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Effect of sulfate ions and associated cation type on the pore solution chemistry in chloride-contaminated plain and blended cements

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Abstract

This paper presents the results of a study conducted to evaluate the effect of chloride and sulfate contamination on the pore solution chemistry in plain and blended cements. The cement paste specimens were admixed with a fixed quantity of sodium chloride and varying quantities of sodium sulfate or magnesium sulfate. The pore solution was extracted from these specimens and analyzed to determine OH^-, Cl^- and SO_4^{2-} concentrations. The OH^- concentration of the pore solution in both the plain and blended cements increased with increasing concentration of sodium sulfate while no increase was noted in the specimens admixed with sodium chloride plus magnesium sulfate. The chloride concentration in the pore solution in plain and blended cements increased with increasing sodium sulfate concentration. In the specimens admixed with magnesium sulfate, the increase was noted up to 1% SO_4^{2-}, beyond which no change was noted. The SO_4^{2-} concentration also increased with increasing quantity of sulfate contamination in the specimens admixed with both sodium and magnesium sulfate. The sulfate concentration in the cements admixed with sodium chloride plus sodium sulfate was more than that in the specimens admixed with sodium chloride or sodium chloride plus magnesium sulfate. The alkalinity of the pore solution influenced both chloride- and sulfate-binding capacity of cements.

Keywords: Blended cements; Chloride concentration; OH^- concentration; Plain cements; Pore solution; Sulfate concentration

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1. Introduction

Concrete provides both physical and chemical protection to the reinforcing steel. The physical protection is provided by its dense and relatively impermeable structure. The chemical protection is provided by the high alkalinity ($pH > 13.5$) of the pore solution. At this high pH, a thin protective layer of γ-Fe_2O_3 is formed which provides electrochemical protection to the reinforcing steel. Another chemical protection provided to the steel by the cement is its capacity to bind chlorides, particularly those present at the time of mixing. Chlorides introduced at the time of mixing or at a later stage are bound by the cement hydration products, particularly C_3A. The chloride-binding capacity of cement reduces the quantity of chlorides available for the initiation and sustenance of reinforcement corrosion.

The presence of the sulfate ions reduces the chloride binding capacity of cement. The earliest investigation to evaluate the effect of sulfate ions on the chloride binding of cements was conducted by Holden et al. [1], who reported a substantial increase in the chloride concentration in the specimens that were admixed with sodium chloride plus sodium sulfate compared to those in which only sodium chloride was admixed. They attributed the reduction in the chloride-binding capacity of cements, in the presence of sulfate ions, to the preferential reaction of sulfate ions with C_3A phase of cement forming calcium sulphoaluminate hydrate. Maslehuddin et al. [2] 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 25–70 °C. It was reported that both temperature and sulfate contamination influenced the chloride binding capacity of plain and blended cements and the chloride concentration increased with exposure temperature and

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sulfate concentration. 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 increase in the chloride concentration in the concrete admixed with chloride plus sulfate, compared with that admixed with only chloride ions may increase the rate of reinforcement corrosion in the former concrete. Maslehuddin et al. [3] reported an increase in 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 a behavior to: (i) decreased chloride binding, and (ii) reduced electrical resistivity, due to the incorporation of sulfate ions in the chloride-admixed concrete.

The studies conducted to date have evaluated the OH^- and Cl^- concentrations using only sodium sulfate with random concentrations as a contaminant. Meager data are available on the effect of the cation type, such as Na^+, associated with sulfate ions on the pore solution composition [1–3]. However, no data are available on the effect of $MgSO_4$ on the pore solution chemistry. A systematic study to evaluate the effect of sulfate concentration and the associated cation type on the pore solution chemistry is beneficial.

This study was conducted to evaluate the effect of sulfate concentration and the associated cation type on the pore solution chemistry, i.e., OH^-, Cl^- and SO_4^{2-} concentrations, in chloride-contaminated plain and blended cements.

