water. The aforementioned studies indicate that sulfate attack is mitigated due to the presence of chloride and sulfate ions. However, other opinions contradicting this position also exist. Smith [95] reported that the
addition of 1% calcium chloride at the mixing stage had generally reduced the sulfate resistance of concrete, particularly in concrete made with Type II cement. Moreover, he reported that temperature seems to play a significant role; concretes made of Type II or Type V cement were more sulfate resistant when mixed and cured at 5 °C (40 °F) than similar concrete mixed and cured at normal room temperatures 25 °C (70 °F). Locher [96] concluded that sulfate attack is generally increased by the addition of chloride to the sulfate solution. The increased sulfate attack due to the presence of chlorides was attributed to:

i) formation of ettringite which is not hindered by the addition of chlorides,

ii) the presence of monochloride, which is attributed to the consumption of monosulfate and tetracalcium aluminate hydrate by part of chloride reacting with the nonhydrated C₃A phase in the cements,

iii) this monochloride is not stable in the presence of sulfate ions; therefore, it is converted to ettringite when sulfate attack commences with time, and

iv) at higher concentrations of chloride, both monochloride and trichloride hydrates are formed, the former reacts with the penetrating sulfate ions to form ettringite without generation of crystallization pressure and the latter hydrate resists sulfate attack.

The formation of trichloride hydrate (3CaO Al₂O₃.3CaCl₂.32H₂O) was reported to be favorable at high chloride concentration by Schwietz et al., as quoted by Hjorth [88].
Figure 2.1: Variation of OH⁻ concentration with exposure temperature in the SRPC mortar specimens [43].

Figure 2.2: Variation of OH⁻ concentration with exposure temperature in the OPC-A mortar specimens [43].
Figure 2.3: Variation of OH⁻ concentration with exposure temperature in the OPC-B mortar specimens [43].

Figure 2.4: Variation of OH⁻ concentration with exposure temperature in the silica fume cement mortar specimens [43].
Figure 2.5: Variation of chloride concentration with exposure temperature in the SRPC mortar specimens [43].

Figure 2.6: Variation of chloride concentration with exposure temperature in the OPC-A mortar specimens [43].
Figure 2.7: Variation of chloride concentration with exposure temperature in the OPC-B mortar specimens [43].

Figure 2.8: Variation of chloride concentration with exposure temperature in the silica fume mortar specimens [43].
Figure 2.9: Influence of sulfate ions associated with 3.6% water-soluble chloride on reinforcement corrosion [13].
CHAPTER 3

METHODOLOGY OF RESEARCH

3.1 INTRODUCTION

This chapter discusses the experimental work conducted to achieve the objectives of this research. The experimental work was divided into the following four series:

Series I: Effect of chloride and sulfate concentration on the pore solution composition.

Series II: Effect of sulfate concentration and the associated cation type on chloride-induced reinforcement corrosion and concrete deterioration.

Series III: Effect of cement alkalinity on pore solution chemistry

Series IV: Effect of cement alkalinity on reinforcement corrosion.

The experimental methods were carefully selected to provide insight into the effects of the quantity of sulfate ions and the associated cation type on pore solution chemistry and reinforcement corrosion. For example, the effect of sulfate contamination on the pore solution chemistry was determined by extracting pore solution and analyzing it for alkalinity (OH⁻), chloride (Cl⁻) and sulfate (SO₄²⁻) concentrations. The concomitant effect of chloride and sulfate ions diffusing from the external environment on reinforcement corrosion was evaluated by measuring corrosion potentials and corrosion current density (I_{corr}). The effect of
cement alkalinity on reinforcement corrosion, due to chloride ions diffusing from the external environment, has not been thoroughly investigated. This aspect was studied by mixing known quantities of sodium hydroxide, as a contamination and placing the specimens in sodium chloride solution, admixed with similar alkalinity. Reinforcement corrosion was evaluated by measuring corrosion potentials and corrosion current density.

The effect of quantity of sulfate ions, both magnesium and sodium, on concrete deterioration was evaluated by visual inspection of the concrete specimens after four years of immersion in the solutions. The morphological changes of cement due to sulfate were evaluated by examining selected specimens under scanning electron microscope.

The materials used, specimen preparation, exposure conditions, and experimental methods adopted in each of the above series will be discussed in detail in the following sections.

3.2 INFLUENCE OF SULFATE CONCENTRATION ON PORE SOLUTION CHEMISTRY IN CHLORIDE-ADMIXED CEMENTS

3.2.1 Materials and Specimen Preparation

Six cements, namely sulfate-resisting Portland cement (SRPC; C₃A: 3.6%), ordinary Portland cement (OPC-A; C₃A: 8.5%), (OPC-B; C₃A: 9.65%), blast furnace slag (BFS), silica fume (SF) and fly ash (FA) cements were used to prepare the cement paste 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.

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

<table>
<thead>
<tr>
<th>Constituent (Wt %)</th>
<th>SRPC¹</th>
<th>OPC-A²</th>
<th>OPC-B³</th>
<th>BFS⁴</th>
<th>SF⁵</th>
<th>FA⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>22.00</td>
<td>20.52</td>
<td>20.00</td>
<td>35.40</td>
<td>92.50</td>
<td>49.72</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.08</td>
<td>5.64</td>
<td>6.00</td>
<td>7.80</td>
<td>0.40</td>
<td>47.58</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4.24</td>
<td>3.80</td>
<td>3.70</td>
<td>0.52</td>
<td>0.40</td>
<td>1.28</td>
</tr>
<tr>
<td>CaO</td>
<td>64.07</td>
<td>64.35</td>
<td>65.90</td>
<td>43.7</td>
<td>0.50</td>
<td>0.48</td>
</tr>
<tr>
<td>MgO</td>
<td>2.21</td>
<td>2.11</td>
<td>0.70</td>
<td>8.50</td>
<td>0.90</td>
<td>0.30</td>
</tr>
<tr>
<td>SO₃</td>
<td>1.96</td>
<td>2.10</td>
<td>2.10</td>
<td>1.13</td>
<td>0.50</td>
<td>0.20</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>0.80</td>
<td>0.70</td>
<td>1.30</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.31</td>
<td>0.36</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.21</td>
<td>0.19</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na₂O equivalent</td>
<td>0.41</td>
<td>0.43</td>
<td>0.36</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₃S</td>
<td>54.57</td>
<td>56.70</td>
<td>64.70</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₂S</td>
<td>21.91</td>
<td>16.05</td>
<td>8.53</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₃A</td>
<td>3.64</td>
<td>8.52</td>
<td>9.65</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₂AF</td>
<td>12.90</td>
<td>11.56</td>
<td>11.26</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

¹ Sulfate-resisting Portland cement (C₃A: 36%)
² Ordinary Portland cement (C₃A: 85%)
³ Ordinary Portland cement (C₃A: 965%)
⁴ Blast furnace slag
⁵ Silica fume
⁶ Fly ash
The required cements and the supplementary cementing materials were obtained from a single source and single batch. The required quantities of these materials were obtained and stored under controlled laboratory conditions (25°C and 50% RH) until their use.

Cylindrical cement paste specimens, 49 mm in diameter and 75 mm in height, were cast from each cement. These specimens were made with effective water to cementitious materials ratio of 0.45. Deionized water was used in these mixtures. The specimens were divided into seven groups and admixed with various dosages of chloride and sulfate salts, as shown in Table 3.2. Three specimens representing same constituent were used throughout this study.

Table 3.2: Level of contamination used in the cement paste specimens utilized for the pore solution study.

<table>
<thead>
<tr>
<th>Group</th>
<th>Contamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.8% Cl(^-) (NaCl was used)</td>
</tr>
<tr>
<td>2</td>
<td>0.8% Cl(^-) + 1% SO(_4)(^-) (NaCl and Na(_2)SO(_4) were used)</td>
</tr>
<tr>
<td>3</td>
<td>0.8% Cl(^-) + 2.5% SO(_4)(^-) (NaCl and Na(_2)SO(_4) were used)</td>
</tr>
<tr>
<td>4</td>
<td>0.8% Cl(^-) + 4% SO(_4)(^-) (NaCl and Na(_2)SO(_4) were used)</td>
</tr>
<tr>
<td>5</td>
<td>0.8% Cl(^-) + 1% SO(_4)(^-) (NaCl and MgSO(_4) were used)</td>
</tr>
<tr>
<td>6</td>
<td>0.8% Cl(^-) + 2.5% SO(_4)(^-) (NaCl and MgSO(_4) were used)</td>
</tr>
<tr>
<td>7</td>
<td>0.8% Cl(^-) + 4% SO(_4)(^-) (NaCl and MgSO(_4) were used)</td>
</tr>
</tbody>
</table>

The selected chloride ion concentration, i.e. 0.8% is twice that allowed by BS 8110 [64]. This was done to accelerate the deterioration process in concrete. The sulfate concentration was varied from 0 to
4% to systematically evaluate the effect of these ions on chloride binding.

The required quantities of analar grade salts were dissolved in the mix water, which was added gradually to the cement during mixing. The constituents were mixed in a blender till uniform consistency was obtained. In the blended cements, the supplementary cementing materials and the cement were first mixed thoroughly and then deionized water was added. The cement paste was poured into the plastic cylindrical vials in two layers with appropriate consolidation to remove entrapped air. The vials were then tightly sealed and kept at a controlled laboratory temperature of $20 \pm 2 \, ^\circ C$ until testing.

3.2.2 Pore Solution Extraction

The pore solution in the cement paste specimens was extracted using a high-pressure pore solution expression device similar to that used by Longuet et al. [97] and Barneyback and Diamond [98]. This technique has the advantage that the pore solution can be extracted and its composition known. Though this is a tedious method, the pore solution so extracted has a uniform concentration, while this advantage is not available with other techniques, such as determining the pore solution composition by water or acid extraction. The pore solution was extracted after 100 days of casting. For this purpose, the specimen was placed on the base of a pore press and the pressure was applied through the piston and gradually increased to a maximum of 150 MPa. This pressure was sustained until sufficient quantity (3 to 4 ml) of the pore fluid was recovered in a hypodermic syringe through the fluid drain located at the
base of the apparatus. Care was taken to avoid undue exposure of the pore solution to air and it was stored in sealed plastic tubes until the time of analysis.

### 3.2.3 Pore Solution Analysis

The expressed pore solution was analyzed to determine $\text{OH}^-$, $\text{Cl}^-$ and $\text{SO}_4^{2-}$ concentration.

**OH$^-$ Concentration**

The $\text{OH}^-$ concentration of the pore solution was evaluated by direct titration against nitric acid. For this purpose, 0.2 to 0.5 ml of the pore solution was diluted with deionized water to 10 ml and the $\text{OH}^-$ concentration was measured by direct titration against 0.01 M nitric acid using phenolphthalein as an indicator. A burette with a least division of 0.02 ml was used for titration. The actual molarity of the nitric acid was determined by titrating it against 0.01 M NaOH.

**Chloride Concentration**

The chloride ion concentration of the pore solution was determined using a spectrophotometric method [99]. For this purpose, 0.2 ml pore solution was diluted to 10 ml with distilled water. To the diluted solution, 2 ml ferric ammonium sulfate and 2 ml mercuric thiocynate, saturated in ethanol, were added. The mixture was mixed slowly and continuously by shaking the beaker and then kept undisturbed for about 30 minutes before the absorption reading was taken on a Spectronic model UV21 spectrophotometer at a wave length of 460 nm against deionized water. The chloride concentration was computed using a computer programme that corresponded to a calibration curve prepared
using a standard chloride solution. Some specimens were serially diluted to maintain the chloride concentration to less than 10 µg/L.

**Sulfate Concentration**

The sulfate concentration was determined using the spectrophotometric method outlined in standard methods for the analysis of water and wastewater, published by the American Water Works Association (AWWA) [100]. For this purpose, 0.5 ml of the pore solution was diluted to 100 ml using deionized water. To the diluted solution, the recommended buffer was added and absorption measured using a spectrophotometer at a wavelength of 420 nm. Barium chloride (BaCl\(_2\)) was then added to the solution and mixed by stirring for one minute. After thorough mixing, the solution was placed in the spectrophotometer and the absorption reading taken after 5 minutes. The sulfate concentrations were calculated from the net absorption using a calibration curve prepared using a standard sulfate solution.

3.3 EFFECT OF SULFATE CONCENTRATION AND THE ASSOCIATED CATION TYPE ON CHLORIDE-INDUCED REINFORCEMENT CORROSION

3.3.1 Materials and Specimen Preparation

The cements used to prepare reinforced concrete specimens were the same as those utilized to prepare the pore solution specimens as described in Section 3.2.1. 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 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.

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.

<table>
<thead>
<tr>
<th>Sieve opening, mm</th>
<th>Percentage passing</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>100</td>
</tr>
<tr>
<td>19.0</td>
<td>90</td>
</tr>
<tr>
<td>12.5</td>
<td>55</td>
</tr>
<tr>
<td>9.5</td>
<td>20</td>
</tr>
<tr>
<td>4.75</td>
<td>5</td>
</tr>
<tr>
<td>2.36</td>
<td>0</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Weight per cubic metre, kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cementitious material</td>
<td>350</td>
</tr>
<tr>
<td>Coarse aggregate</td>
<td>1116</td>
</tr>
<tr>
<td>Fine aggregate</td>
<td>684</td>
</tr>
<tr>
<td>Water</td>
<td>158</td>
</tr>
</tbody>
</table>

3.3.2 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% $\text{SO}_4^{2-}$ 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.](image)

<table>
<thead>
<tr>
<th>Group</th>
<th>Concentration of the test solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5% NaCl</td>
</tr>
<tr>
<td>2</td>
<td>5% NaCl + 1% $\text{SO}_4^{2-}$ (Na$_2$SO$_4$ was used)</td>
</tr>
<tr>
<td>3</td>
<td>5% NaCl + 2.5% $\text{SO}_4^{2-}$ (Na$_2$SO$_4$ was used)</td>
</tr>
<tr>
<td>4</td>
<td>5% NaCl + 4% $\text{SO}_4^{2-}$ (Na$_2$SO$_4$ was used)</td>
</tr>
<tr>
<td>5</td>
<td>5% NaCl + 1% $\text{SO}_4^{2-}$ (MgSO$_4$ was used)</td>
</tr>
<tr>
<td>6</td>
<td>5% NaCl + 2.5% $\text{SO}_4^{2-}$ (MgSO$_4$ was used)</td>
</tr>
<tr>
<td>7</td>
<td>5% NaCl + 4% $\text{SO}_4^{2-}$ (MgSO$_4$ was used)</td>
</tr>
</tbody>
</table>

3.3.3 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 ± 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]:

\[ I_{corr} = \frac{B}{R_p} \]

Where

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

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

\[ B = \frac{\beta_a \beta_c}{2(\beta_a + \beta_c)} \]

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 ±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.

3.3.4 Morphological Changes in Cement due to Sulfate Exposure

The morphological changes in cement due to exposure to sulfate solution were investigated using a JEOL Model JSM-840 scanning electron microscope. Scanning electron microscopy (SEM) is a valuable tool by which it is possible to resolve distances up to less than 10 Å. It has a magnification in the range of 20-150,000 and a depth of field that is 300 times that of ordinary light microscope. The SEM used was also equipped with an energy dispersive X-ray analyzer (EDXA) which provides semi-quantitative information on the elemental composition of the specimen under consideration.

3.4 INFLUENCE OF ALKALINITY ON PORE SOLUTION CHEMISTRY

3.4.1 Materials and Specimen Preparation

Cylindrical cement paste specimens, 49 mm in diameter and 75 mm high, were cast using SRPC and OPC-A with an effective water to
cementitious materials ratio of 0.45. Deionized water was used in these mixtures. These specimens were used to study the effect of cement alkalinity on pore solution composition.

Cement alkalinity was adjusted to 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4% (Na₂O equivalent) and admixed with 0.8% Cl⁻ by weight of cement. Analar grade sodium hydroxide and sodium chloride was mixed with distilled water to obtain the required quantity of alkalinity or chloride ion. Three replicate specimens were cast from each batch.

3.4.2 Pore Solution Extraction and Analysis

The pore solution was extracted from the specimens prepared in Section 3.4.1 and analyzed to determine the concentrations of OH⁻, Cl⁻ and SO₄⁻ concentrations as described in Sections 3.2.2 and 3.2.3.

3.5 INFLUENCE OF ALKALINITY ON REINFORCEMENT CORROSION

3.5.1 Materials and Specimen Preparation

The concrete specimens were prepared using sulfate resisting Portland cement (SRPC) and ordinary Portland cement (OPC-A). To study the effect of alkalinity on reinforcement corrosion, reinforced concrete specimens similar to those described in Section 3.3.1 were prepared. Cement alkalinity was adjusted to 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4% (Na₂O equivalent) by adding the required quantities of sodium hydroxide. Analar grade sodium hydroxide was mixed with distilled water to obtain the required alkalinity. Concrete cylindrical specimens, 75 mm diameter and 150 mm high, were cast using concrete with an effective water to cementitious materials ratio of 0.45. The mixture proportions and the quantities of ingredients used in the preparation
of concrete specimens of this series are the same as those described in Section 3.3.1 and detailed in Table 3.4. Three replicate specimens were cast from each batch.

3.5.2 Exposure Solutions

The concrete specimens were divided into six groups, each group consisted of three specimens from each cement. The specimens in each group were placed in solution containing 5% NaCl and varying alkalinity as detailed in Table 3.6.

Table 3.6: Composition of the Test Solution for Series III and IV Specimens.