2. Experimental program

2.1. Materials and specimen preparation

Six cements, namely sulfate-resisting Portland cement (SRPC; C_3A: 3.6%), ordinary Portland cement (OPC-A; C_3A: 8.5%), ordinary Portland cement (OPC-B; C_3A: 9.65%), blast furnace slag (BFS), silica fume (SF) and fly ash (FA) were used to prepare cement paste specimens. In the fly ash cement paste specimens, 20% fly ash was used as a replacement of OPC-A. In the silica fume cement paste specimens, 10% OPC-A 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 pozzolanic materials is shown in Table 1.

Cylindrical cement paste specimens, 49 mm in diameter and 75 mm high, were cast from each cement. These specimens were prepared with an 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 a fixed quantity of chloride and varying dosages of sulfate salts, as shown in Table 2. Three specimens representing similar mixture composition were prepared for pore solution expression and analysis.

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 pozzolanic materials

Table 1
Composition of cements and pozzolonic materials

Constituent (wt. %)	SRPC[a]	OPC-A[b]	OPC-B[c]	BFS[d]	SF[e]	FA[f]
SiO_2	22.0	20.5	20.0	35.4	92.5	49.7
Al_2O_3	4.1	5.6	6.0	7.8	0.4	47.6
Fe_2O_3	4.2	3.8	3.7	0.5	0.4	1.3
CaO	64.1	64.4	65.9	43.7	0.5	0.5
MgO	2.2	2.1	0.7	8.5	0.9	0.3
SO_3	1.9	2.10	2.1	1.1	0.5	0.2
Loss on ignition	0.8	0.7	1.3	–	–	–
K_2O	0.3	0.4	–	–	–	–
Na_2O	0.2	0.2	–	–	–	–
Na_2O equivalent	0.4	0.4	0.4	–	–	–
C_3S	54.6	56.7	64.7	–	–	–
C_2S	21.9	16.1	8.5	–	–	–
C_3A	3.6	8.5	9.7	–	–	–
C_4AF	12.9	11.6	11.3	–	–	–

[a] Sulfate-resisting Portland cement (C_3A: 3.6%).
[b] Ordinary Portland cement (C_3A: 8.5%).
[c] Ordinary Portland cement (C_3A: 9.7%).
[d] Blast furnace slag.
[e] Silica fume.
[f] Fly ash.

Table 2
Details of chloride and sulfate contamination used in the cement paste specimens

Group	Contamination
1	0.8% Cl^- (NaCl)
2	0.8% $Cl^- + 1\%\ SO_4^{2-}$ (NaCl and Na_2SO_4)
3	0.8% $Cl^- + 2.5\%\ SO_4^{2-}$ (NaCl and Na_2SO_4)
4	0.8% $Cl^- + 4\%\ SO_4^{2-}$ (NaCl and Na_2SO_4)
5	0.8% $Cl^- + 1\%\ SO_4^{2-}$ (NaCl and $MgSO_4$)
6	0.8% $Cl^- + 2.5\%\ SO_4^{2-}$ (NaCl and $MgSO_4$)
7	0.8% $Cl^- + 4\%\ SO_4^{2-}$ (NaCl and $MgSO_4$)

were first mixed thoroughly with the cement 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 ± 2 °C until testing.

2.2. Pore solution extraction

The pore solution was extracted using a high-pressure pore solution expression device similar to that utilized by Longuet et al. [4] and Barneyback and Diamond [5]. The pore solution was extracted after 100 days of casting when it is known that the pore solution concentration is fairly stable [5]. 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.

2.3. Pore solution analysis

The pore solution was extracted from three replicate specimens and analyzed to determine OH^-, Cl^- and SO_4^{2-} concentrations. The methods of analysis are briefly described in the following paragraphs.

2.3.1. OH^- concentration

The 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 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 standard 0.01 M NaOH.

2.3.2. Chloride concentration

The chloride ion concentration of the pore solution was determined using a spectrophotometric method [6]. 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 min before the absorption reading was taken on a Spectronic model UV21 spectrophotometer at a wavelength of 460 nm against deionized water [6]. The chloride concentration was computed using a computer program that corresponded to a calibration curve prepared using a standard chloride solution. Some specimens were serially diluted to reduce the chloride concentration to less than 10 μg/l.

2.3.3. Sulfate concentration

The sulfate concentration was determined using the spectrophotometric method outlined in the standard methods for the analysis of water and wastewater published by the American Water Works Association (AWWA) [7]. 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 min. The sulfate concentration was calculated from the net absorption from a calibration curve that was prepared using a standard sulfate solution.

3. Results

3.1. OH^- concentration

The OH^- concentration in the plain cement paste specimens admixed with sodium chloride plus sodium sulfate or sodium chloride plus magnesium sulfate is plotted in Fig. 1. 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 or sodium chloride plus magnesium sulfate. The OH^- concentration in the specimens admixed with sodium chloride plus sodium sulfate increased significantly with increasing sodium sulfate contamination. However, the increase was marginal when the sulfate concentration was increased from 2.5%

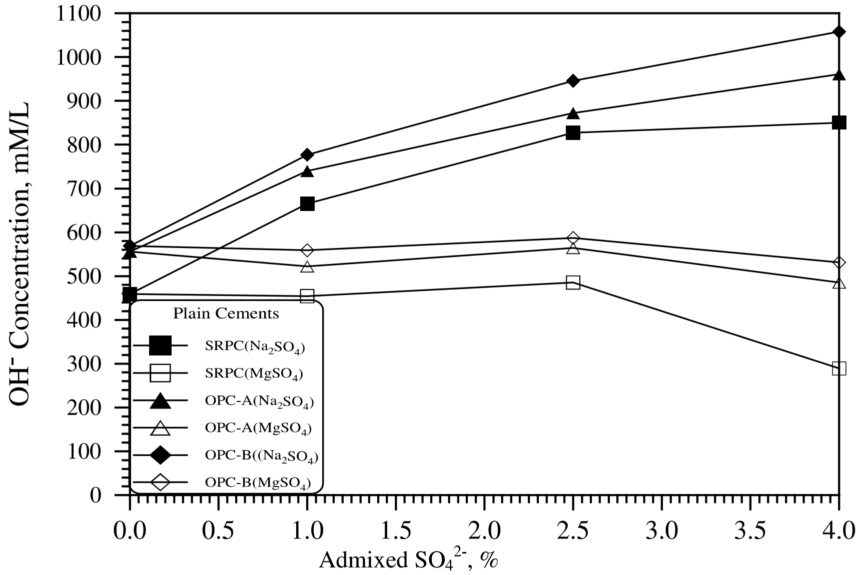

Fig. 1. Variation of OH⁻ concentration with sulfate contamination in the plain cement paste specimens.

to 4% SO_4^{2-}. 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 admixed with 4% SO_4^{2-}. The data in Fig. 1 indicate clearly that the OH⁻ concentration is the highest in the OPC-B specimens and the lowest in the SRPC specimens.

The OH⁻ concentration in the blended cement paste specimens admixed with sodium chloride plus sodium sulfate or sodium chloride plus magnesium sulfate is shown in Fig. 2. These data also indicate a trend similar to that noted in the plain cement paste specimens. The OH⁻ concentration increased significantly with increasing sulfate concentration of up to 2.5%, while there was a marginal change in the OH⁻ concentration when the sulfate concentration was increased from 2.5% to 4%.

Figs. 3 and 4 compare the OH⁻ concentration in the plain and blended cement paste specimens admixed with sodium chloride plus sodium sulfate or sodium chloride plus magnesium sulfate, respectively. The OH⁻ concentration in the plain and BFS cements was more than that in the SF and FA cements. The lower OH⁻ con-