<table>
<thead>
<tr>
<th>Group</th>
<th>Composition of exposure solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5%NaCl + 0.4% Na2O equivalent (control)</td>
</tr>
<tr>
<td>2</td>
<td>5% NaCl + 0.6% Na2O equivalent</td>
</tr>
<tr>
<td>3</td>
<td>5% NaCl + 0.8% Na2O equivalent</td>
</tr>
<tr>
<td>4</td>
<td>5% NaCl + 1.0% Na2O equivalent</td>
</tr>
<tr>
<td>5</td>
<td>5% NaCl + 1.2% Na2O equivalent</td>
</tr>
<tr>
<td>6</td>
<td>5% NaCl + 1.4% Na2O equivalent</td>
</tr>
</tbody>
</table>

3.5.3 Monitoring of Reinforcement Corrosion

Reinforcement corrosion was evaluated by measuring corrosion potentials and corrosion current density, using procedures outlined in Section 3.3.3.
Figure 3.1: Schematic diagram of the experimental set up used to monitor corrosion potentials and corrosion current density.
CHAPTER 4
EFFECT OF CHLORIDE AND SULFATE CONCENTRATION ON THE PORE SOLUTION CHEMISTRY

4.1 INTRODUCTION

To evaluate the effect of chloride and sulfate contamination on the pore solution chemistry, cylindrical cement paste specimens 49 mm diameter and 75 mm high were prepared as described in Section 3.2.1 (Series I). These specimens were admixed with a fixed quantity of sodium chloride and varying dosages of sodium sulfate or magnesium sulfate, as discussed in Section 3.2.1 and detailed in Table 3.2. Pore solution was extracted from these specimens and analyzed to determine OH\(^{-}\), Cl\(^{-}\) and SO\(_4\)\(^{2-}\) concentrations, as described in Sections 3.2.2 and 3.2.3. The pore solution was extracted from three replicate specimens, and average value was reported. Statistical analysis revealed that the coefficient of variation was low and within acceptable limits. However, in limited instances where spurious readings were obtained, they were excluded while calculating the average value. Tables 4.1 through 4.6 present typical statistical analysis of OH\(^{-}\), Cl\(^{-}\) and SO\(_4\)\(^{2-}\), concentrations in the SRPC paste specimens admixed with sodium chloride plus sodium sulfate or magnesium sulfate. Similar statistical analysis of OH\(^{-}\), Cl\(^{-}\), and SO\(_4\)\(^{2-}\) concentrations of OPC-A, OPC-B, BFS, SF, and FA cement paste specimens were performed.
### Table 4.1: Statistical analysis of OH\(^-\) concentration in the SRPC paste specimens admixed with sodium chloride plus sodium sulfate.

<table>
<thead>
<tr>
<th>Contamination</th>
<th>OH(^-) concentration, mM/L</th>
<th>Coefficient of variation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
<td>Sample 2</td>
</tr>
<tr>
<td>0.8% Cl(^-)</td>
<td>457</td>
<td>465</td>
</tr>
<tr>
<td>0.8%Cl(^-)+1%SO(_4)^-</td>
<td>658</td>
<td>673</td>
</tr>
<tr>
<td>0.8%Cl(^-)+2.5%SO(_4)^-</td>
<td>814</td>
<td>850</td>
</tr>
<tr>
<td>0.8%Cl(^-)+4%SO(_4)^-</td>
<td>837</td>
<td>867</td>
</tr>
</tbody>
</table>

### Table 4.2: Statistical analysis of OH\(^-\) concentration in the SRPC paste specimens admixed with sodium chloride plus magnesium sulfate.

<table>
<thead>
<tr>
<th>Contamination</th>
<th>OH(^-) concentration, mM/L</th>
<th>Coefficient of variation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
<td>Sample 2</td>
</tr>
<tr>
<td>0.8% Cl(^-)</td>
<td>457</td>
<td>465</td>
</tr>
<tr>
<td>0.8%Cl(^-)+1%SO(_4)^-</td>
<td>440</td>
<td>465</td>
</tr>
<tr>
<td>0.8%Cl(^-)+2.5%SO(_4)^-</td>
<td>475</td>
<td>495</td>
</tr>
<tr>
<td>0.8%Cl(^-)+4%SO(_4)^-</td>
<td>300</td>
<td>275</td>
</tr>
</tbody>
</table>

### Table 4.3: Statistical analysis of chloride concentration in the SRPC paste specimens admixed with sodium chloride plus sodium sulfate.

<table>
<thead>
<tr>
<th>Contamination</th>
<th>Chloride concentration, mM/L</th>
<th>Coefficient of variation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
<td>Sample 2</td>
</tr>
<tr>
<td>0.8% Cl(^-)</td>
<td>312</td>
<td>328</td>
</tr>
<tr>
<td>0.8%Cl(^-)+1%SO(_4)^-</td>
<td>450</td>
<td>454</td>
</tr>
<tr>
<td>0.8%Cl(^-)+2.5%SO(_4)^-</td>
<td>623</td>
<td>634</td>
</tr>
<tr>
<td>0.8%Cl(^-)+4%SO(_4)^-</td>
<td>695</td>
<td>710</td>
</tr>
</tbody>
</table>
Table 4.4: Statistical analysis of chloride concentration in the SRPC paste specimens admixed with sodium chloride plus magnesium sulfate.

<table>
<thead>
<tr>
<th>Contamination</th>
<th>Chloride concentration, mM/L</th>
<th>Coefficient of variation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
<td>Sample 2</td>
</tr>
<tr>
<td>0.8% Cl⁻</td>
<td>312</td>
<td>328</td>
</tr>
<tr>
<td>0.8%Cl⁻+1%SO₄⁻</td>
<td>394</td>
<td>392</td>
</tr>
<tr>
<td>0.8%Cl⁻+2.5%SO₄⁻</td>
<td>238</td>
<td>235</td>
</tr>
<tr>
<td>0.8%Cl⁻+4%SO₄⁻</td>
<td>186</td>
<td>195</td>
</tr>
</tbody>
</table>

Table 4.5: Statistical analysis of SO₄²⁻ concentration in the SRPC paste specimens admixed with sodium chloride plus sodium sulfate.

<table>
<thead>
<tr>
<th>Contamination</th>
<th>Sulfate concentration, mM/L</th>
<th>Coefficient of variation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
<td>Sample 2</td>
</tr>
<tr>
<td>0.8% Cl⁻</td>
<td>18</td>
<td>21</td>
</tr>
<tr>
<td>0.8%Cl⁻+1%SO₄⁻</td>
<td>174</td>
<td>149</td>
</tr>
<tr>
<td>0.8%Cl⁻+2.5%SO₄⁻</td>
<td>415</td>
<td>380</td>
</tr>
<tr>
<td>0.8%Cl⁻+4%SO₄⁻</td>
<td>673</td>
<td>665</td>
</tr>
</tbody>
</table>

Table 4.6: Statistical analysis of SO₄²⁻ concentration in the SRPC paste specimens admixed with sodium chloride plus magnesium sulfate.

<table>
<thead>
<tr>
<th>Contamination</th>
<th>Sulfate concentration, mM/L</th>
<th>Coefficient of variation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
<td>Sample 2</td>
</tr>
<tr>
<td>0.8% Cl⁻</td>
<td>18</td>
<td>21</td>
</tr>
<tr>
<td>0.8%Cl⁻+1%SO₄⁻</td>
<td>50</td>
<td>46</td>
</tr>
<tr>
<td>0.8%Cl⁻+2.5%SO₄⁻</td>
<td>109</td>
<td>96</td>
</tr>
<tr>
<td>0.8%Cl⁻+4%SO₄⁻</td>
<td>259</td>
<td>254</td>
</tr>
</tbody>
</table>
4.2 OH\(^-\) CONCENTRATION

4.2.1 Results

The OH\(^-\) concentration in the plain cement paste specimens admixed with sodium chloride plus sodium sulfate or magnesium sulfate is plotted in Figures 4.1 through 4.3. The OH\(^-\) concentration in the specimens admixed with sodium chloride plus sodium sulfate was more than that in the specimens admixed with only sodium chloride and much more than that in the specimens admixed with sodium chloride plus magnesium sulfate. The OH\(^-\) concentration in the former specimens increased significantly with increasing sulfate contamination, although at reduced rate above 2.5%. The OH\(^-\) concentration in the specimens admixed with sodium chloride plus magnesium sulfate was more or less similar to that in the specimens admixed with only sodium chloride. However, it decreased slightly in the specimens with 4% SO\(_4\)^{2-}.

The increase in the OH\(^-\) concentration in the specimens admixed with sodium chloride plus sodium sulfate may be attributed to the cation type associated with the sulfate and chloride ions. When sodium chloride and sodium sulfate are added to cement, Cl\(^-\) and SO\(_4\)^{2-} ions react with the cement hydration products, such as Ca(OH)\(_2\) and C\(_3\)A, while Na\(^+\) cations are released in the pore solution, thereby increasing its alkalinity.

The OH\(^-\) concentration in the blended cement paste specimens admixed with sodium chloride plus sodium sulfate or magnesium sulfate is shown in Figures 4.4 through 4.6. These data also indicated a trend similar to that noted in the plain cement specimens. The OH\(^-\) concentration increased significantly with increasing contamination of sodium sulfate up to 2.5%, while there was a marginal change in the OH\(^-\)
concentration when the sodium sulfate contamination was increased from 2.5 to 4%.

The OH\textsuperscript{−} concentration in the three plain cements (SRPC, OPC-A, and OPC-B) specimens are compared in Figure 4.7. The OH\textsuperscript{−} concentration is highest in the OPC-B specimens, and lowest in the SRPC specimens. In Figures 4.8 and 4.9, the OH\textsuperscript{−} concentration is plotted against tricalcium aluminate content (C\textsubscript{3}A) for the specimens admixed with sodium chloride plus sodium or magnesium sulfate, respectively. In the specimens admixed with magnesium sulfate also the OH\textsuperscript{−} concentration was the highest in OPC-B and lowest in the SRPC. The data indicate clearly that the OH\textsuperscript{−} concentration in the plain cements, admixed with sodium chloride plus sodium sulfate or magnesium sulfate increases with increasing C\textsubscript{3}A content of cements.

Figure 4.10 compares the OH\textsuperscript{−} concentration in the blended cements admixed with sodium chloride plus sodium sulfate or magnesium sulfate. The OH\textsuperscript{−} concentration increased significantly with the quantity of sodium sulfate but changed little with the magnesium sulfate contamination. The OH\textsuperscript{−} concentration was the highest in the blast furnace slag cement admixed with sodium chloride plus sodium sulfate and the lowest in the fly ash cement with similar contamination. However, the OH\textsuperscript{−} concentration in the silica fume cement admixed with only sodium chloride was the least. The OH\textsuperscript{−} concentration in the blast furnace slag cement admixed with sodium chloride plus magnesium sulfate was the highest, while it was the lowest in the silica fume cement specimens with similar contamination.

Figures 4.11 and 4.12 compare the OH\textsuperscript{−} concentration in the plain and blended cement paste specimens admixed with sodium sulfate and
magnesium sulfate, respectively. These data show that OH\(^-\) concentration was the highest in the plain cements with both salts. The decrease in the OH\(^-\) concentration in the blended cements, compared to plain cements, may be attributed to the reaction of Ca(OH)\(_2\) with the pozzolanic material.

Table 4.7 summarizes the OH\(^-\) concentrations of the pore solution in plain and blended cement paste specimens admixed with sodium chloride or sodium chloride plus sodium or magnesium sulfate.

Table 4.7: OH\(^-\) concentration in the plain and blended cement paste specimens.

<table>
<thead>
<tr>
<th>Contamination</th>
<th>OH(^-) concentration, mM/L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SRPC</td>
</tr>
<tr>
<td>0.8 Cl(^-)</td>
<td>459</td>
</tr>
<tr>
<td>0.8 Cl(^-)+1% SO(_4)^(-) (Na(_2)SO(_4))</td>
<td>665</td>
</tr>
<tr>
<td>0.8 Cl(^-)+2.5% SO(_4)^(-) (Na(_2)SO(_4))</td>
<td>827</td>
</tr>
<tr>
<td>0.8 Cl(^-)+4% SO(_4)^(-) (Na(_2)SO(_4))</td>
<td>850</td>
</tr>
<tr>
<td>0.8 Cl(^-)+1% SO(_4)^(-) (MgSO(_4))</td>
<td>454</td>
</tr>
<tr>
<td>0.8 Cl(^-)+2.5% SO(_4)^(-) (MgSO(_4))</td>
<td>485</td>
</tr>
<tr>
<td>0.8 Cl(^-)+4% SO(_4)^(-) (MgSO(_4))</td>
<td>289</td>
</tr>
</tbody>
</table>

4.2.2 Discussion of the Effect of Sodium Sulfate Contamination on OH\(^-\) Concentration

As shown in Figures 4.1 through 4.12 and Table 4.7, the OH\(^-\) concentration in the plain and blended cement paste specimens admixed with sodium chloride plus sodium sulfate was more than that in the specimens admixed with only sodium chloride. This increase in the OH\(^-\)
concentration due to the conjoint presence of sodium chloride and sodium sulfate is attributed to the cation type associated with the sulfate and chloride ions. When sodium chloride and sodium sulfate are added to cement, Cl$^-$ and SO$_4^{2-}$ react with the cement hydration products, such as Ca(OH)$_2$ and C$_3$A, while Na$^+$ and OH$^-$ ions are released in the pore solution.

According to Yonezawa et al. [104] NaCl first reacts with Ca(OH)$_2$, to form CaCl$_2$ releasing Na$^+$ and OH$^-$ in the pore solution. The CaCl$_2$ so formed reacts with tricalcium aluminate (C$_3$A) to form calcium-chloroaluminate hydrate (Friedel's salt) as indicated in the following equations:

$$2\text{NaCl} + \text{Ca(OH)}_2 \rightarrow \text{CaCl}_2 + 2\text{Na}^+ + 2\text{OH}^- \quad (4.1)$$

$$3\text{CaO Al}_2\text{O}_3.10\text{H}_2\text{O} + \text{CaCl}_2 \rightarrow 3\text{CaO Al}_2\text{O}_3.\text{CaCl}_2.10\text{H}_2\text{O} \quad (4.2)$$

Several researchers [5,7,43,46] have reported an increase in the OH$^-$ concentration in the pore solution of cement paste or mortar specimens admixed with sodium chloride and/or sodium sulfate. Maslehuudin [43] reported an increase in the OH$^-$ concentration in the pore solution of mortar specimens admixed with sodium chloride or sodium sulfate compared with unadmixed specimens. The OH$^-$ concentration in the specimens admixed with sodium chloride plus sodium sulfate was much more than that in the specimens admixed with either sodium chloride or sodium sulfate. Kayyali et al. [46] reported an increase in the OH$^-$ concentration in the pore solution of cement paste specimens admixed with sodium chloride and increased with the quantity of sodium chloride. Hussain [7] demonstrated that the OH$^-$ concentration increased with increasing quantity of sodium chloride and it was higher in the specimens admixed with sodium chloride plus sodium sulfate compared
with those admixed with only sodium chloride. However, the increase was marginal when the sodium sulfate concentration increased from 4% to 8%. Holden et al. [5] indicated that the OH⁻ concentration in the specimens admixed with sodium chloride was more than that in the specimens without any contamination and it was higher in the specimens admixed with sodium chloride plus sodium sulfate compared with those admixed with only sodium chloride.

The OH⁻ concentration in the blended cement specimens admixed with sodium chloride plus sodium sulfate also increased with increasing concentration of sodium sulfate. However, the increase in the OH⁻ concentration was marginal when the sulfate concentration increased from 2.5 to 4%. Several studies [7,23,43] indicated an increase in the OH⁻ concentration in the blended cements due to incorporation of sodium chloride and/or sodium sulfate. Maslehuddin [43] reported an increase in the OH⁻ concentration in the blended cements due to the addition of sodium chloride and/or sodium sulfate. He attributed the increase in the OH⁻ concentration in the blended cements, due to incorporation of sodium chloride and/or sodium sulfate to the fixation of chloride and sulfate ions with the cement hydration products and to the pozzolonic reaction. Hussain [7] and Talib [23] reported similar results.

The OH⁻ concentration in all the blended cement specimens admixed with sodium chloride was much less than that in the plain cements with similar contamination and in the silica fume cement specimens it was the lowest. Similarly, the OH⁻ concentration in all the blended cement specimens admixed with sodium chloride plus sodium sulfate or magnesium sulfate was less than that in the plain cement specimens with similar contamination. Further, the OH⁻ concentration in the silica fume
cement specimens admixed with sodium chloride plus magnesium sulfate was the lowest.

The lower OH\(^-\) concentration in the pore solution of blended cements, compared to plain cement, may be attributed to the reaction between Ca(OH)\(_2\) in cement and the pozzolanic materials. Such a phenomenon has been reported by several researchers [5, 20, 23, 68, 105]. Nixon et al. [105] reported a reduction in the OH\(^-\) concentration of cements blended with PFA, the OH\(^-\) concentration decreased with increasing quantity of fly ash. Further, it was reported that the pore solution composition is significantly affected by the cement alkalinity and the fly ash content. Holden et al. [5] and Diamond [68] reported that the addition of fly ash to Portland cement paste causes a reduction in the OH\(^-\) concentration of its pore solution. A recent study [23] indicated that the OH\(^-\) concentration in the silica fume cement decreased with increasing cement replacement by silica fume up to 15%, beyond this quantity the alkalinity decreased marginally. Similar results were reported by Page and Vennesland [20] who indicated a decrease in the pH of the pore solution with increasing addition of silica fume to cement paste.

Rasheeduzzafar et al. [69], Maslehuddin [43] and Byfors et al. [70] reported a reduction in the OH\(^-\) concentration of the pore solution of cement paste specimens incorporating silica fume. Byfors [70] attributed the reduction in the pH of the pore solution in the silica fume cements to the diluting effect when cement is replaced by silica fume. Sellevold [106] reported that the silica fume reacts with the calcium hydroxide formed during the hydration process due to which the OH\(^-\) concentration decreases.
Table 4.8 summarizes the OH\(^-\) concentration of the pore solution in cements admixed with sodium chloride and sodium chloride plus sodium sulfate. The data developed in this study and other related studies [5, 43, 45] are utilized for comparison. The data in Table 4.8 indicate that for a similar chloride contamination the OH\(^-\) concentration increases with the addition of sulfate ions. It should be noted that the data presented in Table 4.8 related to cements admixed with sodium chloride or sodium chloride plus sodium sulfate salts. The increase in the OH\(^-\) concentration, due to the addition of sodium sulfate, may be attributed to the reaction of sulfate ions with cement hydration products, as discussed earlier. When sulfate ions react with Ca(OH)\(_2\) and C\(_3\)A leading to the formation of gypsum and calcium sulfoaluminate hydrate, respectively. In this process, sodium ions are liberated into the pore solution, thereby increasing its alkalinity.

From the data in Table 4.8 it is apparent that the data developed in this study is comparable with that developed by Maslehuiddin [43] and Hussain et al. [45]. The OH\(^-\) concentration of SRPC used in this study and admixed with 0.8% Cl\(^-\) was 459 mM/L, while Maslehuiddin [43] reported a value of 324 mM/L. Hussain et al. [45] reported a value of 265 mM/L. This lower value is obvious since they admixed the cement with 0.6% Cl\(^-\). Holden et al. [5] reported a value of OH\(^-\) concentration of 501 mM/L in SRPC admixed with 0.4% Cl\(^-\). The high value of OH\(^-\) concentration reported by Holden et al. [5] compared to that obtained in this study and those reported by Maslehuiddin [43] and Hussain et al. [45] may be attributed to the variation of chemical composition of the cements used.
Table 4.8: Comparison of OH\(^{-}\) concentration of the pore solution obtained in the present study and other related studies [5, 43, 45].

<table>
<thead>
<tr>
<th>Researcher</th>
<th>Contamination</th>
<th>SRPC (mM/L)</th>
<th>% increase in OH(^{-})</th>
<th>OPC (mM/L)</th>
<th>% increase in OH(^{-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present study</td>
<td>0.8 Cl(^{-})</td>
<td>459</td>
<td>-</td>
<td>556</td>
<td>-</td>
</tr>
<tr>
<td>SRPC (C(_3)A: 3.6%)</td>
<td>0.8 Cl(^{-})+1.2%SO(_3)(^{-})*</td>
<td>665</td>
<td>44.9</td>
<td>740</td>
<td>33.1</td>
</tr>
<tr>
<td>OPC (C(_3)A: 8.5%)</td>
<td>0.8 Cl(^{-})+3%SO(_3)(^{-})*</td>
<td>827</td>
<td>80.2</td>
<td>872</td>
<td>56.8</td>
</tr>
<tr>
<td></td>
<td>0.8 Cl(^{-})+4.8%SO(_3)(^{-})*</td>
<td>850</td>
<td>85.2</td>
<td>961</td>
<td>72.8</td>
</tr>
<tr>
<td>Holden et al. [5]</td>
<td>0.4 Cl(^{-})</td>
<td>501</td>
<td>-</td>
<td>741</td>
<td>-</td>
</tr>
<tr>
<td>SRPC (C(_3)A: 1.9%)</td>
<td>0.4 Cl(^{-})+1.5%SO(_3)(^{-})</td>
<td>1000</td>
<td>99.6</td>
<td>1318</td>
<td>77.9</td>
</tr>
<tr>
<td>OPC (C(_3)A: 7.7%)</td>
<td>0.8 Cl(^{-})</td>
<td>324</td>
<td>-</td>
<td>401</td>
<td>-</td>
</tr>
<tr>
<td>Maslehuddin [43]</td>
<td>0.8 Cl(^{-})+1.5%SO(_3)(^{-})</td>
<td>609</td>
<td>88.0</td>
<td>725</td>
<td>80.8</td>
</tr>
<tr>
<td>Hussain et al. [45]</td>
<td>0.6 Cl(^{-})</td>
<td>265</td>
<td>-</td>
<td>391</td>
<td>-</td>
</tr>
<tr>
<td>SRPC (C(_3)A: 2.4%)</td>
<td>0.6 Cl(^{-})+1.5%SO(_3)(^{-})</td>
<td>770</td>
<td>190.6</td>
<td>786</td>
<td>101.02</td>
</tr>
<tr>
<td>OPC (C(_3)A: 7.59%)</td>
<td>0.6 Cl(^{-})+5.5%SO(_3)(^{-})</td>
<td>786</td>
<td>196.6</td>
<td>960</td>
<td>145.5</td>
</tr>
</tbody>
</table>

* SO\(_4\)\(^{-}\) was converted to SO\(_3\) to compare with other data

Another point to be noted from the comparison of data in Table 4.8 is that the OH\(^{-}\) concentration increases with the addition of sodium sulfate to chloride admixed cements. Holden et al. [5] and Maslehuddin [43] reported 99.6 and 88% increase in the OH\(^{-}\) concentration when 1.5% SO\(_3\) was added to chloride admixed SRPC. Hussain et al. [45] reported an
increase of 191 and 197%, respectively, when 1.5 and 5.5% SO₃ was added to SRPC admixed with 0.6% Cl⁻. In the present study, the OH⁻ concentration increased by 45, 80, and 85%, respectively, when SRPC admixed with 0.8% Cl⁻ was admixed with 1.2, 3, and 4.8% SO₃. The common feature of the data developed in this study and that reported by Hussain et al. [45] is that addition of excess amount of SO₃ marginally increased the OH⁻ concentration of the pore solution. This is apparent by the fact that the OH⁻ concentration, noted in this study, increased by only 5% when the SO₃ concentration was increased from 3 to 4.8%, while the OH⁻ concentration increased by about 35% when the SO₃ concentration was increased from 1.2 to 3%. In the data reported by Hussain et al. [45] the OH⁻ concentration increased by about 6% when the SO₃ concentration was increased from 1.5 to 5.5%.

Table 4.8 also summarizes the OH⁻ concentrations in the OPC admixed with sodium chloride and sodium chloride plus sodium sulfate. As in the case of SRPC, the data developed in this study are comparable to that reported by Maslehuddin [43] and Hussain et al. [45], of course for similar contamination. However, an important point to be noted from the data in Table 4.8 is that the OH⁻ concentration in the OPC was more than that in the SRPC with similar contamination. This trend was noted in this study and by other researchers [5,43, 45]. The increase in the OH⁻ concentration of OPC, compared to SRPC, is indicative of chloride-binding of cements due to a higher C₃A in the former cement compared to the latter cement.
4.2.3 Discussion of the Effect of Magnesium Sulfate Contamination on OH⁻ Concentration

The OH⁻ concentration in all the plain and blended cements, admixed with sodium chloride plus magnesium sulfate, was less than that in the specimens admixed with sodium chloride plus sodium sulfate. Further, the OH⁻ concentration in the specimens admixed with sodium chloride plus magnesium sulfate was more or less similar to that in the specimens admixed with only sodium chloride. In fact the OH⁻ concentration decreased when the magnesium sulfate concentration increased from 2.5 to 4%. The insignificant change in the alkalinity of the pore solution, due to the incorporation of magnesium sulfate, may be attributed to the non-alkaline nature of magnesium hydroxide formed as a byproduct of the reaction between magnesium sulfate and the calcium hydroxide in the cement, as indicated by the following reaction.

\[
\text{MgSO}_4 + \text{Ca(OH)}_2 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{Mg(OH)}_2
\]  

(4.3)

The alkalinity of magnesium hydroxide (Mg(OH)₂) is low (pH<10.5), which marginally reduces the OH⁻ concentration of the pore solution in the specimens admixed with magnesium sulfate. Further, when the magnesium sulfate concentration is increased up to 4% SO₄²⁻, the quantity of magnesium hydroxide also increases thereby reducing the OH⁻ concentration. This phenomenon was generally noticed in both plain and blended cements, admixed with sodium chloride plus magnesium sulfate.
4.3 CHLORIDE CONCENTRATION

4.3.1 Results

The chloride concentration in the plain cement paste specimens admixed with sodium chloride plus sodium sulfate or magnesium sulfate is shown in Figures 4.13 through 4.15. The chloride concentration in the specimens admixed with sodium chloride plus sodium sulfate was more than that in the specimens admixed with only sodium chloride or those admixed with sodium chloride plus magnesium sulfate. Further, the chloride concentration in the specimens admixed with sodium chloride plus sodium sulfate increased with increasing sulfate contamination. It also increased with magnesium sulfate up to 1% SO$_4^{2-}$, but decreased at higher levels.

Figures 4.16 through 4.18 depict the chloride concentration in the blended cements admixed with sodium chloride plus sodium sulfate or magnesium sulfate. The trend of these data is similar to that observed in the plain cement paste specimens.

It is noteworthy to mention that the reduction in the chloride-binding capacity of the blended cements, especially silica fume cement, due to sulfate contamination, was much more than that in the plain cement specimens. For instance, the chloride concentration in the silica fume cement specimens admixed with only sodium chloride was 98 mM/L, while it was 317 mM/L in the SRPC specimens with similar contamination. The chloride concentration in the SRPC specimens admixed with sodium chloride plus 4% SO$_4^{2-}$, derived from sodium sulfate, was 701 mM/L while it was 703 mM/L in the silica fume cement specimens with similar contamination. The increase in the chloride concentration, due to incorporation of sodium sulfate, in the SRPC
specimens was 220%, while it was 720% in the silica fume cement specimens.

Table 4.9 summarizes chloride concentrations of the pore solution in plain and blended cement paste specimens admixed with sodium chloride or sodium chloride plus sodium or magnesium sulfate.

**Table 4.9: Chloride concentrations in the plain and blended cement paste specimens.**

<table>
<thead>
<tr>
<th>Contamination</th>
<th>Chloride concentration, mM/L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SRPC</td>
</tr>
<tr>
<td>0.8 Cl⁻</td>
<td>317</td>
</tr>
<tr>
<td>0.8 Cl⁻+1% SO₄²⁻ (Na₂SO₄)</td>
<td>436</td>
</tr>
<tr>
<td>0.8 Cl⁻+2.5% SO₄²⁻ (Na₂SO₄)</td>
<td>628</td>
</tr>
<tr>
<td>0.8 Cl⁻+4% SO₄²⁻ (Na₂SO₄)</td>
<td>701</td>
</tr>
<tr>
<td>0.8 Cl⁻+1% SO₄²⁻ (MgSO₄)</td>
<td>393</td>
</tr>
<tr>
<td>0.8 Cl⁻+2.5% SO₄²⁻ (MgSO₄)</td>
<td>236</td>
</tr>
<tr>
<td>0.8 Cl⁻+4% SO₄²⁻ (MgSO₄)</td>
<td>191</td>
</tr>
</tbody>
</table>

4.3.2 Discussion of the Effect of Sulfate Contamination on Chloride Binding in Plain Cements

The chloride concentration in the plain cement specimens (SRPC, OPC-A, and OPC-B) admixed with sodium chloride plus sodium sulfate or magnesium sulfate is plotted against sulfate concentration in Figure 4.19, while it is plotted against C₃A content of cement in Figures 4.20 and 4.21. The chloride concentration in the plain cements, admixed with sodium chloride plus sodium sulfate, increased with increasing sulfate contamination. However, in the specimens admixed with sodium
chloride plus magnesium sulfate, the chloride concentration increased up to 1% $\text{SO}_4^{2-}$. Further increase in the $\text{SO}_4^{2-}$ concentration resulted in a decrease in the chloride concentration. The chloride concentration in the SRPC paste specimens was more than that in the OPC-A, which was more than that in the OPC-B cement. This indicates that cements with high $\text{C}_3\text{A}$ bind more admixed chloride ions than the low $\text{C}_3\text{A}$ cements, even in the presence of sulfate contamination. Further, the chloride concentration increased with the quantity of sodium sulfate contamination. These results are in agreement with the findings of previous studies conducted by several investigators on chloride-binding of cements [5,44]. These studies concluded that the chloride-binding capacity of cement increases with increasing $\text{C}_3\text{A}$ content. Holden et al. [5] reported a substantial difference in the performance of low and high $\text{C}_3\text{A}$ cements in binding chlorides. Rasheeduzzafar et al. [44] indicated that the chloride concentration in the pore solution decreases significantly with increasing $\text{C}_3\text{A}$ content of cement.

The chloride concentration in the plain cement specimens admixed with sodium chloride plus magnesium sulfate increased with increasing quantity of magnesium sulfate up to 1%, then decreased with increasing quantity of these salts up to 2.5%, beyond which the chloride concentration remained more or less similar. The reduction in the chloride concentration, when the magnesium sulfate concentration is more than 1%, may be attributed to the low OH$^-$ concentration associated with the formation of magnesium hydroxide (pH<10.5).

The chloride concentrations in SRPC and OPC admixed with sodium chloride or sodium chloride plus sodium sulfate as obtained in this study and that reported by others [5,43,45] are summarized in Table 4.10.
These data indicate that the chloride concentration in the SRPC and OPC admixed with chloride salts increases when sodium sulfate is added to these cements.

Table 4.10: Comparison of chloride concentration of the pore solution developed in the present study and other related studies [5,43,45].

<table>
<thead>
<tr>
<th>Researcher</th>
<th>Contamination</th>
<th>SRPC</th>
<th>OPC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cl⁻ (mM/L)</td>
<td>% increase in Cl⁻</td>
</tr>
<tr>
<td>Present study</td>
<td>0.8 Cl⁻</td>
<td>317</td>
<td>-</td>
</tr>
<tr>
<td>SRPC (C₃A: 3.6%)</td>
<td>0.8 Cl⁻ + 1.2%SO₄</td>
<td>436</td>
<td>37.5</td>
</tr>
<tr>
<td>OPC (C₃A: 8.5%)</td>
<td>0.8Cl⁻ + 3%SO₃</td>
<td>628</td>
<td>98.1</td>
</tr>
<tr>
<td></td>
<td>0.8 Cl⁻ + 4.8%SO₃</td>
<td>701</td>
<td>121.1</td>
</tr>
<tr>
<td>Holden et al. [5]</td>
<td>0.4 Cl⁻</td>
<td>110</td>
<td>-</td>
</tr>
<tr>
<td>SRPC (C₃A: 1.9%)</td>
<td>0.4 Cl⁻ + 1.5%SO₃</td>
<td>257</td>
<td>133.6</td>
</tr>
<tr>
<td>OPC (C₃A: 7.7%)</td>
<td>0.8 Cl⁻</td>
<td>350</td>
<td>-</td>
</tr>
<tr>
<td>Maslehuddin [43]</td>
<td>0.8 Cl⁻</td>
<td>555</td>
<td>58.6</td>
</tr>
<tr>
<td>SRPC (C₃A: 3.5%)</td>
<td>0.6 Cl⁻</td>
<td>210</td>
<td>-</td>
</tr>
<tr>
<td>OPC (C₃A: 8.5%)</td>
<td>0.6 Cl⁻ + 1.5%SO₃</td>
<td>267</td>
<td>27.1</td>
</tr>
<tr>
<td>Hussain et al. [45]</td>
<td>0.6 Cl⁻ + 5.5%SO₃</td>
<td>300</td>
<td>42.9</td>
</tr>
</tbody>
</table>

*SO₄⁻ was converted to SO₃ to compare with other data.
The data developed in this study are comparable with that reported by Maslehuddin [43]. The chloride concentration in SRPC and OPC admixed with 0.8% Cl\(^-\) was 317 and 297 mM/L, respectively. Maslehuddin [43] reported a Cl\(^-\) concentration of 350 and 302 mM/L in SRPC and OPC admixed with 0.8% Cl\(^-\), respectively. Increase in the chloride concentration was reported by all the researchers when sulfate ions were added to chloride admixed cements. In the present study the Cl\(^-\) concentration increased by 121% when 4.8% SO\(_3\) was added to SRPC admixed with 0.8% Cl\(^-\). Holden et al. [5] reported 134% increase in the Cl\(^-\) concentration when 1.5% SO\(_3\) was added to SRPC admixed with 0.4% Cl\(^-\). Hussain et al. [45] reported only 43% increase in the chloride concentration when SRPC admixed with 0.6% Cl\(^-\) was admixed with 5.5% SO\(_3\). Another point to be noted from the data in Table 4.10 is that the Cl\(^-\) concentration in OPC is less than that in SRPC. This is attributed to the increased chloride binding by OPC compared to SRPC. Similar trend was noted by other researchers [5, 43, 45].

4.3.3 Discussion of the Effect of Sulfate Contamination on Chloride binding Capacity of Blended Cements

Figure 4.22 shows the chloride concentration in the blended cement specimens admixed with sodium chloride plus sodium sulfate or magnesium sulfate. The chloride concentration in the blended cements admixed with sodium chloride plus sodium sulfate was more than that in the specimens admixed with only sodium chloride. The chloride concentration in the silica fume cement specimens admixed with only sodium chloride was the lowest while it was the highest in the fly ash cement specimens with similar contamination. The chloride concentration in the blast furnace slag cement specimens admixed with sodium chloride plus sodium sulfate was the lowest, while it was the
highest in the fly ash cement paste specimens with similar contamination. The chloride concentration in the blended cement specimens also increased with the addition of magnesium sulfate, up to 1% $\text{SO}_4^{2-}$ concentration. Any further increase in the sulfate addition resulted in a decrease in the chloride concentration.

The data in Figures 4.13 through 4.22 indicate that the chloride concentration in the blended cements was less than that in the plain cement specimens with similar contamination. This indicates the superior performance of blended cements, compared to plain cements, in binding admixed chlorides. Holden et al. [5] investigated the effect of chloride addition, on the chloride-binding capacity of fly ash and blast furnace slag cements. Their results [5] indicated higher chloride-binding in the fly ash and blast furnace slag cements compared to SRPC and OPC. Andrade and Page [107] investigated the effect of cation type on the chloride-binding capacity of OPC and blast furnace slag cements. The chloride binding in the blast furnace slag cement was more than that in the ordinary Portland cements. Kayyali [46] reported a marginal increase in the chloride binding of cements due to the incorporation of fly ash in the mortar specimens admixed with NaCl and CaCl$_2$. Hussain [7] reported greater chloride-binding in the fly ash and blast furnace slag cements compared to ordinary Portland cement. It is understood that the chloride binding in the slag cements takes place by mechanism other than the formation of Friedel’s salt, possibly the slag itself is capable of binding some of the chlorides. It is also probable that the chloride ions are adsorbed on the C-S-H gel in the slag cements. However, the chloride bound by the C-S-H is less stable than that bound with the C$_3$A [47].
The increased chloride binding by silica fume cements compared to plain cements has been reported by Page and Vennesland [20]. Their results showed that incorporation of increasing percentages of silica fume in Portland cement paste would lead to a progressive reduction in the extent to which chloride ions, introduced during mixing, are excluded from the pore solution. Also, the data from differential thermal analysis coupled with differential thermogravimetric analysis indicated that an increase in the silica fume content brought about not only an expected systematic reduction in the quantity of Ca(OH)$_2$, but also a regular diminution in the quantity of calcium chloro-aluminate hydrates [20]. They [20] attributed the decreased chloride-binding to the increased solubility of Friedel's salt due to a reduction in the pH as a result of incorporation of silica fume in the cement. Diamond [68] referring to the hypothesis of Page and Vennesland [20] regarding the lowering of the chloride binding due to reduction in the alkalinity reported that the reduced chloride-binding capacity in the silica fume cements, among other phenomena, may be attributed to the reduction in the mix water due to the formation of hydration products. However, results contradicting the above findings were reported by Byfors et al. [70], who indicated higher chloride-binding by the silica fume cements than the ordinary Portland cement. They [70] attributed this increase to the specific area of the gel in the silica fume cement paste. Talib [23] indicated that chloride-binding capacity of silica fume cement was higher than the plain cement, up to 15% silica fume, while the chloride-binding capacity decreased when the silica fume replacement was more than 15%.
4.3.4 Discussion of the Effect of Sulfate Contamination on Chloride Binding Capacity of Plain and Blended Cements

The data developed in the present study suggest that the chloride-binding capacity of both plain and blended cements decreases due to the concomitant presence of chloride and sulfate salts. The chloride-binding capacity of both plain and blended cements decreased with increasing sodium sulfate concentration, while it was not affected with increasing concentrations of magnesium sulfate. Further, the chloride-binding capacity of plain cements increased with the C₃A content of cement. Also, the chloride-binding capacity of blended cements was more than that of plain cements.