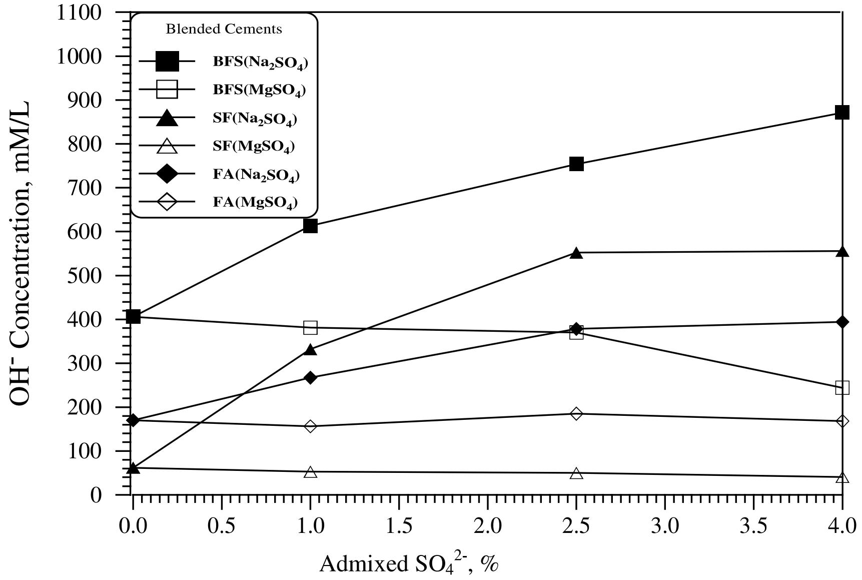

Fig. 2. Variation of OH⁻ concentration with sulfate contamination in the blended cement paste specimens.

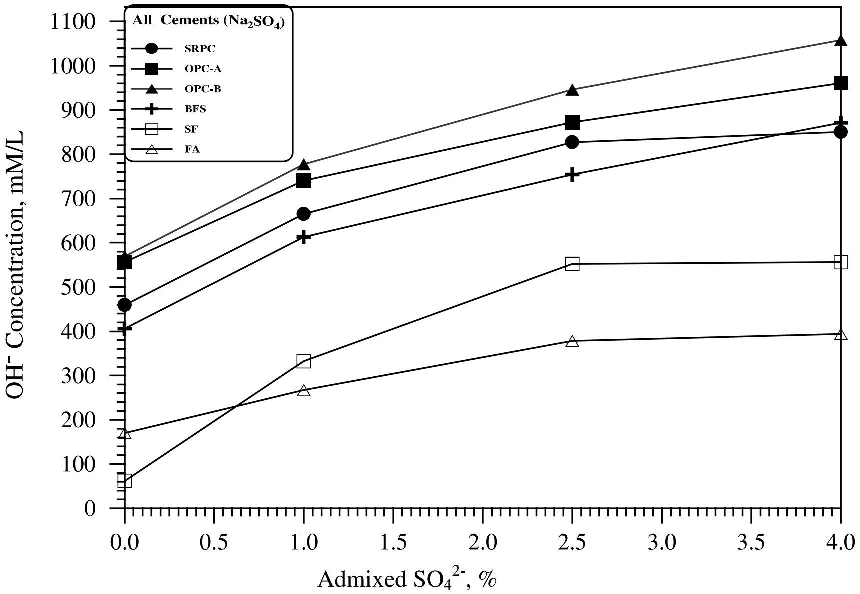

Fig. 3. OH^- concentration in plain and blended cement paste specimens admixed with sodium chloride plus sodium sulfate.

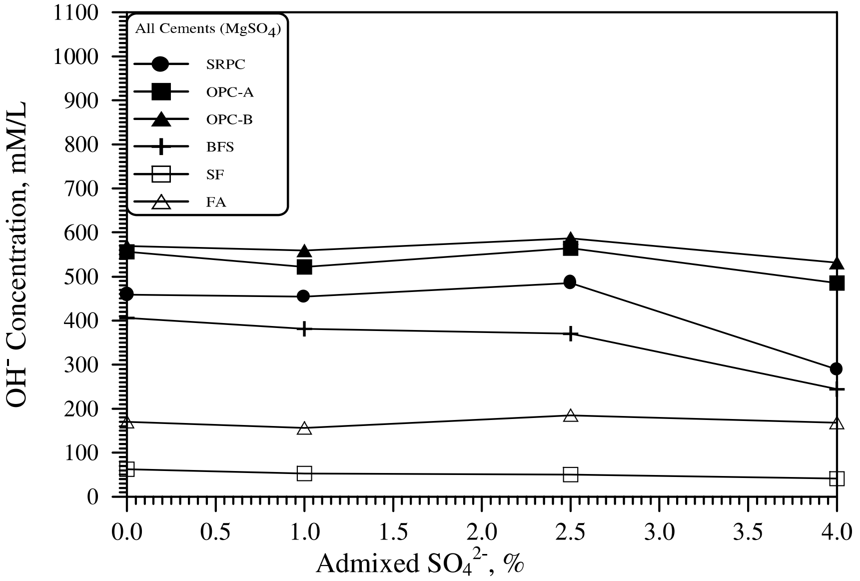

Fig. 4. OH^- concentration in the plain and blended cement paste specimens admixed with sodium chloride plus magnesium sulfate.

centration in the SF and FA cements, compared to plain cements, may be attributed to the reaction of $Ca(OH)_2$ with the pozzolanic materials.