The decrease in the chloride-binding capacity of cements due to the concomitant presence of chloride and sulfate salts, particularly sodium sulfate, may be attributed to the reaction of sulfate ions with the C₃A phase thus inhibiting the formation of Friedel's salt. Several investigators [5, 7, 43, 44, 45] reported similar results. Holden et al. [5] reported a substantial decrease in the chloride-binding capacity of both plain and blended cements due to the concomitant presence of chloride and sulfate salts. They [5] attributed the reduction in the chloride-binding capacity of cements, in the presence of sulfates, to the tendency of sulfate ions to react with the C₃A phase of cement forming calcium sulfo-aluminate hydrate and inhibiting the formation of calcium chloro-aluminate (Friedel's salt). Maslehuddin [64] attributed the reduction in the chloride-binding capacity of cements, due to the concomitant presence of chloride and sulfate ions, to the parallel reaction of sulfate and chloride ions with C₃A to form both calcium sulfo-aluminate hydrate, and calcium chloro-aluminate hydrate, respectively. Hussain [7] indicated that chloride-binding capacity increases with increasing C₃A
content of cement and decreases with increasing concentration of sodium sulfate.

4.3.5 Discussion of the Effect of Cement Alkalinity on Chloride Binding

Another factor that may affect the chloride-binding capacity of cements is the alkalinity of the pore solution. As discussed in Section 4.1, the alkalinity (OH⁻ concentration) of the pore solution increased due to the addition of sodium chloride plus sodium sulfate that may affect the chloride-binding capacity. Several researchers [7, 23, 108] have reported a significant inhibiting effect of a strong alkaline pore solution on the chloride-binding capacity of cements.

Figures 4.23 through 4.26 show the chloride concentration plotted against alkalinity (OH⁻ concentration) in the plain and blended cement specimens admixed with sodium chloride plus sodium or magnesium sulfate. The chloride concentration in the pore solution of all cements, admixed with sodium chloride plus sodium sulfate, increased linearly with the OH⁻ concentration. However, no trend was observed in the specimens admixed with sodium chloride plus magnesium sulfate. Figures 4.23 and 4.24 show a linear relationship between chloride concentration and OH⁻ concentration ($R^2 = 0.95$ to 1).

Studies conducted earlier [5, 7, 43, 45] on the role of sulfate ions on chloride-binding have used sodium sulfate to derive sulfate ions, on the assumption that this is the major form of sulfate salt. However, sulfate ions can also be associated with magnesium and calcium cations. Magnesium sulfate is commonly prevalent in the sabkha soil and sea dredged aggregate. Though sulfate ions can exist in the form of calcium
sulfate, its solubility is very low. Therefore, the deteriorating action of this salt is rarely considered.

The data developed in the present study have, however, indicated that the chloride-binding in the cements admixed with sodium chloride plus sodium sulfate decreases with the sulfate concentration, while such a behaviour was not noted in the cements admixed with sodium chloride plus magnesium sulfate. This indicates that the cation type associated with sulfate ion significantly influences the chloride-binding of cements, apparently by changing the alkalinity of the pore solution. This is obvious from the fact that the alkalinity of the pore solution increased with increasing concentration of sodium sulfate, while it did not change significantly with increasing concentration of magnesium sulfate. As shown in Figures 4.23 through 4.26 the chloride concentration in the specimens admixed with sodium chloride plus sodium sulfate increased linearly with the OH⁻ concentration of the pore solution, while such a relationship was not observed in the specimens admixed with sodium chloride plus magnesium sulfate. These data, therefore, indicate that alkalinity of the pore solution significantly influences the chloride-binding capacity of cements. It may be presumed that Friedel's salt is unstable at high pH and that the chloride binding decreases proportionately with the pH of the pore solution. The following expression represents the effect of alkalinity on the stability of calcium chloro-aluminate hydrate (Friedel's' salt).

\[
Ca(OH)_2 + (Mg, Na)Cl \rightleftharpoons_{pH}^{pH} CaCl_2 + (Mg, Na)(OH)_2 \\
CaCl_2 + 3CaO.Al_2O_3 + 10H_2O \rightleftharpoons_{pH}^{pH} 3CaO.Al_2O_3.CaCl_2.10H_2O
\]
From the previous reactions it can be deduced that alkalinity controls the reaction between chloride ions and the cement hydration products, particularly Ca(OH)$_2$. When cement is admixed with magnesium sulfate, the calcium sulfate formed is stable, due to the low pH of the pore solution, the chloride-binding of cements is not affected. However, when the pH of the pore solution is high, for instance when it is admixed with sodium sulfate, the calcium sulfate is not stable, as a result the sulfate ions are free to react with the cement hydration products, C$_3$A in plain cements and C-S-H in the blended cements, thereby decreasing the chloride-binding. The influence of alkalinity on chloride-binding is further discussed in Chapter 6.

4.4 **Cl/OH$^-$ RATIO**

4.4.1 *Results*

The chloride to hydroxyl ion ratio (Cl$^-$/OH$^-$) of the pore solution in the plain cement paste specimens admixed with sodium chloride plus sodium sulfate or magnesium sulfate are shown in Figures 4.27 through 4.29. The Cl$^-$/OH$^-$ values in the specimens admixed with sodium chloride plus sodium sulfate increased with increasing quantity of sodium sulfate. In the specimens admixed with sodium chloride plus magnesium sulfate these values increased with increasing quantity of magnesium sulfate up to 1% SO$_4^{2-}$, beyond which they decreased.

The Cl$^-$/OH$^-$ values in the blended cement paste specimens admixed with sodium chloride plus sodium sulfate or magnesium sulfate are plotted against sulfate concentration in Figures 4.30 through 4.32. The Cl$^-$/OH$^-$ values in the BFS cement paste specimens admixed with sodium chloride plus sodium sulfate or magnesium sulfate increased with increasing quantity of these salts. The Cl$^-$/OH$^-$ in the silica fume cement
specimens admixed with sodium chloride plus sodium sulfate was less than that in the specimens admixed with only sodium chloride, while the Cl'/OH⁻ in the specimens admixed with sodium chloride plus magnesium sulfate increased with increasing quantity of magnesium sulfate.

The Cl'/OH⁻ values in the fly ash cement specimens admixed with sodium chloride plus sodium sulfate were almost similar to those in the specimens admixed with only sodium chloride, but the ratio with magnesium sulfate increased up to 1% SO₄²⁻ and then decreased at higher SO₄²⁻ concentrations.

4.4.2 Discussion of the Effect of Sulfate Contamination on Cl'/OH⁻

Despite the importance of the OH⁻ and Cl⁻ concentration of the pore solution, they alone do not provide any indication of corrosion risk. The Cl'/OH⁻ ratio of the pore solution is therefore considered to be a rough measure of the relative corrosion risk, particularly the time to initiation of reinforcement corrosion. Several researchers [18, 19, 44, 68] have proposed threshold Cl'/OH⁻ values for the depassivation of steel. Hausman [18] proposed a threshold Cl'/OH⁻ value of 0.6. Gouda [19] evaluated the maximum NaCl threshold concentration for six pH values ranging from 11.75 to 13.95. Diamond [68] converted the data developed by Gouda [19] to compare the Cl'/OH⁻ values for various pH ranges. His results indicated that the threshold Cl'/OH⁻ ratios were 0.57, 0.48, 0.29, 0.27 and 0.3 for pH values of 11.75, 12.1, 12.6, 13, and 13.3, respectively. Based on this study, Diamond [68] recommended a depassivation threshold Cl'/OH⁻ of 0.3 for concrete alkaline pore solution. Rasheeduzzafar et al. [44] adopted a Cl'/OH⁻ threshold of 0.3 proposed by Diamond [68] to signify the onset of depassivation and corrosion in concrete admixed with chloride ions.
In other studies, Hussain et al. [110,114] evaluated the threshold Cl'/OH⁻ ratios in the specimens exposed to 5% NaCl solution. The results of these studies revealed that the threshold Cl'/OH⁻ depends on the pH of the pore solution of concrete. These results also indicated that a Cl'/OH⁻ ratio of 0.3 can be adopted for concrete with admixed chloride. Hussain et al. [110] demonstrated that the threshold Cl'/OH⁻ value for the pore solution pH in the range of 13.26 to 13.36 varies from 1.28 to 2.0. Lambert et al. [66] indicated that the threshold Cl'/OH⁻ ratio in concrete exposed to external chloride was 3. Kayyali and Haque [109] emphasized the importance of Cl'/OH⁻ threshold to predict the time to initiation of reinforcement corrosion. They [109] provided charts giving safe regions of Cl'/OH⁻ values for various concretes. According to their charts, a Cl'/OH⁻ value of more than 0.6, for concrete with admixed chloride is considered unsafe. Similarly, a Cl'/OH⁻ value of greater than 3.0 for concrete exposed to external chloride is considered unsafe.

The Cl'/OH⁻ ratios in all the plain and blended cement paste specimens, except blast furnace slag cement specimens, were greater than 0.3, the threshold value proposed by Diamond [68]. The high Cl'/OH⁻ values, more than 0.3 noted in all the plain and blended cements, may lead to depassivation of steel and hence initiate reinforcement corrosion. Further, the increase in the sulfate contamination did not significantly increase the Cl'/OH⁻ value in the plain and BFS cements. However, a change in the Cl'/OH⁻ value was noted in the silica fume and fly ash cements with increasing sulfate contamination.

Figure 4.33 shows the variation of Cl'/OH⁻ values in the plain and blended cement specimens admixed with sodium chloride plus sodium sulfate. These data indicate that the Cl'/OH⁻ values in the fly ash cement
specimens were the highest. This can be attributed to the low alkalinity of the pore solution in these cements. The Cl'/OH' values were the lowest in the blast furnace slag cement specimens. This can be ascribed to the ability of blast furnace slag cement to bind more chloride in addition to the high alkalinity of pore solution of this cement. Among the plain cement specimens, the Cl'/OH' ratios in the SRPC specimens were the highest, while they were the lowest in the OPC-B specimens. This can be attributed to the C₃A content and low chloride and high OH' concentrations in these cements, as discussed in Sections 4.1 and 4.2.

Figure 4.34 depicts the variation of Cl'/OH' ratios in the plain and blended cement specimens admixed with sodium chloride plus magnesium sulfate. The trend of these data is similar to that observed in the plain and blended cement specimens admixed with sodium chloride plus sodium sulfate. A comparison of the data in Figures 4.27 through 4.34 shows that the Cl'/OH' values in the specimens admixed with sodium chloride plus magnesium sulfate were more than those admixed with sodium chloride plus sodium sulfate, particularly up to 1% SO₄²⁻. However, when the sulfate contamination was more than 1%, the Cl'/OH' values in the specimens admixed with sodium chloride plus magnesium sulfate were less than those admixed with sodium chloride plus sodium sulfate. Thus the chances of depassivation of steel are high in the concrete specimens admixed with sodium chloride plus magnesium sulfate, particularly for SO₄²⁻ concentration of up to 1%. However, when the SO₄²⁻ concentration is more than 1%, steel depassivation will be earlier in the specimens admixed with sodium chloride plus sodium sulfate compared to those admixed with sodium chloride plus magnesium sulfate.
4.5 SULFATE CONCENTRATION

4.5.1 Results

The sulfate concentration in the plain cement paste specimens admixed with sodium chloride plus sodium sulfate or magnesium sulfate is shown in Figures 4.35 through 4.37. The sulfate concentration increased approximately linearly in the specimens admixed with sodium chloride plus sodium sulfate or magnesium sulfate, although the rate was much higher with the former.

The sulfate concentration in the blended cement paste specimens admixed with sodium chloride plus sodium sulfate or magnesium sulfate is plotted in Figures 4.38 through 4.40. The sulfate concentration in BFS cement paste specimens increased with the quantity of sodium sulfate, while no change in the sulfate concentration was noted in the specimens admixed with magnesium sulfate. However, the sulfate concentration in the blended cement paste specimens was much less than that in the plain cement paste specimens.

Figures 4.41 and 4.42 compare the sulfate concentration in the plain and blended cement paste specimens admixed with sodium chloride plus sodium or magnesium sulfate. The $\text{SO}_4^{2-}$ concentration in the plain cement paste specimens was more than that in the blended cement in both sodium and magnesium sulfate.

The sulfate concentration is plotted against OH$^-$ concentration in Figures 4.43 through 4.46. The sulfate concentration in the specimens admixed with sodium chloride plus sodium sulfate increased significantly with the OH$^-$ concentration of the pore solution, while such a relationship was not observed in the specimens admixed with sodium chloride plus magnesium sulfate.
4.5.2 Discussion of the Effect of Sulfate Contamination on the Sulfate Concentration

The data in Figures 4.35 through 4.42 indicate that the sulfate concentration in the plain and blended cement paste specimens, admixed with sodium chloride plus sodium sulfate or magnesium sulfate, increased with increasing sulfate contamination. This increase may be attributed to the addition of sulfate salts to the mix. Further, the sulfate concentration in the specimens admixed with sodium chloride plus sodium sulfate was much more than that in the specimens admixed with sodium chloride plus magnesium sulfate indicating that more sulfates are bound with the cement hydration products when they are associated with magnesium ions. This may be attributed to the high alkalinity of the pore solution in the specimens admixed with sodium sulfate. It is possible that at high pH the reaction between the sulfate ions and the cement hydration products does not take place and therefore the sulfate ions are released in the pore solution.

The high alkalinity of the pore solution in the specimens admixed with sodium sulfate inhibits the reaction between the sulfate ions and the cement hydration products. In the specimens admixed with magnesium sulfate, the reaction between calcium hydroxide and magnesium sulfate leads to the formation of gypsum and magnesium hydroxide as indicated below:

\[ \text{MgSO}_4 + \text{Ca(OH)}_2 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4.2\text{H}_2\text{O} + \text{Mg(OH)}_2 \]  \hspace{1cm} (4.6)

The magnesium hydroxide so formed is insoluble and its alkalinity is low (pH <10.5). Further, gypsum reacts with calcium aluminate hydrate to form additional ettringite, as indicated by the following reaction:

\[ 3(\text{CaSO}_4\text{.2H}_2\text{O}) + \text{C}_3\text{AH}_12 + 13\text{H}_2 \rightarrow \text{C}_3\text{A}.3\text{CaSO}_4\text{.H}_32 \]  \hspace{1cm} (4.7)
Furthermore, the magnesium sulfate reacts with calcium silicate hydrate to form calcium sulfate and magnesium hydroxide. The sulfate concentration in the specimens admixed with magnesium sulfate is therefore, much less than that in the specimens admixed with sodium sulfate.

Another important feature of the data in Figures 4.38 through 4.40 is the binding of sulfate ions by the blended cements. The sulfate-binding capacity of the blended cements was excellent when associated with the magnesium cation. Most of the admixed sulfate ions were bound by the cement hydration products in this case, whereas considerable quantity of these ions were free when they were added in the form of sodium sulfate. This sulfate-binding may be attributed to the alkalinity of the pore solution. Furthermore, as the quantity of C₃A and Ca(OH)₂ in the blended cements is much less, compared to plain cements, it is expected that the sulfate ions are bound by the C-S-H.

The data on sulfate concentration also indicate that binding of sulfate ions is dependent on the alkalinity of the pore solution. A high pH of the pore solution leads to destabilization of gypsum and/or calcium sulpho-aluminate hydrate. A similar effect of the alkalinity of the pore solution was noted on chloride binding, as discussed in Section 4.2.

Therefore, the influence of pore solution pH on the reaction between SO₄⁻ ions and the C-S-H can be expressed as follows:

\[(\text{Mg, Na}_2)\text{SO}_4 + \text{C-S-H} \xrightleftharpoons{\text{pH}} \text{CaSO}_4 + (\text{Mg, Na}_2)\text{(OH)}_2 + \text{SiO}_2 \quad (4.8)\]

The data on free sulfate concentration in the pore solution of the cement paste specimens admixed with sodium chloride plus sodium sulfate or magnesium sulfate can also be discussed with regard to
reinforcement corrosion and sulfate attack. The increase in the sulfate concentration, when sodium sulfate is added may lead to depassivation of steel and decrease the electrical resistivity of concrete, thus increasing the rate of reinforcement corrosion. The decrease in the sulfate concentration, due to the addition of MgSO₄, is indicative of the reaction of sulfate salts with the cement hydration products, principally C₃A and Ca(OH)₂ in the plain cements and C-S-H in the blended cements and the formation of ettringite and gypsum, leading to concrete degradation in the form of softening of the matrix in the blended cements and/or expansive type of cracking in the plain cements. In the blended cements, magnesium cations may also contribute to the disintegration of calcium silicate hydrate. Such a phenomenon has been noticed to be more intense in the blended cements placed in the magnesium sulfate environments as will be discussed in Chapter 7.
Figure 4.1: Variation of OH⁻ concentration with sulfate contamination in the SRPC paste specimens.

Figure 4.2: Variation of OH⁻ concentration with sulfate contamination in the OPC-A paste specimens.
Figure 4.3: Variation of OH$^-$ concentration with sulfate contamination in the OPC-B paste specimens.

Figure 4.4: Variation of OH$^-$ concentration with sulfate contamination in the blast furnace slag cement paste specimens.
Figure 4.5: Variation of $OH^-$ concentration with sulfate contamination in the silica fume cement paste specimens.

Figure 4.6: Variation of $OH^-$ concentration with sulfate contamination in the fly ash cement paste specimens.
Figure 4.7: Variation of OH⁻ concentration with sulfate contamination in the plain cement paste specimens.

Figure 4.8: Variation of OH⁻ concentration with C₃A in plain cement paste specimens admixed with sodium chloride plus sodium sulfate.
Figure 4.9: Variation of OH\(^-\) concentration with C\(_3\)A in the plain cement specimens admixed with sodium chloride plus magnesium sulfate.

Figure 4.10: Variation of OH\(^-\) concentration with sulfate contamination in the blended cement paste specimens.
Figure 4.11: OH⁻ concentration in plain and blended cement paste specimens admixed with sodium chloride plus sodium sulfate.

Figure 4.12: OH⁻ concentration in the plain and blended cement paste specimens admixed with sodium chloride plus magnesium sulfate.
Figure 4.13: Variation of chloride concentration with sulfate contamination in the SRPC paste specimens.

Figure 4.14: Variation of chloride concentration with sulfate contamination in the OPC-A specimens.
Figure 4.15: Variation of chloride concentration with sulfate contamination in the OPC-B specimens.

Figure 4.16: Variation of chloride concentration with sulfate contamination in the BFS cement paste specimens.
Figure 4.17: Variation of chloride concentration with sulfate contamination in the SF cement paste specimens.

Figure 4.18: Variation of chloride concentration with sulfate contamination in the FA cement paste specimens.
Figure 4.19: Variation of chloride concentration with sodium sulfate or magnesium sulfate contamination in the plain cement paste specimens.

Figure 4.20: Variation of chloride concentration with C₃A in the plain cement paste specimens admixed with sodium chloride plus Na₂SO₄.
Figure 4.21: Variation of chloride concentration with C₃A in plain cement specimens admixed with sodium chloride plus magnesium sulfate.

Figure 4.22: Variation of chloride concentration with sodium or magnesium sulfate contamination in the blended cement paste specimens.
Figure 4.23: Variation of chloride concentration with OH⁻ concentration in the plain cement paste specimens admixed with NaCl plus Na₂SO₄.

Figure 4.24: Variation of chloride concentration with OH⁻ concentration in the blended cement paste specimens admixed with NaCl plus Na₂SO₄.
Figure 4.25: Variation of chloride concentration with OH$^-$ concentration in the plain cement paste specimens admixed with NaCl plus MgSO$_4$.

Figure 4.26: Variation of chloride concentration with OH$^-$ concentration in the blended cement paste specimens admixed with NaCl plus MgSO$_4$. 
Figure 4.27: Variation of Cl'/OH' with sulfate contamination in the SRPC paste specimens.

Figure 4.28: Variation of Cl'/OH' with sulfate contamination in the OPC-A paste specimens.
Figure 4.29: Variation of Cl/OH⁻ with sulfate contamination in the OPC-B paste specimens.

Figure 4.30: Variation of Cl/OH⁻ with sulfate contamination in the blast furnace slag cement paste specimens.
Figure 4.31: Variation of Cl'/OH⁻ with sulfate concentration in the silica fume cement paste specimens.

Figure 4.32: Variation of Cl'/OH⁻ with sulfate concentration in the fly ash cement paste specimens.
Figure 4.33: Variation of Cl\(^+\)/OH\(^-\) in the plain and blended cement paste specimens admixed with sodium chloride plus sodium sulfate.

Figure 4.34: Variation of Cl\(^+\)/OH\(^-\) in the plain and blended cement paste specimens admixed with sodium chloride plus magnesium sulfate.
Figure 4.35: Effect of sulfate contamination on the sulfate concentration in the SRPC paste specimens.

Figure 4.36: Effect of sulfate contamination on the sulfate concentration in the OPC-A paste specimens.
Figure 4.37: Effect of sulfate contamination on the sulfate concentration in the OPC-B paste specimens.

Figure 4.38: Effect of sulfate contamination on the sulfate concentration in the blast furnace slag cement specimens.
Figure 4.39: Effect of sulfate contamination on the sulfate concentration in the silica fume cement paste specimens.

Figure 4.40: Effect of sulfate contamination on the sulfate concentration in the fly ash cement paste specimens.
Figure 4.41: Effect of sodium sulfate contamination on the sulfate concentration in the plain and blended cement paste specimens.

Figure 4.42: Effect of magnesium sulfate contamination on the sulfate concentration in the plain and blended cement paste specimens.
Figure 4.43: Variation of $SO_4^{2-}$ concentration with OH$^-$ concentration in the plain cement paste specimens admixed with NaCl plus Na$_2$SO$_4$.

Figure 4.44: Variation of $SO_4^{2-}$ concentration with OH$^-$ concentration in the blended cement paste specimens admixed with NaCl plus Na$_2$SO$_4$. 
Figure 4.45: Variation of $\text{SO}_4^{2-}$ concentration with $\text{OH}^-$ concentration in the plain cement paste specimens admixed with NaCl plus Na$_2$SO$_4$.

Figure 4.46: Variation of $\text{SO}_4^{2-}$ concentration with $\text{OH}^-$ concentration in the blended cement paste specimens admixed with NaCl plus Na$_2$SO$_4$. 
CHAPTER 5

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

5.1 INTRODUCTION

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 (Na⁺ or Mg²⁺) 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.
5.2 CORROSION POTENTIALS

5.2.1 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 ($C_3A$: 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

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1 Figures: A-1 through A-28 are included in Appendix A
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 (C₃A: 9.65%) concrete specimens exposed to 5% NaCl solution containing 0, 1, 2.5 and 4% SO₄²⁻, 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% SO₄²⁻, 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.

5.2.2 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% SO₄²⁻, 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% SO₄²⁻, 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 $S^-$, $S_2O_3$, 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% $SO_4^-$ 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% $\text{SO}_4^{2-}$, 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% $\text{SO}_4^{2-}$, 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% $\text{SO}_4^{2-}$, derived from magnesium sulfate, respectively. The potentials decreased with time and were stable at later times.

5.3 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 C₃A content of cement. The delay in corrosion initiation in the plain cements, with increasing C₃A content, may be attributed to the chloride-binding capacity of cements with high C₃A 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 5.1: Time to initiation of reinforcement corrosion in the concrete specimens exposed to sodium chloride plus sodium sulfate or magnesium sulfate solutions.

<table>
<thead>
<tr>
<th>Exposure Solution</th>
<th>Time to initiation of reinforcement corrosion, days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SRPC</td>
</tr>
<tr>
<td>5% NaCl</td>
<td>118</td>
</tr>
<tr>
<td>5% NaCl + 1% SO₄²⁻ (Na₂SO₄)</td>
<td>113</td>
</tr>
<tr>
<td>5% NaCl + 2.5% SO₄²⁻ (Na₂SO₄)</td>
<td>137</td>
</tr>
<tr>
<td>5% NaCl + 4% SO₄²⁻ (Na₂SO₄)</td>
<td>119</td>
</tr>
<tr>
<td>5% NaCl + 1% SO₄²⁻ (MgSO₄)</td>
<td>111</td>
</tr>
<tr>
<td>5% NaCl + 2.5% SO₄²⁻ (MgSO₄)</td>
<td>116</td>
</tr>
<tr>
<td>5% NaCl + 4% SO₄²⁻ (MgSO₄)</td>
<td>127</td>
</tr>
</tbody>
</table>
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.

5.4 CORROSION CURRENT DENSITY

5.4.1 Corrosion Current Density in Plain Cement Concrete Specimens

The variation of corrosion current density ($I_{corr}$) with time on steel in the SRPC concrete specimens exposed to 5% NaCl solutions containing 0, 1, 2.5 and 4% SO$_4$$^-$, derived from sodium sulfate, is plotted against period of exposure in Figure 5.17. The $I_{corr}$ 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 $I_{corr}$ 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 $I_{corr}$ with time in the SRPC concrete specimens exposed to 5% NaCl solutions admixed with 0, 1, 2.5, and 4% SO$_4$$^-$, derived from magnesium sulfate. Almost a linear increase in the $I_{corr}$ 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 $I_{corr}$ 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 $I_{corr}$ 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 (C$_3$A: 8.5%) and OPC-B (C$_3$A: 9.65%) concrete specimens exposed to 5% NaCl plus 0, 1, 2.5, and 4% 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% 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.

5.4.2 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% 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 $I_{corr}$ on steel in the blast furnace slag cement concrete specimens exposed to 5% NaCl solutions containing 0, 1, 2.5 and 4% $SO_4^{2-}$, derived from magnesium sulfate. The $I_{corr}$ increased with period of exposure. Initially, the $I_{corr}$ was very low and similar in all the specimens up to 150 days of exposure beyond which the $I_{corr}$ started to increase. The $I_{corr}$ 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 $I_{corr}$ increased with increasing concentration of magnesium sulfate up to 2.5% $SO_4^{2-}$, beyond which the $I_{corr}$ decreased slightly. This trend is similar to that noted in the plain cement concrete specimens exposed to sodium chloride plus magnesium sulfate solution.

The $I_{corr}$ 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% $SO_4^{2-}$, 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 $I_{corr}$ on steel in the silica fume and fly ash cement concrete specimens exposed to 5% NaCl solution containing 0, 1, 2.5 and 4% $SO_4^{2-}$, 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.

5.4.3 Corrosion Current Density in Plain and Blended Cement Concrete Specimens

The $I_{corr}$ 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 $I_{corr}$ in the plain cement concrete specimens was much
higher than that in the blended cement specimens. Further, the $I_{corr}$ on steel in the concrete specimens exposed to chloride plus sulfate solution was more than that in the specimens exposed to chloride solution.

The $I_{corr}$ 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 $I_{corr}$ increased almost linearly with increasing concentration of sodium sulfate. The $I_{corr}$ 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 $I_{corr}$ increased with increasing concentration of magnesium sulfate up to 2.5% $SO_4^{2-}$. However, it decreased slightly when the magnesium sulfate concentration was increased from 2.5 to 4%.

The $I_{corr}$ on steel in the concrete specimens exposed to sodium chloride plus sodium sulfate is plotted against $C_3A$ in Figure 5.33. The $I_{corr}$ decreased significantly with increasing $C_3A$ content. Figure 5.34 shows the relationship between $I_{corr}$ 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 5.2: Corrosion Current Density after 1200 days of exposure.

<table>
<thead>
<tr>
<th>Exposure solution</th>
<th>Corrosion current density, μA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SRPC</td>
</tr>
<tr>
<td>5% NaCl</td>
<td>1.83</td>
</tr>
<tr>
<td>5% NaCl + 1% SO₄⁻ (Na₂SO₄)</td>
<td>2.13</td>
</tr>
<tr>
<td>5% NaCl + 2.5% SO₄⁻ (Na₂SO₄)</td>
<td>2.48</td>
</tr>
<tr>
<td>5% NaCl + 4% SO₄⁻ (Na₂SO₄)</td>
<td>2.6</td>
</tr>
<tr>
<td>5% NaCl + 1% SO₄⁻ (MgSO₄)</td>
<td>2.89</td>
</tr>
<tr>
<td>5% NaCl + 2.5% SO₄⁻ (MgSO₄)</td>
<td>3.25</td>
</tr>
<tr>
<td>5% NaCl + 4% SO₄⁻ (MgSO₄)</td>
<td>3.06</td>
</tr>
</tbody>
</table>

5.5 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] reported 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 Ca(OH)$_2$ solution. Morgan [51] found that addition of 50 ppm of SO$_4^-$ brought about pitting at lower chloride concentrations than when sulfate was absent. Gouda and Halaka [50] reported that small concentrations of Na$_2$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 °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 Cl$^-$ ions in plain and blended cements was twice that of 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 SO$_4^{2-}$ ions is 2 to 5 times that of Na$^+$ ions. Bakker [59] indicated that the diffusion of chloride anions is considerably faster than
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 $I_{corr}$ increased with increasing sulfate concentration.

The increase in the $I_{corr}$ 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$_3$A with both chloride and sulfate ions. Chloride ions normally react with C$_3$A in cement to form an insoluble compound known as calcium chloro-aluminate hydrate (C$_3$A.CaCl$_2$.10H$_2$O), 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$_3$A 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 C₃A forming calcium sulfo-aluminate hydrate. Maslehuddin et al. [6] indicated that C₃A 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 Icorr 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 kΩ.cm when sulfate contamination was increased from 7.2 to 43.2 kg/m³. 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/m³. 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 Ω.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 Ω.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 $I_{corr}$ 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\textsubscript{corr} is influenced by the cation type associated with the sulfate ions. The I\textsubscript{corr} increased with increasing concentration of sodium sulfate. Similarly, the I\textsubscript{corr} increased as the concentration of magnesium sulfate increased. However, the I\textsubscript{corr} decreased slightly when the concentration of magnesium sulfate was increased from 2.5 to 4.0%. The decrease in the I\textsubscript{corr} due to excess of magnesium sulfate may be attributed to the formation of Mg(OH)\textsubscript{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.
Figure 5.1: Variation of corrosion potentials with time on steel in the SRPC concrete specimens exposed to 5% NaCl solution.

Figure 5.2: Variation of corrosion potentials with time on steel in the SRPC concrete specimens exposed to 5% NaCl plus 1% SO₄⁻² (Na₂SO₄) solution.
Figure 5.3: Variation of corrosion potentials with time on steel in the SRPC concrete specimens exposed to 5% NaCl plus 2.5% SO$_4^{2-}$ (Na$_2$SO$_4$) solution.

Figure 5.4: Variation of Corrosion Potentials with time on steel in the SRPC concrete specimens exposed to 5% NaCl plus 4% SO$_4^{2-}$ (Na$_2$SO$_4$) solution.
Figure 5.5: Variation of corrosion potentials with time on steel in the SRPC concrete specimens exposed to 5% NaCl plus 1% SO$_4^-$ (MgSO$_4$) solution.

Figure 5.6: Variation of corrosion potentials with time on steel in the SRPC concrete specimens exposed to 5% NaCl plus 2.5% SO$_4^-$ (MgSO$_4$) solution.
Figure 5.7: Variation of corrosion potentials with time on steel in the SRPC concrete specimens exposed to 5% NaCl plus 4%SO₄⁻(MgSO₄) solution.

Figure 5.8: Variation of corrosion potentials with time on steel in the BFS concrete specimens exposed to 5% NaCl solution.
Figure 5.9: Variation of corrosion potentials with time on steel in the BFS concrete specimens exposed to 5% NaCl plus 1% SO$_4^{--}$ (Na$_2$SO$_4$) solution.

Figure 5.10: Variation of corrosion potentials with time on steel in the BFS concrete specimens exposed to 5% NaCl plus 2.5% SO$_4^{--}$ (Na$_2$SO$_4$) solution.
Figure 5.11: Variation of corrosion potentials with time on steel in the BFS concrete specimens exposed to 5% NaCl plus 4% SO$_4^{2-}$ (Na$_2$SO$_4$) solution.

Figure 5.12: Variation of corrosion potentials with time on steel in the BFS concrete specimens exposed to 5% NaCl plus 1% SO$_4^{2-}$ (MgSO$_4$) solution.
Figure 5.13: Variation of corrosion potentials with time on steel in the BFS concrete specimens exposed to 5% NaCl plus 2.5% \( \text{SO}_4^- \) (MgSO\(_4\)) solution.

Figure 5.14: Variation of corrosion potentials with time on steel in the BFS concrete specimens exposed to 5% NaCl plus 4% \( \text{SO}_4^- \) (MgSO\(_4\)) solution.
Figure 5.15: Time to initiation of reinforcement corrosion against SO$_4^{2-}$ concentration in the specimens exposed to 5% NaCl plus Na$_2$SO$_4$ solution.

Figure 5.16: Time to initiation of reinforcement corrosion against SO$_4^{2-}$ concentration in the specimens exposed to 5% NaCl plus MgSO$_4$ solution.
Figure 5.17: Variation of $I_{corr}$ with period of exposure in the SRPC concrete specimens exposed to 5% NaCl plus sodium sulfate solution.

Figure 5.18: Variation of $I_{corr}$ with period of exposure in the SRPC concrete specimens exposed to 5% NaCl plus magnesium sulfate solution.
Figure 5.19: Variation of $I_{\text{corr}}$ with period of exposure in the OPC-A concrete specimens exposed to 5% NaCl plus sodium sulfate solution.

Figure 5.20: Variation of $I_{\text{corr}}$ with period of exposure in the OPC-B concrete specimens exposed to 5% NaCl plus sodium sulfate solution.
Figure 5.21: Variation of $I_{\text{corr}}$ with period of exposure in the OPC-A concrete specimens exposed to 5% NaCl plus magnesium sulfate solution.

Figure 5.22: Variation of $I_{\text{corr}}$ with period of exposure in the OPC-B concrete specimens exposed to 5% NaCl plus magnesium sulfate solution.
Figure 5.23: Variation of $I_{\text{corr}}$ with period of exposure in the BFS cement concrete specimens exposed to 5% NaCl plus sodium sulfate solution.

Figure 5.24: Variation of $I_{\text{corr}}$ with period of exposure in the BFS cement concrete specimens exposed to 5% NaCl plus magnesium sulfate solution.
Figure 5.25: Variation of $I_{corr}$ with period of exposure in the SF cement concrete specimens exposed to 5% NaCl plus sodium sulfate solution.

Figure 5.26: Variation of $I_{corr}$ with period of exposure in the FA cement concrete specimens exposed to 5% NaCl plus sodium sulfate solution.
Figure 5.27: Variation of $I_{\text{corr}}$ with period of exposure in the SF cement concrete specimens exposed to 5% NaCl plus magnesium sulfate solution.

Figure 5.28: Variation of $I_{\text{corr}}$ with period of exposure in the FA cement concrete specimens exposed to 5% NaCl plus magnesium sulfate solution.
Figure 5.29: Variation of $I_{\text{corr}}$ with sulfate concentration in the plain cement concrete specimens exposed to 5% NaCl plus sodium sulfate solution.

Figure 5.30: Variation of $I_{\text{corr}}$ with sulfate concentration in the blended cement concrete specimens exposed to 5% NaCl plus sodium sulfate solution.
Figure 5.31: Variation of $I_{\text{corr}}$ with sulfate concentration in the plain cement concrete specimens exposed to 5% NaCl plus magnesium sulfate solution.

Figure 5.32: Variation of $I_{\text{corr}}$ with sulfate concentration in the blended cement concrete specimens exposed to 5% NaCl plus magnesium sulfate solution.
Figure 5.33: Variation of $I_{\text{corr}}$ with C\textsubscript{3}A in the plain cement concrete specimens exposed to 5% NaCl plus sodium sulfate solution.

Figure 5.34: Variation of $I_{\text{corr}}$ with C\textsubscript{3}A contents in the plain cement concrete specimens exposed to 5% NaCl plus magnesium sulfate solution.
CHAPTER 6

EFFECT OF CEMENT ALKALINITY ON PORE SOLUTION CHEMISTRY AND REINFORCEMENT CORROSION

The effect of cement alkalinity on durability of SRPC and OPC was evaluated by measuring the pore solution composition and reinforcement corrosion. The measurements were conducted on replicate specimens and the values were presented. The three readings were very similar and the coefficient of variation was low and within acceptable limits. However, in the limited instances where spurious readings were obtained, they were excluded while calculating the average value.