3.2. Chloride concentration

The chloride concentration in the plain cement paste specimens admixed with sodium chloride plus sodium sulfate or sodium chloride plus magnesium sulfate is depicted in Fig. 5. 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. The chloride concentration in the specimen admixed with magnesium sulfate increased up to a sulfate concentration of 1% SO_4^{2-}. Thereafter, the chloride concentration decreased with further increase in the sulfate concentration.

Fig. 6 depicts the chloride concentration in the blended cement paste specimens admixed with sodium

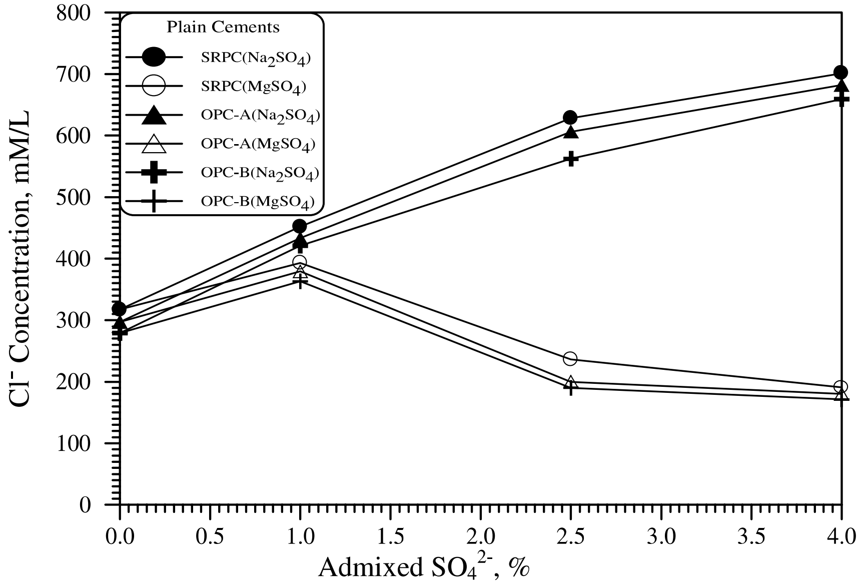

Fig. 5. Variation of chloride concentration with sodium sulfate or magnesium sulfate contamination in the plain cement paste specimens.

chloride plus sodium sulfate or sodium chloride plus magnesium sulfate. The trend of these data is similar to that noted in the plain cement paste specimens with similar contamination.

3.3. Sulfate concentration

The sulfate concentration in the plain and blended cements admixed with sodium chloride plus sodium sulfate and sodium chloride plus magnesium sulfate is shown in Figs. 7 and 8, respectively. While the sulfate concentration increased significantly in the cement paste specimens admixed with sodium chloride plus sodium sulfate, the change in the sulfate concentration in the specimens admixed with sodium chloride plus magnesium sulfate was insignificant. Further, the sulfate concentration in the blended cement paste specimens was much less than that in the plain cement paste specimens.