6.1 EFFECT OF CEMENT ALKALINITY ON THE PORE SOLUTION CHEMISTRY

6.1.1 Results

To evaluate the influence of cement alkalinity on the pore solution composition, cylindrical cement paste specimens 49 mm diameter and 75 mm high were prepared, as described in Section 3.4.1. The cement paste was admixed with fixed quantity of sodium chloride (0.8% Cl⁻ by weight of cement) and various dosages of alkalinity (in the range of 0.4 to 1.4% Na₂O equivalent), as described in Section 3.4.1 and detailed in Table 3.5. The pore solution was extracted from these cement paste specimens and analyzed to determine OH⁻, Cl⁻ and SO₄²⁻ concentrations, as described in Section 3.4.2.

The OH⁻ concentration in the SRPC and OPC-A paste specimens admixed with 0.8% Cl⁻ and admixed with various dosages of alkalinity is plotted in Figure 6.1. The OH⁻ concentration increased almost linearly with increasing alkalinity of cement. These values in the OPC-A paste
specimens were slightly more than that in the SRPC paste specimens up to an alkalinity of 1.2%. However, they were similar when the alkalinity was 1.4%.

Figure 6.2 depicts the chloride concentration in the SRPC and OPC-A paste specimens admixed with sodium chloride and different alkali contents. The chloride concentration increased with the alkalinity content in both the cements. These values in the SRPC paste specimens were slightly more than those in the OPC-A specimens up to an alkali content of 1%. Beyond this alkalinity, the chloride concentration in both the cements was almost the same.

The Cl⁻/OH⁻ ratio of the pore solution in the SRPC and OPC-A paste specimens admixed with 0.8% Cl⁻ and different alkali contents is plotted in Figure 6.3. These values decreased with increasing alkali content of up to 0.8% Na₂O equivalent, beyond which the Cl⁻/OH⁻ increased slightly with increasing alkali content. The values in the SRPC paste specimens were slightly higher than those in the OPC-A paste specimens. The decrease in the Cl⁻/OH⁻ ratio, with increasing alkalinity of cement, up to 0.8%, may be attributed to an increase in the OH⁻ concentration. Beyond 0.8%, the increase in both OH⁻ and Cl⁻ is very marginal. This results in a slight increase in the Cl⁻/OH⁻ ratio.

The sulfate concentration in the SRPC and OPC-A paste specimens is depicted in Figure 6.4. The sulfate concentration increased almost linearly with increasing alkali content of cement. The sulfate concentration in the control specimens (Na₂O equivalent of 0.4%) was the same in both the cements. However, the sulfate concentration in the OPC-A specimens with other alkali contents was slightly higher than that in the SRPC specimens with similar alkali contents.
6.1.2 Discussion of the Effect of Cement Alkalinity on the Pore Solution Chemistry

The data in Figures 6.1, 6.2 and 6.4 indicate that the OH', Cl' and SO₄⁻ concentrations increased with increasing alkali content in the cement. Similar data have been reported by Hussain [7] who reported an increase in the OH' concentration with increasing alkali content of cement. Also, the concentration of free-chloride ions increased with the alkali content. He attributed the reduction in chloride-binding capacity of cements to the reduced formation of Friedel’s salt due to increased solubility of calcium chloro-aluminate with increasing alkalinity of the pore solution. Roberts [72] used different solutions at various temperatures and alkalinity to study the solubility of Friedel’s salt. The solutions were prepared using 0.5 and 1% NaOH and 0.5 and 1% KOH containing crystalline Ca(OH)₂. The results indicated that the solubility of calcium chloro-aluminate increased when the concentration of the alkali hydroxides increased from 0.5 to 1%. Tritthart [22] used CaCl₂, MgCl₂ and HCl to induct 1% Cl', by weight of cement, to study the chloride-binding capacity of OPC, and reported that the free-chloride concentration in the pore solution was proportional to the alkalinity of the pore solution. Talib [23] investigated the effect of alkalinity on the pore solution composition of plain and silica fume cements. The results indicated that the OH' and Cl' concentrations in the pore solution increased with increasing alkali contents in both plain and silica fume cements. Gunkel [21] indicated that the alkali effect on weakening of the chloride binding of cement may be more than the sulfate effect. In a 0.5 w/c ratio cement paste with 0 to 0.4% chloride, derived from NaCl, the chloride concentration in the pore solution increased from 2900 ppm to 3200 ppm when alkali-free 1.36% CaSO₄ was added, while this
concentration increased to 4100 ppm when 0.62% Na₂O was added to the cement through the mix water. However, the free-chloride concentration increased to 5700 ppm when both alkalis and sulfates were added.

Way and Shayan [73] studied the effect of adding 0.5 to 4.5% NaOH on sulfate concentrations. They concluded that the early (first day) sulfate concentration increased significantly with the cement alkalinity. At higher alkalinity levels, a substantial proportion of the increased sulfate concentration was maintained throughout the relatively brief period evaluated (48 hrs). Ong and Diamond [74] indicated that the addition of a high alkali cement (1.14% Na₂O equivalent) to mix water containing pre-dissolved NaOH actually reduced the OH⁻ concentration that was already present in the mix water. They observed that the pre-dissolved NaOH reacts almost immediately with gypsum in cement to form dissolved Na₂SO₄, and if NaOH is added in excess of that required to dissolve the gypsum, the excess NaOH remains in solution to increase the OH⁻ concentration in the pore solution. Diamond and Ong [75] reported that the addition of alkali hydroxide to cement mix water results in high concentration of sulfate ions in the pore solution, while the increase in OH⁻ concentration was less than expected.

The data developed in the present study indicated a significant increase in the OH⁻, Cl⁻ and SO₄²⁻ concentrations with increasing alkalinity. The OH⁻, Cl⁻ and SO₄²⁻ concentrations were almost similar in the SRPC and OPC-A paste specimens when the cement alkalinity was high. Further, the OH⁻, Cl⁻ and SO₄²⁻ concentrations increased with increasing alkali content. The increase in the OH⁻ concentration may be attributed to the NaOH added through the mix water. The increase in the
chloride concentration with increasing alkalinity may be ascribed to the solubility of calcium chloro-aluminate hydrate (Friedel's salt) due to increasing alkalinity. The $\text{SO}_4^{2-}$ concentration in the SRPC and OPC-A paste specimens also increased linearly with the alkalinity. This increase in sulfate concentration may be attributed to the formation of $\text{Na}_2\text{SO}_4$ due to the reaction between the added sodium hydroxide and gypsum available in the cement. In other words, both calcium chloroaluminate and calcium sulfo-aluminate hydrates are unstable in a highly alkaline environment.

These results confirm the hypothesis presented in Chapter 4 on the effect of alkalinity on chloride- and sulfate-binding of cement. An increase in the alkalinity of cement, particularly when the alkaline materials are added as contaminants, influences the chloride- and sulfate binding of cements.

While a decrease in chloride binding of cements results in accelerated reinforcement corrosion, the reduction in the sulfate binding is beneficial as it reduces the chances of concrete deterioration due to sulfate attack. Another concern with regards the increase in alkalinity of cements is the acceleration of the alkali-aggregate reaction when reactive aggregates are used. To avoid deterioration of concrete due to alkali-aggregate reaction, the cement alkalinity, expressed as $\text{Na}_2\text{O}$, is limited to 0.6%.

### 6.2 EFFECT OF CEMENT ALKALINITY ON REINFORCEMENT CORROSION

To evaluate the influence of cement alkalinity on reinforcement corrosion, cylindrical reinforced concrete specimens 75 mm in diameter and 150 mm high with a 12 mm diameter steel bar centered in the middle were prepared, as described in Section 3.5.1. The alkali content in the
cement was adjusted to 0.4 (control), 0.6, 0.8, 1.0, 1.2 and 1.4% Na$_2$O equivalent and exposed to 5% NaCl solution with similar alkalinity, as discussed in Section 3.5.2 and detailed in Table 3.5. The effect of cement alkalinity on reinforcement corrosion was evaluated by measuring corrosion potentials and corrosion current density, as detailed in Section 3.3.3.

6.2.1 Corrosion Potentials

The corrosion potentials on steel in the SRPC concrete specimens with alkalinity of 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4% Na$_2$O equivalent and exposed to 5% NaCl solution containing similar alkalinity are plotted against the period of exposure in Figures 6.5 through 6.10, respectively. The corrosion potentials on steel in the concrete specimens made with this cement were initially high (less negative). However, they decreased with the period of exposure of up to about 600 days, beyond this period these values were more or less stable.

The corrosion potentials on steel in the OPC-A concrete specimens with alkalinity of 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4% are shown in Figures 6.11 through 6.16. These data also indicate a trend similar to that noted in the SRPC concrete specimens.

6.2.2 Time to Initiation of Reinforcement Corrosion

The corrosion potential curves, discussed in Section 6.2.1, were utilized to evaluate the time to initiation of reinforcement corrosion based on the ASTM C876 criterion of -270 mV SCE. These values are summarized in Table 6.1 and plotted against alkalinity in Figure 6.17. The time to initiation of reinforcement corrosion in both the cements increased with increasing alkali content of up to 0.8%. However, it
decreased in the concrete specimens with alkalinity of more than 0.8%. This indicates that cement alkalinity of up to 0.8% is beneficial from corrosion initiation point of view. However, a further increase in alkalinity may not improve the corrosion-resistance.

**Table 6.1. Time to initiation of reinforcement corrosion in concrete specimens with varying alkalinity.**

<table>
<thead>
<tr>
<th>Exposure Solution</th>
<th>Time-to-initiation of reinforcement corrosion, days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SRPC</td>
</tr>
<tr>
<td>5% NaCl + 0.4% Na₂O</td>
<td>101</td>
</tr>
<tr>
<td>5% NaCl + 0.6% Na₂O</td>
<td>125</td>
</tr>
<tr>
<td>5% NaCl + 0.8% Na₂O</td>
<td>168</td>
</tr>
<tr>
<td>5% NaCl + 1.0% Na₂O</td>
<td>127</td>
</tr>
<tr>
<td>5% NaCl + 1.2% Na₂O</td>
<td>114</td>
</tr>
<tr>
<td>5% NaCl + 1.4% Na₂O</td>
<td>100</td>
</tr>
</tbody>
</table>

**6.2.3 Corrosion Current Density**

The variation of $I_{corr}$ on steel in the SRPC concrete specimens with varying alkalinity is depicted in Figure 6.18. The $I_{corr}$ values were initially very low and similar up to 100 to 120 days of exposure in all the concrete specimens. After this time, the $I_{corr}$ started to deviate and increased with increasing period of exposure. The $I_{corr}$ on steel in the control specimens (cement with Na₂O equivalent of 0.4%) was more than that in the concrete specimens with higher alkalinity. However, the
$I_{\text{corr}}$ on steel in the concrete specimens with an alkalinity of 0.8% was the lowest.

The $I_{\text{corr}}$ on steel in the OPC-A concrete specimens with varying alkalinity is plotted against period of exposure in Figure 6.19. These data also exhibited a trend similar to that noted in the SRPC concrete specimens. The $I_{\text{corr}}$ on steel in the SRPC and OPC-A concrete specimens is plotted against alkalinity in Figure 6.20. The $I_{\text{corr}}$ decreased with increasing alkali content of up to 0.8%, beyond which the $I_{\text{corr}}$ increased slightly. These results together with those in Figure 6.17 indicate that the resistance of concrete to reinforcement corrosion is improved up to an alkali content of 0.8%. However, when the alkalinity is more than 0.8% this improvement is reduced.

### 6.2.4 Discussion of the Effect of Cement Alkalinity on Reinforcement Corrosion

The influence of cement alkalinity on reinforcement corrosion is not very well documented and no data are available regarding the effect of cement alkalinity on time to initiation of reinforcement corrosion and corrosion current density in concrete. Limited studies [7,23] conducted to date have concentrated on the effect of cement alkalinity on the pore solution chemistry.

The data developed in this study have indicated that the alkalinity of cement plays an important role in reinforcement corrosion. The corrosion potentials in the SRPC and OPC-A concrete specimens decreased with increasing alkalinity of cement. The time to initiation of reinforcement corrosion in both the cements also increased with increasing alkalinity content of up to 0.8%. However, the time to initiation of reinforcement corrosion decreased with further increase in the cement alkalinity.
Similarly, the $I_{corr}$ on steel in the SRPC and OPC-A concrete specimens decreased with increasing cement alkalinity of up to 0.8%. Beyond this alkalinity no appreciable change in the $I_{corr}$ was noted. However, the $I_{corr}$ in the specimens with alkalinity of 1.0, 1.2 and 1.4 was also lower than that in the concrete specimens made with an alkalinity of 0.4 and 0.6%. The results of this study indicate that alkalinity, improves the resistance to reinforcement corrosion in both SRPC and OPC-A. However, the highest improvement was noted when the alkalinity was 0.8%.

The improvement of resistance to corrosion in concrete due to the addition of alkalinity may be attributed to the increase of pH in the pore solution, which stabilize the protective layer on the steel bar. However, a decrease in the corrosion resistance when alkalinity was more than 0.8% may be attributed to the decrease in chloride binding due to high alkalinity. Goni and Andrade [116] reported that as the alkalinity increases the pH increases and the $I_{corr}$ decreases. The other important factor to which the corrosion resistance improvement may be attributed, is the Cl'/OH⁻ ratio of the pore solution as discussed in Section 6.1.

The Cl'/OH⁻ ratio of the pore solution in the cement paste specimens admixed with sodium chloride and admixed with alkalinity decreased with increasing alkali content of cement up to 0.8% Na₂O, and then increased slightly with increasing alkali content up to 1.4% Na₂O as shown in Figure 6.3. The $I_{corr}$ exhibited a similar behavior. The results of the Cl'/OH⁻ ratio of the pore solution as shown in Figure 6.3 together with those reported by Goni and Andrade [116] support the results of the $I_{corr}$ obtained in this study. Further, the concrete specimens were investigated visually by splitting them and the bars were taken out which indicated that the corrosion on steel bars in both cements exhibited a
trend similar to that noted in the Cl'/OH⁻ ratio of the pore solution, as shown in Figure 6.3. The corrosion was the highest in the control specimens while it was the lowest in the specimens admixed with 0.8% Na₂O equivalent.

A maximum limit of 0.6% cement alkalinity, expressed as Na₂O equivalent, is normally imposed by many international standards, such as ASTM and BS. This limitation is purely adopted to avoid alkali-aggregate reaction, when alkali-reactive aggregates are utilized in concrete. The results of this study show that the alkali content can be increased to 0.8%, to enhance the corrosion-resistance of concrete. This will be beneficial if it is known that the aggregates are not reactive. Therefore, the limits on alkali content in cement should be case specific as shown below:

**Limitations on cement alkalinity (Na₂O equivalent):**

Potentially alkali-reactive aggregate: < 0.6%

Inert aggregate: 0.6 to 0.8%
Figure 6.1: Variation of OH⁻ concentration with alkalinity (Na₂O equivalent) in the SRPC and OPC paste specimens.

Figure 6.2: Variation of Cl⁻ concentration with alkalinity (Na₂O equivalent) in the SRPC and OPC paste specimens.
Figure 6.3: Variation of Cl/OH⁻ ratio with alkalinity (Na₂O equivalent) in the SRPC and OPC paste specimens.

Figure 6.4: Variation of SO₄²⁻ concentration with alkalinity (Na₂O equivalent) in the SRPC and OPC paste specimens.
Figure 6.5: Variation of corrosion potentials with time on steel in the SRPC concrete specimens exposed to 5% NaCl plus 0.4% Na₂O solution.

Figure 6.6: Variation of corrosion potentials with time on steel in the SRPC concrete specimens exposed to 5% NaCl plus 0.6% Na₂O solution.
Figure 6.7: Variation of corrosion potentials with time on steel in the SRPC concrete specimens exposed to 5% NaCl plus 0.8% Na$_2$O solution.

Figure 6.8: Variation of corrosion potentials with time on steel in the RPC concrete specimens exposed to 5% NaCl plus 1.0% Na$_2$O solution.
Figure 6.9: Variation of corrosion potentials with time on steel in the SRPC concrete specimens exposed to 5% NaCl plus 1.2% Na$_2$O solution.

Figure 6.10: Variation of corrosion potentials with time on steel in the SRPC concrete specimens exposed to 5% NaCl plus 1.4% Na$_2$O solution.
Figure 6.11: Variation of corrosion potentials with time on steel in the OPC concrete specimens exposed to 5% NaCl plus 0.4% Na$_2$O solution.

Figure 6.12: Variation of corrosion potentials with time on steel in the OPC concrete specimens exposed to 5% NaCl plus 0.6% Na$_2$O solution.
Figure 6.13: Variation of corrosion potentials with time on steel in the OPC concrete specimens exposed to 5% NaCl plus 0.8% Na$_2$O solution.

Figure 6.14: Variation of corrosion potentials with time on steel in the PC concrete specimens exposed to 5% NaCl plus 1% Na$_2$O solution.
Figure 6.15: Variation of corrosion potentials with time on steel in the OPC concrete specimens exposed to 5% NaCl plus 1.2% Na$_2$O solution.

Figure 6.16: Variation of corrosion potentials with time on steel in the OPC concrete specimens exposed to 5% NaCl plus 1.4% Na$_2$O solution.
Figure 6.17: Variation of time to initiation of reinforcement corrosion with alkalinity in the SRPC and OPC concrete specimens.

Figure 6.18: Variation of $I_{corr}$ with period of exposure in the SRPC concrete specimens exposed to 5% NaCl plus Na$_2$O solution.
Figure 6.19: Variation of $I_{corr}$ with period of exposure in the OPC concrete specimens exposed to 5% NaCl plus Na$_2$O solution.

Figure 6.20: Variation of $I_{corr}$ with alkalinity (Na$_2$O equivalent) in the SRPC and OPC concrete specimen.
CHAPTER 7

EFFECT OF SULFATE CATION TYPE ON MORPHOLOGICAL CHANGES IN CEMENTS AND CONCRETE DETERIORATION DUE TO SULFATE ATTACK

7.1 INTRODUCTION

To evaluate the effect of sulfate cation type on morphological changes in cement and concrete and its deterioration due to sulfate attack, the concrete specimens which were prepared for Series II tests, as described in Section 3.3.1, were used. These concrete specimens were exposed to 5% NaCl solutions containing 0, 1, 2.5 and 4% $SO_4^{2-}$ derived from sodium sulfate or magnesium sulfate, as outlined in Section 3.3.2 and detailed in Table 3.4. After four years of exposure to these solutions the concrete specimens were visually examined to determine the extent of concrete deterioration due to sulfate attack. Some selected specimens were also examined under scanning electron microscope (SEM) to evaluate the morphological changes occurring in the cement due to sulfate exposure.

7.2 MORPHOLOGICAL CHANGES

7.2.1 Morphological Changes in the Specimens Exposed to Sodium Sulfate

Selected specimens were analyzed using SEM to evaluate the morphological changes in cement due to sulfate exposure. Figure 7.1 shows the SEM micrograph of OPC-A concrete specimen exposed to 5% NaCl solution containing 1% $SO_4^{2-}$, derived from sodium sulfate. A platy type of C-S-H was noted, with few needle shaped ettringite crystals, and $CaSO_4$ (white crystals). The energy dispersive X-ray analysis (EDXA) of the area, shown in Figure 7.2, indicated the presence
of mainly Ca in addition to small quantities of Si, Fe and S. The SEM micrograph of OPC-A concrete specimens exposed to 4% $\text{SO}_4^{2-}$, is shown in Figure 7.3. This indicates a normal morphology of the C-S-H with isolated crystals of CaSO$_4$. The EDXA of the area, shown in Figure 7.4, indicated mainly the presence of Ca in addition to small quantities of Si and S.

Figure 7.5 shows the SEM micrograph of silica fume cement concrete specimens exposed to 5% NaCl solution containing 1% $\text{SO}_4^{2-}$, derived from sodium sulfate. A compact structure of the C-S-H was indicated with the presence of ettringite crystals and isolated flowery crystals of CaSO$_4$. The EDXA, shown in Figure 7.6, indicated mainly the presence of Ca and small quantities of Si, Cl and S. The SEM micrograph of SF cement concrete specimens exposed to 4% SO$_4^{2-}$ is shown in Figure 7.7. This micrograph indicates a normal structure of the C-S-H with isolated crystals of gypsum. The EDXA, shown in Figure 7.8, indicates mainly the presence of Ca in addition to Si and S.

### 7.2.2 Morphological Changes in Specimens Exposed to Magnesium Sulfate

Figure 7.9 shows the SEM micrograph of OPC-A concrete specimen exposed to 5% NaCl solution containing 1% $\text{SO}_4^{2-}$, in the form of magnesium sulfate. A fairly dense structure of the C-S-H was indicated which may be due to the formation of magnesium hydroxide. The EDXA, shown in Figure 7.10, indicated mainly the presence of Ca in addition to Si, Mg and Al. The SEM micrograph of OPC-A concrete specimen exposed to 4% SO$_4^{2-}$ is shown in Figure 7.11. A very heterogeneous structure of the C-S-H with the formation of gypsum crystals was indicated. The EDXA of the area shown in Figure 7.12 indicated mainly the presence of Ca in addition to S.
The SEM micrograph of silica fume cement concrete specimens exposed to 5% NaCl solution containing 1% SO₄⁻, derived from magnesium sulfate, is shown in Figure 7.13. A dense morphology of the C-S-H was indicated. However, the C-S-H was ruptured at isolated locations due to the formation of monosulfate. The EDXA of the area, shown in Figure 7.14, indicated mainly the presence of Ca in addition to Si and S. Figure 7.15 shows the SEM micrograph of SF cement concrete specimen exposed to 4% SO₄⁻, which indicated a very heterogeneous structure.

In general a dense C-S-H was noted in plain and silica fume cement concrete specimens exposed to sodium chloride plus sodium sulfate solution. However, a heterogeneous structure of C-S-H was noted in the specimens exposed to magnesium sulfate solution. While a marginal deterioration of C-S-H was noted in OPC-A concrete specimens exposed to 5% NaCl plus 1% MgSO₄ solution, deterioration of C-S-H in silica fume concrete specimens exposed to similar solution due to the formation of calcium sulfate was noted at isolated spots. Disintegration of the C-S-H was noted in both OPC and SF cement concrete specimens exposed to 5% NaCl plus 4% MgSO₄ solution.

7.3 CONCRETE DETERIORATION

7.3.1 Deterioration of Concrete Specimens Exposed to Sodium Sulfate

Plain and blended cement concrete specimens were exposed to 5% NaCl solutions containing different concentrations of sodium or magnesium sulfate. These specimens exhibited varying levels of deterioration, depending on the cation type and the sulfate concentration. Figures 7.16 through 7.21 show the plain (SRPC, OPC-A and OPC-B) and blended (BFS, SF, FA) cement concrete specimens after 4 years of
exposure to 5% NaCl solution containing 0, 1, 2.5 and 4% SO₄⁻, in the form of sodium sulfate. No deterioration was noted on the surface of plain and blended cement concrete specimens exposed to 5% NaCl plus sodium sulfate solutions. However, some surface scaling was noted on the concrete specimens exposed to 5% NaCl solution containing 2.5 and 4% SO₄⁻, derived from sodium sulfate.

7.3.2 Deterioration of Concrete Specimens Exposed to Magnesium Sulfate

The appearance of SRPC concrete specimens after 4 years of exposure to 5% NaCl plus magnesium sulfate solution is shown in Figure 7.22. Signs of deterioration were observed on all the concrete specimens and the severity of deterioration increased with increasing magnesium sulfate concentration. Figures 7.23 and 7.24 show the OPC-A and OPC-B concrete specimens after 4 years of exposure to 5% NaCl plus magnesium sulfate solution. In this group of specimens deterioration was higher in the specimens exposed to sodium chloride plus 2.5 and 4% SO₄⁻ solutions than those exposed to sodium chloride plus 0 and 1% SO₄⁻ solution.

Figures 7.25 through 7.27 show the appearance of blended cement concrete specimens after 4 years of exposure to sodium chloride plus magnesium sulfate solutions. The deterioration in the blended cement concrete specimens was severe even when the magnesium sulfate concentration was 1% and the damage increased with further increase in the magnesium sulfate concentration. Further, the severity of deterioration in the blended cement concrete specimens exposed to sodium chloride plus magnesium sulfate was much higher than that in the plain cement concrete specimens exposed to similar solutions.
7.4 DISCUSSION

The effect of sulfate cation type on deterioration of concrete was primarily evaluated by visual examination. However, limited studies were also conducted to evaluate the effect of sulfate cation type on the morphological changes in cement. The morphological studies have indicated the formation of gypsum due to the reaction of sodium or magnesium sulfate with the cement hydration products, particularly Ca(OH)$_2$. The EDX analyses of concrete specimens exposed to magnesium sulfate solution indicated the presence of magnesium ions, which may be attributed to the formation of brucite (Mg(OH)$_2$) and magnesium sulfate hydrate (M-S-H).

Visual inspection of concrete specimens after 4 years of exposure to the sulfate solution has shown that magnesium sulfate is more aggressive than sodium sulfate. These results corroborate the findings of other researchers [76-86], notably by Rasheeduzzafar et al. [76] and Bonen and Cohen [80-81]. However, most of these studies were conducted on cement paste or cement mortar specimens. Further, the effect of sulfate concentration and cation type, on sulfate attack, was not evaluated.

Deterioration of concrete, due to sulfate attack, is predominantly noted in two forms. In the first type of deterioration, etching of the concrete skin, which ultimately leads to the exposure of aggregates, is noted. This type of sulfate attack is acidic in nature and is normally associated with the formation of gypsum. The second type of sulfate attack manifests itself in the form of expansion and cracking of concrete. The former type of sulfate attack is attributed to the formation of gypsum, while the second type is attributed to the formation of tricalcium sulphoaluminate hydrate. When concrete is exposed to
sulfate-bearing soil or ground water, the sulfate ions react with the cement hydration products, particularly Ca(OH)$_2$ and C$_3$A, forming either gypsum or calcium sulfoaluminate hydrate, also known as ettringite. The nature and extent of deterioration is dependent on: (i) the cation type associated with the sulfate ions, (ii) sulfate concentration and (iii) cement composition. In soil and ground water, sulfates exist in three forms, namely sodium sulfate, magnesium sulfate and calcium sulfate. Since the solubility of calcium sulfate is very low, studies on sulfate attack in concrete have been conducted using sodium and magnesium sulfate.

When concrete is exposed to magnesium sulfate, Ca(OH)$_2$ is converted to gypsum and magnesium hydroxide, as shown below:

$$CH + M\bar{S} + 2H \rightarrow C\bar{S}H_2 + MH$$ \hspace{1cm} (7.1)

The magnesium hydroxide formed in Equation 7.1 has a low solubility and a low pH of 10.5. This low level of alkalinity destabilizes the C-S-H, which tends to liberate lime to establish its equilibrium and stability of pH.

In blended cements, particularly silica fume and blast furnace slag, lack of CH encourages magnesium sulfate (M\bar{S}) to react with C-S-H leading to the formation of non cementitious magnesium silicate hydrate (M-S-H), as shown below:

$$C-S-H + M\bar{S} + 2H \rightarrow M-S-H + C\bar{S}H_2$$ \hspace{1cm} (7.2)

When cement is exposed to sodium sulfate (M\bar{S}) bearing soil or ground water, the sulfate ions first react with CH to form gypsum as shown below:
\[ CH + N\bar{S} + 2H \rightarrow C\bar{S}H_2 + NH \] (7.3)

The gypsum produced in Eq. 7.3 reacts with calcium aluminate hydrate, monosulfate, or the unhydrated C\(_3\)A to produce ettringite, as shown below:

\[ C_4AH_{13} + 3C\bar{S}H_2 + 14H \rightarrow C_6A\bar{S}_3H_{32} + CH \] (7.4)

\[ C_4AH_{12} + 3C\bar{S}H_2 + 16H \rightarrow C_6A\bar{S}_3H_{32} \] (7.5)

\[ C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_6A\bar{S}_3H_{32} \] (7.6)

The ettringite formed in the above equations, which is dependent on the quantity of CH and C\(_3\)A, leads to expansion and cracking of concrete.

Sulfate attack in concrete may lead to a strength reduction in concrete. Al-Amoudi et al. [82-85] reported strength reduction in plain and blended cement mortar specimens exposed to M\(\bar{S}\) environment more than those exposed to N\(\bar{S}\). The strength reduction in the blended cements was more than that in the plain cements. The expansion in plain and blended cements exposed to N\(\bar{S}\) solution was more than that in the specimens exposed to M\(\bar{S}\) environment.

According to Bonen and Cohen [80-81] increasing the magnesium sulfate concentration from 2.1% to 4.2% did not change the course of attack. However, the increase in concentration of magnesium sulfate resulted in the appearance of M-S-H in the silica fume cements. Based on chemical and mineralogical analyses, they indicated that the sulfate attack due to M\(\bar{S}\) is noticeable up to a certain distance, which they term it as transition zone, beyond it, i.e. in the interior zone, only small chemical and mineralogical changes were detected. According to them
[80-81] the decrease in the Ca/Si ratio of the C-S-H gel can serve as a chemical criterion of the rate of magnesium sulfate attack. Another important conclusion of these studies [80-81] was that the formation of the massive continuous surface double layer ultimately suppresses diffusion of $\text{SO}_4^{2-}$ ions and protects the interior zone of the paste from further attack.

According to Turker et al. [86] deterioration of concrete due to magnesium sulfate attack proceeds in three stages. In the early stages, the detrimental effect of $\text{MS}$ is not clearly evidenced. In fact an increase in the strength, probably due to crystallization of salts in the pores, is noted. Further, increase in concentration does not cause acceleration of damage processes at this stage. In the secondary stage, a change in the physical properties is noted, exhibiting signs of deterioration. The initiation of the final stage of deterioration is dependent on the sulfate concentration.

Almost all codes of practices, such as ACI 318 [62], BS 8110 [64] etc., provide guidelines on the quality of concrete and the type of cement to be used for sulfate exposure. These guidelines are based on the concentration of sulfate ions in the soil or ground water. However, these standards, such as ACI and BS, are not informative on the precautions to be taken when the sulfate ions are associated with magnesium cation. This information is provided in the BRE Digest 363 entitled, “Sulfate and Acid Resistance of Concrete in the Ground,” [117]. However, these guidelines do not include the use of silica fume cement.

From the data developed in this study, it is apparent that the severity of sulfate attack is dependent on: (i) the concentration of sulfate ion, (ii) the cation type associated with the sulfate ions and (iii) the type of
cement. For example, deterioration was not noted in plain and blended cement concrete specimens exposed to sodium sulfate solution, while considerable concrete deterioration was observed on the specimens exposed to magnesium sulfate solution. Appreciable deterioration was noted in the plain cement concrete specimens when the SO$_4^{--}$ concentration, associated with magnesium ions, was 2.5% or more. In the blended cements, concrete deterioration was noted for a SO$_4^{--}$ concentration of 1% and above.

Therefore, when blended cements are used in structures exposed to SO$_4^{--}$ concentration of 1% or above and magnesium ions are present, they should be adequately protected. Similarly when plain cement concrete is exposed to SO$_4^{--}$ concentration of 2.5% or more, the structures should be adequately protected. Such a protection may include good tanking to exclude the ground water from the structure and/or applying a good coating. Al-Amoudi et al. [15] recommend an epoxy-based coating for this purpose.
Figure 7.1: Scanning electron micrograph of OPC-A concrete specimen exposed to 5% NaCl solution containing 1% SO$_4^{2-}$ ($\text{Na}_2\text{SO}_4$).

Figure 7.2: EDXA of OPC-A concrete specimen exposed to 5% NaCl solution containing 1% SO$_4^{2-}$ ($\text{Na}_2\text{SO}_4$).
Figure 7.3: Scanning electron micrograph of OPC-A concrete specimen exposed to 5% NaCl solution containing 4% SO₄⁻ (Na₂SO₄).

Figure 7.4: EDXA of OPC-A concrete specimen exposed to 5% NaCl solution containing 4% SO₄⁻ (Na₂SO₄).
Figure 7.5: Scanning electron micrograph of SF cement concrete specimen exposed to 5% NaCl solution containing 1% SO$_4^{2-}$ (Na$_2$SO$_4$).

Figure 7.6: EDXA of silica fume cement concrete specimen exposed to 5% NaCl solution containing 1% SO$_4^{2-}$ (Na$_2$SO$_4$).
Figure 7.7: Scanning electron micrograph of SF cement concrete specimen exposed to 5% NaCl solution containing 4% SO$_4^{–}$ (Na$_2$SO$_4$). 

Figure 7.8: EDXA of silica fume cement concrete specimen exposed to 5% NaCl solution containing 4% SO$_4^{–}$ (Na$_2$SO$_4$).
Figure 7.9: Scanning electron micrograph of OPC-A concrete specimen exposed to 5% NaCl solution containing 1% $\text{SO}_4^{2-}$ ($\text{MgSO}_4$).

Figure 7.10: EDXA of OPC-A concrete specimen exposed to 5% NaCl solution containing 1% $\text{SO}_4^{2-}$ ($\text{MgSO}_4$).
Figure 7.11: Scanning electron micrograph of OPC-A concrete specimen exposed to 5% NaCl solution containing 4% SO\textsubscript{4}\textsuperscript{2-} (MgSO\textsubscript{4}).

Figure 7.12: EDXA of OPC-A concrete specimen exposed to 5% NaCl solution containing 4% SO\textsubscript{4}\textsuperscript{2-} (MgSO\textsubscript{4}).
Figure 7.13: Scanning electron micrograph of SF cement concrete specimen exposed to 5% NaCl solution containing 1% SO$_4^{−}$ (MgSO$_4$).

Figure 7.14: EDXA of silica fume cement concrete specimen exposed to 5% NaCl solution containing 1% SO$_4^{−}$ (MgSO$_4$).
Figure 7.15: Scanning electron micrograph of SF cement concrete specimen exposed to 5% NaCl solution containing 4% SO$_4^{2-}$ (MgSO$_4$).
Figure 7.16: SRPC concrete specimens after 4 years of exposure to 5% NaCl plus Na$_2$SO$_4$ solutions.

Figure 7.17: OPC-A concrete specimens after 4 years of exposure to 5% NaCl plus Na$_2$SO$_4$ solutions.
Figure 7.18: OPC-B concrete specimens after 4 years of exposure to 5% NaCl plus Na₂SO₄ solutions.

Figure 7.19: BFS cement concrete specimens after 4 years of exposure to 5% NaCl plus Na₂SO₄ solution.
Figure 7.20: SF cement concrete specimens after 4 years of exposure to 5% NaCl plus Na$_2$SO$_4$ solutions.

Figure 7.21: FA cement concrete specimens after 4 years of exposure to 5% NaCl plus Na$_2$SO$_4$ solutions.
Figure 7.22: SRPC concrete specimens after 4 years of exposure to 5% NaCl plus MgSO₄ solutions.

Figure 7.23: OPC-A concrete specimens after 4 years of exposure to 5% NaCl plus MgSO₄ solutions.
Figure 7.24: OPC-B concrete specimens after 4 years of exposure to 5% NaCl plus MgSO₄ solutions.

Figure 7.25: BFS cement concrete specimens after 4 years of exposure to 5% NaCl plus MgSO₄ solutions.
Figure 7.26: SF cement concrete specimens after 4 years of exposure to 5% NaCl plus MgSO₄ solutions.

Figure 7.27: FA cement concrete specimens after 4 years of exposure to 5% NaCl plus MgSO₄ solutions.
CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 CONCLUSIONS

As stated earlier in Chapter 1, the objective of this study was to investigate the effect of sulfate ions and cement alkalinity on pore solution chemistry, and chloride-induced reinforcement corrosion. The specific objectives were:

Objective 1: to evaluate the effect of sulfate concentration and associated cation type on pore solution chemistry, i.e., $\text{OH}^-$, $\text{Cl}^-$ and $\text{SO}_4^{2-}$ concentrations;

Objective 2: to assess the effect of sulfate ion concentration on chloride-induced reinforcement corrosion;

Objective 3: to study the effect of cement alkalinity on reinforcement corrosion and pore solution chemistry, i.e., $\text{OH}^-$, $\text{Cl}^-$ and $\text{SO}_4^{2-}$ concentrations; and

Objective 4: to investigate the effect of sulfate cation type on concrete deterioration due to sulfate attack and the resulting morphological changes to cement.

The experimental work conducted in this study was designed to achieve the aforesaid objectives. The following sections present the conclusions that can be drawn from the data and results developed in the present study relevant to these objectives.
8.1.1 Main Conclusions

1. The OH\textsuperscript{−} concentration of the pore solution in plain and blended cements increased with increasing sodium sulfate, while no increase was noted in the case of magnesium sulfate contamination.