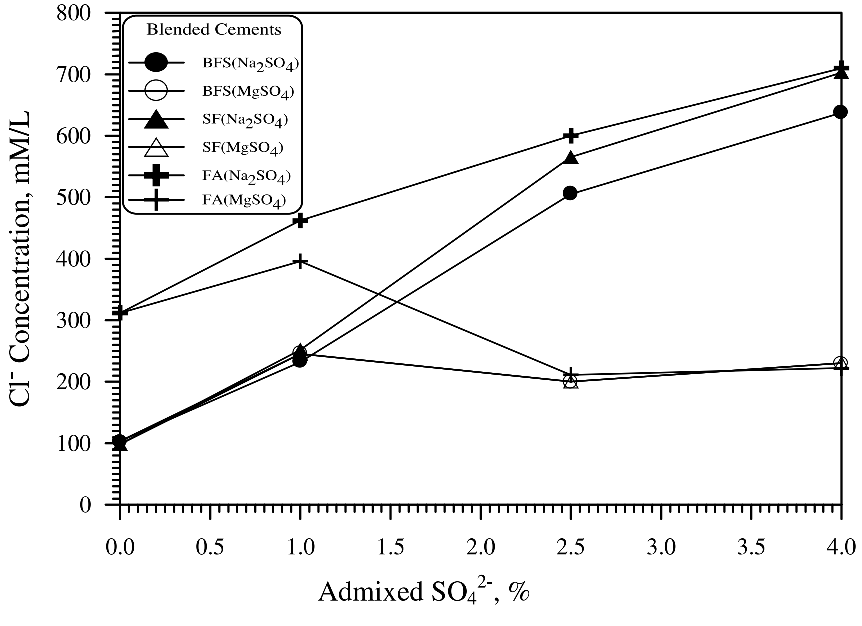

Fig. 6. Variation of chloride concentration with sodium or magnesium sulfate contamination in the blended cement paste specimens.

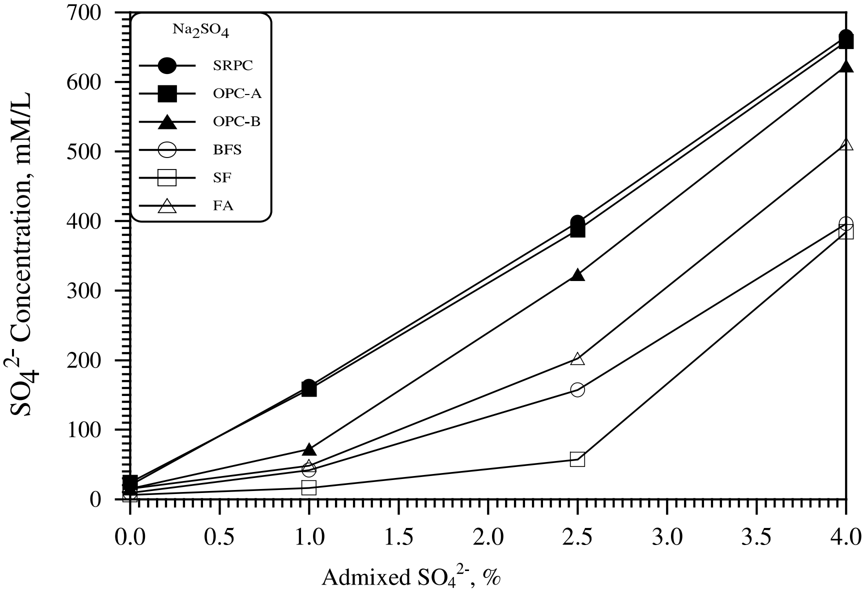

Fig. 7. Effect of sodium sulfate contamination on the sulfate concentration in the plain and blended cement paste specimens.