2. The chloride concentration of the pore solution in plain and blended cements increased with increasing sodium sulfate contamination. In the case of magnesium sulfate, the increase was noted up to 1% SO\textsubscript{4}\textsuperscript{2−}, beyond which no change was noted.

3. The chloride concentration increased linearly with the OH\textsuperscript{−} concentration in cements admixed with sodium chloride plus sodium sulfate. However, such a trend was not observed in the cements admixed with sodium chloride plus magnesium sulfate.

4. The SO\textsubscript{4}\textsuperscript{2−} concentration of the pore solution in the plain and blended cements increased almost linearly with increasing sulfate contamination. However, the SO\textsubscript{4}\textsuperscript{2−} concentration increased significantly with increasing OH\textsuperscript{−} concentration of the pore solution.

5. 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_{corr} increased with increasing sodium sulfate or magnesium sulfate. In the specimens exposed to magnesium sulfate solution, the increase continued up to 2.5% SO\textsubscript{4}\textsuperscript{2−}, beyond which, the I_{corr} decreased slightly.
6. The OH\(^{-}\), Cl\(^{-}\), and SO\(_4^{2-}\) concentrations in the pore solution of the SRPC and OPC increased with increasing alkali contents of cement.

7. The corrosion resistance of SRPC and OPC concrete specimens increased with increasing alkali content of cement of up to 0.8% Na\(_2\)O equivalent.

8. No signs of deterioration were noted in the concrete specimens exposed to sodium chloride or sodium chloride plus sodium sulfate. However, deterioration was noted in plain and fly ash cement concrete specimens exposed to 2.5% magnesium sulfate or more, while in silica fume and blast furnace slag cement concrete specimens deterioration was noted when the SO\(_4^{2-}\) concentration in the magnesium sulfate solution was 1% or above.

8.1.2 Detailed Conclusions

Effect of Sulfate Concentration on the Pore Solution Chemistry in Chloride-Admixed Cements

1. The OH\(^{-}\) concentration of the pore solution in plain and blended cements, admixed with sodium chloride plus sodium sulfate, was more than that in the cements admixed with only sodium chloride. The OH\(^{-}\) concentration increased significantly with increasing quantity of sodium sulfate contamination of up to 2.5%, beyond which it increased marginally. The data developed in this study compare well with that reported by other researchers [5, 43, 45] for similar chloride and sulfate contamination.

2. The OH\(^{-}\) concentration of the pore solution in plain and blended cements admixed with sodium chloride plus magnesium sulfate
was more or less similar to that in the cements admixed with only sodium chloride.

3. The OH$^-$ concentration in all the blended cements, admixed with sodium chloride plus sodium sulfate or sodium chloride plus magnesium sulfate, was much less than that in plain cements with similar contamination. The decrease in the OH$^-$ concentration in blended cements may be attributed to the reaction of pozzolans with Ca(OH)$_2$.

4. The chloride concentration in the pore solution of plain and blended cements admixed with sodium chloride plus sodium sulfate was more than that in the cements admixed with only sodium chloride. Further, the chloride concentration increased with increasing quantity of sodium sulfate. The data on the effect of sulfate contamination on the chloride concentration developed in this study compare well with that reported by other researchers [5, 43, 45] for similar chloride and sulfate contamination.

5. In plain and blended cements admixed with sodium chloride plus magnesium sulfate, the chloride concentration of the pore solution increased with increasing magnesium sulfate contamination of up to 1% SO$_4^{2-}$. However, no appreciable change in the chloride concentration was noted with a further increase in the magnesium sulfate contamination.

6. The chloride concentration in the blended cements was less than that in the plain cements with similar contamination.

7. The chloride-binding capacity of plain and blended cements decreased with increasing sodium sulfate contamination.
8. The chloride-binding capacity of plain cements was influenced significantly by the cement composition and increased with increasing C₃A content of cement.

9. The chloride concentration increased linearly with the OH⁻ concentration in cements admixed with sodium chloride plus sodium sulfate. However, such a trend was not observed in the cements admixed with sodium chloride plus magnesium sulfate.

10. The Cl⁻/OH⁻ ratio in plain cements admixed with sodium chloride plus magnesium sulfate, increased with increasing quantity of magnesium sulfate, of up to 1% SO₄⁻. For SO₄⁻ concentrations of more than 1%, a decrease in Cl⁻/OH⁻ was noted.

11. The Cl⁻/OH⁻ values in plain cements admixed with sodium chloride plus sodium sulfate, increased slightly with increasing sodium sulfate concentration and these values were more than those in the cements admixed with only sodium chloride.

12. The SO₄⁻ concentration of the pore solution in the plain and blended cements admixed with sodium chloride plus sodium sulfate or sodium chloride plus magnesium sulfate, increased almost linearly with increasing sulfate contamination.

13. The SO₄⁻ concentration in cements admixed with sodium chloride plus sodium sulfate was more than that in the cements admixed with sodium chloride plus magnesium sulfate.

14. In blended cements, the SO₄⁻ concentration was much less than that in the plain cements, particularly in those cements admixed with sodium chloride plus magnesium sulfate.
15. The $\text{SO}_4^{-}$ concentration of the pore solution in plain and blended cements increased significantly with increasing $\text{OH}^-$ concentration of the pore solution, particularly in the blended cements. These results indicate that sulfate-binding of cements is influenced by the alkalinity of the pore solution i.e., calcium sulphaaluminate hydrate is not stable at high alkalinity. Similarly, an increase in the chloride concentration with increasing alkalinity points towards the instability of calcium choroaluminate hydrate. The increase in the chloride and sulfate concentration, in cements admixed with chloride and sulfate ions, enhances the chances of reinforcement corrosion. These salts are normally contributed at the mixing stage by concrete mixture ingredients, particularly aggregates and mix water.

**Effect of Sulfate Concentration on Chloride-Induced Reinforcement Corrosion**

16. 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.

17. The concurrent presence of chloride and sulfate ions, however, increased the rate of reinforcement corrosion.

18. 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.
19. 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.

20. 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.

21. 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% $\text{SO}_4^{2-}$, beyond this concentration, the $I_{\text{corr}}$ decreased slightly.

22. 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.

23. 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.

24. 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.

25. The $I_{corr}$ 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.

26. The $I_{corr}$ 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 specimens compared to plain cement concrete specimens.

Effect of Cement Alkalinity on Pore Solution Composition and Reinforcement Corrosion

27. The $OH^-$, $Cl^-$ and $SO_4^{2-}$ concentration of the pore solution increased with increasing alkali content of the cement. The increase in the chloride and sulfate concentration due to increasing alkalinity indicates that both calcium chloroaluminate and calcium sulphoaluminate hydrates are not stable at high alkalinity.

28. The time-to-initiation of reinforcement corrosion in the SRPC and OPC-A concrete specimens increased with increasing alkalinity of
up to 0.8% Na₂O equivalent. However, when the alkalinity was more than 0.8% Na₂O equivalent, a decrease in time-to-initiation of reinforcement corrosion was noted.

29. The $I_{corr}$ on steel in SRPC and OPC-A concrete specimens with varying alkali content was initially very low and similar in all the specimens. However, it changed with alkali content and period of exposure. The $I_{corr}$ was the lowest in both SRPC and OPC-A concrete specimens when the alkalinity was 0.8% Na₂O equivalent. However, it increased with further increase in the alkalinity. This suggests that the alkali content of cement can be increased to 0.8% (Na₂O equivalent) to increase the corrosion-resistance of concrete. However, the present limit of 0.6% should be adhered to when it is expected that the aggregates are alkali-reactive.

Effect of Sulfate Cation Type on the Morphological Changes in Cements and Concrete Deterioration Due to Sulfate Attack

30. Plain and blended cement concrete specimens exposed to only sodium chloride or sodium chloride plus sodium sulfate solution, did not show any signs of deterioration even when the $SO_4^{−}$ concentration was as high as 4%. However, concrete deterioration was observed on the concrete specimens exposed to magnesium sulfate solution.

31. In plain and fly ash cement concrete specimens exposed to magnesium sulfate solution, deterioration was noted when the $SO_4^{−}$ concentration was 2.5% and above.
32. In silica fume and blast furnace slag cement concrete specimens, exposed to magnesium sulfate solution, deterioration was noted when the \( \text{SO}_4^{\text{-}} \) concentration was as low as 1%. Therefore, structures made with these cements and exposed to magnesium sulfate should be adequately protected, perhaps by the application of an epoxy-based coating.

8.2 IMPLICATIONS FOR CONCRETE DURABILITY IN CHLORIDE-SULFATE ENVIRONMENTS

1. The data developed in this study indicated that the combined presence of chloride and sulfate ions significantly influences concrete durability. The chloride concentrations of the pore solution in cements admixed with chloride plus sulfate ions was more than in those admixed with only chloride ions. Therefore, contamination of concrete by sulfate ions should be minimized, as is the case with chloride ions. The mix constituents, such as aggregates, cement, mix water and admixtures may contribute the sulfate ions.

2. The combined presence of chloride and sulfate ions also influences reinforcement corrosion in the concrete specimens exposed to chloride-sulfate environment. In such situations, the diffusion of both chloride and sulfate ions, into the interior matrix, should be minimized either by using a dense and impermeable concrete or coating such structures with a protective coating.

3. The results of this study indicated that a \( \text{SO}_4^{\text{-}} \) concentration of 2.5% and more, associated with magnesium anions, leads to deterioration of plain and fly ash cement concrete. However,
concrete deterioration is possible in silica fume and blast furnace slag cement concrete when the $\text{SO}_4^{--}$ concentration is as low as 1%. Therefore, reinforced concrete structures made with these cements and exposed to sulfate salts should be adequately protected.

4. The alkalinity of cement significantly affects the pore solution alkalinity and reinforcement corrosion. The data developed in this study indicated that cement alkalinity of up to 0.8% ($\text{Na}_2\text{O}$ equivalent) is beneficial in decreasing reinforcement corrosion. Therefore, cements with this alkalinity level, i.e. 0.8% ($\text{Na}_2\text{O}$ equivalent), can be utilized when the aggregates are not alkali-reactive.

8.3 RECOMMENDATIONS

8.3.1 Recommendations for Practice

1. Both chloride and sulfate contamination in concrete mixture ingredients should be minimized to reduce the deterioration due to reinforcement corrosion. This can be achieved by washing aggregates using potable water and avoid using chloride-admixed admixtures or brackish water in mixing.

2. Concrete specifications for environments admixed with chlorides and sulfates, such as sabkha soils or marine environments should emphasize the need for cleaning mixture ingredients from these salts, particularly washing aggregates and using potable water.

3. Concrete structures exposed to chloride and sulfate salts should be protected to avoid reinforcement corrosion. This can be achieved by using a dense and impermeable concrete or coating the
structural components with a protective coating, particularly substructures.

4. Silica fume and blast furnace slag cements should not be used in the concrete structural components exposed to more than 1% SO$_4^{2-}$ (associated with magnesium anion). If such cements are used, the structural components should be adequately protected by the application of an epoxy-based coating.

5. When plain and fly ash cements are used, extra precautions should be taken when the SO$_4^{2-}$ concentration is 2.5% and above.

6. Alkali content of cement can be increased to 0.8% Na$_2$O equivalent to enhance the corrosion-resistance of concrete. However, if the aggregates are alkali-reactive, the alkali content in cement should be kept less than 0.6% Na$_2$O equivalent.

8.3.2 Recommendations for Future Study

1. The data developed in this study indicated that sulfate salts, particularly sodium sulfate, influences the pore solution composition, specially Cl'/OH' ratio, which is an important indicator of initiation of reinforcement corrosion. While several standards, such as ACI 318 [62], ACI 224 [63], BS 8110 [64] etc. impose limitations on acceptable chloride levels, no such restrictions are put forward for sulfate ions. The present limit normally utilized by the industry is that given by BS 8110 which is 4% SO$_3$ by weight of cement. This limit is provided from the point of view of cement chemistry and is not related to pore solution composition and its implication on reinforcement
corrosion. Therefore, there is a need to conduct a systematic study to establish limits on sulfate contamination in concrete.

2. In this study the effect of sulfate concentration and the associated cation type on chloride-induced reinforcement corrosion and concrete deterioration due to sulfate attack has been established for a selected concrete composition. The interactive effect of concrete quality and the allowable sulfate concentration in the soil and ground water, particularly those associated with magnesium ions, needs to be established.

3. The results of this study and those by Al-Amoudi et al. [15] and Cohen and Bentur [77] indicated the possibility of deterioration of silica fume and blast furnace slag cement concrete when exposed to magnesium sulfate. In such environments, it is recommended to apply a protective coating on the structural components. The efficiency of coatings, in such severe environments is not adequately evaluated. Therefore, the performance of some coatings, such as epoxy-based, bituminous, acrylic etc., in sulfate environments, particularly magnesium sulfate, should be evaluated in order to develop an efficient concrete protection system for concrete structures serving in severe chloride-sulfate environments, such as sabkha.

4. The effect of cation type associated with sodium sulfate or magnesium sulfate on chloride-binding, pore solution chemistry and chloride-induced reinforcement corrosion was investigated in this study. The effect of other cations, such as calcium, associated with sulfate ions on chloride-binding, pore solution chemistry and
chloride-induced reinforcement corrosion is not well documented in the literature. Further studies on this aspect will be beneficial.

5. The effect of cement alkalinity on chloride-induced reinforcement corrosion was evaluated in the present study and the results provided useful data on the effect of cement alkalinity on chloride-induced reinforcement corrosion. Further research is required to validate the results of the present study.
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APPENDIX A
Figure A-1: Variation of corrosion potentials with time on steel in the OPC-A concrete specimens exposed to 5% NaCl solution.

Figure A-2: Variation of corrosion potentials with time on steel in the OPC-A concrete specimens exposed to 5% NaCl plus 1% SO₄²⁻(Na₂SO₄) solution.
Figure A-3: Variation of corrosion potentials with time on steel in the OPC-A concrete specimens exposed to 5% NaCl + 2.5% SO\textsubscript{4}\textsuperscript{2-} (Na\textsubscript{2}SO\textsubscript{4}) solution.

Figure A-4: Variation of corrosion potentials with time on steel in the OPC-A concrete specimens exposed to 5% NaCl plus 4% SO\textsubscript{4}\textsuperscript{2-} (Na\textsubscript{2}SO\textsubscript{4}) solution.
Figure A-5: Variation of corrosion potentials with time on steel in the OPC-A concrete specimens exposed to 5% NaCl plus 1% $\text{SO}_4^{-}$ (MgSO$_4$) solution.

Figure A-6: Variation of corrosion potentials with time on steel in the OPC-A concrete specimens exposed to 5% NaCl + 2.5% $\text{SO}_4^{-}$ (MgSO$_4$) solution.
Figure A-7: Variation of corrosion potentials with time on steel in the OPC-A concrete specimens exposed to 5% NaCl plus 4%SO₄²⁻(MgSO₄) solution.

Figure A-8: Variation of corrosion potentials with time on steel in the OPC-B concrete specimens exposed to 5% NaCl solution.
Figure A-9: Variation of corrosion potentials with time on steel in the OPC-B concrete specimens exposed to 5% NaCl plus 1% SO₄⁻ (Na₂SO₄) solution.

Figure A-10: Variation of corrosion potentials with time on steel in the OPC-B concrete specimens exposed to 5% NaCl plus 2.5% SO₄⁻ (Na₂SO₄) solution.
Figure A-11: Variation of corrosion potentials with time on steel in the OPC-B concrete specimens exposed to 5% NaCl plus 4% SO$_4^{2-}$ (Na$_2$SO$_4$) solution.

Figure A-12: Variation of corrosion potentials with time on steel in the OPC-B concrete specimens exposed to 5% NaCl plus 1% SO$_4^{2-}$ (MgSO$_4$) solution.
Figure A-13: Variation of corrosion potentials with time on steel in the OPC-B concrete specimens exposed to 5% NaCl plus 2.5% SO$_4^-$(MgSO$_4$) solution.

Figure A-14: Variation of corrosion potentials with time on steel in the OPC-B concrete specimens exposed to 5% NaCl plus 4% SO$_4^-$(MgSO$_4$) solution.
Figure A-15: Variation of corrosion potentials with time on steel in the SF concrete specimens exposed to 5% NaCl solution.

Figure A-16: Variation of corrosion potentials with time on steel in the SF concrete specimens exposed to 5% NaCl plus 1% $\text{SO}_4^{2-}$ ($\text{Na}_2\text{SO}_4$) solution.
Figure A-17: Variation of corrosion potentials with time on steel in the SF concrete specimens exposed to 5% NaCl plus 2.5% \( \text{SO}_4^- \) (\( \text{Na}_2\text{SO}_4 \)) solution.

Figure A-18: Variation of corrosion potentials with time on steel in the SF concrete specimens exposed to 5% NaCl plus 4% \( \text{SO}_4^- \) (\( \text{Na}_2\text{SO}_4 \)) solution.
Figure A-19: Variation of corrosion potentials with time on steel in the SF concrete specimens exposed to 5% NaCl plus 1% SO₄²⁻ (MgSO₄) solution.

Figure A-20: Variation of corrosion potentials with time on steel in the SF concrete specimens exposed to 5% NaCl plus 2.5% SO₄²⁻ (MgSO₄) solution.
Figure A-21: Variation of corrosion potentials with time on steel in the SF concrete specimens exposed to 5% NaCl plus 4% SO₄⁻ (MgSO₄) solution.

Figure A-22: Variation of corrosion potentials with time on steel in the FA concrete specimens exposed to 5% NaCl solution.
Figure A-23: Variation of corrosion potentials with time on steel in the FA concrete specimens exposed to 5% NaCl plus 1% SO₄²⁻ (Na₂SO₄) solution.

Figure A-24: Variation of corrosion potentials with time on steel in the FA concrete specimens exposed to 5% NaCl plus 2.5% SO₄²⁻ (Na₂SO₄) solution.
Figure A-25: Variation of corrosion potentials with time on steel in the FA concrete specimens exposed to 5% NaCl plus 4% SO$_4^{2-}$ (Na$_2$SO$_4$) solution.

Figure A-26: Variation of corrosion potentials with time on steel in the FA concrete specimens exposed to 5% NaCl plus 1% SO$_4^{2-}$ (MgSO$_4$) solution.
Figure A-27: Variation of corrosion potentials with time on steel in the FA concrete specimens exposed to 5% NaCl plus 2.5% SO$_4^{2-}$ (MgSO$_4$) solution.

Figure A-28: Variation of corrosion potentials with time on steel in the FA concrete specimens exposed to 5% NaCl plus 4% SO$_4^{2-}$ (MgSO$_4$) solution.