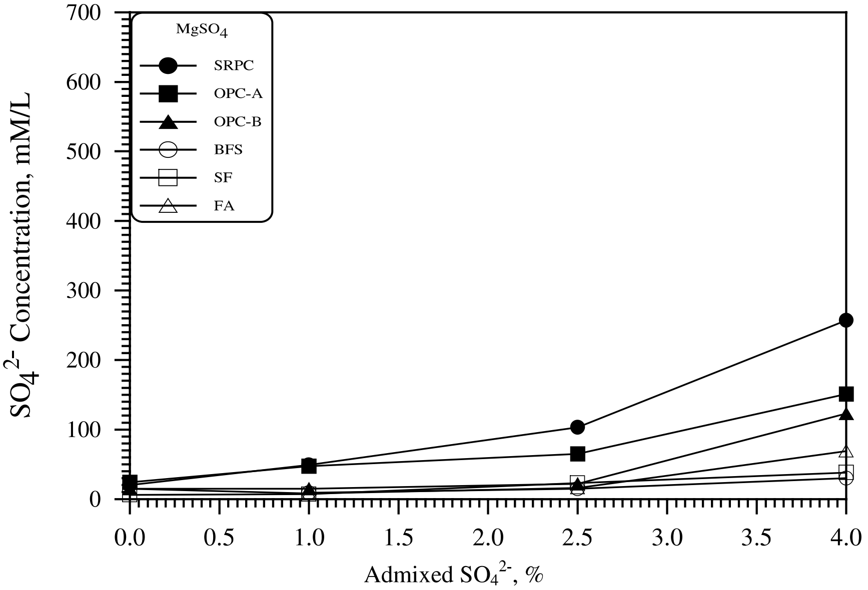

Fig. 8. Effect of magnesium sulfate contamination on the sulfate concentration in the plain and blended cement paste specimens.

4. Discussion

4.1. OH^- concentration

The data in Figs. 1 and 2 indicate that the OH^- concentration in the plain and blended cements 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, namely $Ca(OH)_2$ and C_3A, forming calcium-chloroaluminate, ettringite and monosulfate while Na^+ and OH^- ions are released in the pore solution, thereby increasing its alkalinity.

According to Yonezawa et al. [8], 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_3A) to form calcium-chloroaluminate hydrate (Friedel's salt) as indicated in the following equations:

$$2NaCl + Ca(OH)_2 \rightarrow CaCl_2 + 2Na^+ + 2OH^- \quad (1)$$

$$3CaO \cdot Al_2O_3 \cdot 10H_2O + CaCl_2 \rightarrow 3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O \quad (2)$$

$$(Mg, Na_2)SO_4 + Ca(OH)_2 \rightarrow CaSO_4 \cdot 2H_2O + (Mg, Na_2)(OH)_2 \quad (3)$$

$$3(CaSO_4 \cdot 2H_2O) + C_3AH_{12} \rightarrow C_3A \cdot 3CaSO_4 \cdot H_{32} \quad (4)$$

Several researchers [1–3,9,10] 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. Maslehuddin et al. [2] reported an increase in the OH^- concentration in the pore solution of mortar specimens admixed with sodium chloride or sodium sulfate compared with the specimens without contamination. The OH^- concentration in the specimens admixed with sodium chloride plus sodium sulfate was reported to be much more than that in the specimens admixed with either sodium chloride or sodium sulfate alone. Kayyali et al. [10] reported an increase in the OH^- concentration of the pore solution in the cement paste specimens admixed with sodium chloride compared to the specimens without any contamination. Hussain [9] demonstrated that the OH^- concentration increased with increasing concentration of sodium chloride. Further, 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. However, the increase was marginal when the sodium sulfate concentration was increased from 4% to 8%.

As shown in Fig. 2, the OH^- concentration in the blended cement specimens admixed with sodium chloride plus sodium sulfate also increased with increasing concentration of sodium sulfate. Several studies [2,9,11] indicated an increase in the OH^- concentration in the blended cements due to incorporation of sodium chloride and/or sodium sulfate. Maslehuddin et al. [2] 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. Hussain [9] and Talib [11] reported similar results.

The data in Figs. 3 and 4 indicate that the OH^- concentration in all blended cement paste specimens admixed with sodium chloride was much less than that in the plain cement paste specimens with similar contamination. Similarly, the OH^- concentration in all 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.

The lower OH^- concentration in the pore solution of blended cements, particularly SF and FA compared to plain cements, 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 [1,11–14]. Nixon et al. [12] reported a reduction in the OH^- concentration of cements blended with fly ash, the OH^- concentration decreased with increasing quantity of fly ash. Further, it was reported that the pore solution composition is significantly influenced by the cement alkalinity and the fly ash content. Holden et al. [1] and Diamond [13] reported that the addition of fly ash to Portland cement paste causes a reduction in the OH^- concentration of its pore solution. Talib [11] 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 [14] who indicated a decrease in the pH of the pore solution with increasing addition of silica fume to cement paste.

Rasheeduzzafar et al. [15], Maslehuddin et al. [2] and Byfors et al. [16] reported a reduction in the OH^- concentration of the pore solution of cement paste specimens incorporating silica fume. Byfors [16] 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 [17] reported that the silica fume reacts with the calcium hydroxide formed during the hydration process due to which the OH^- concentration decreases.

The increase in the pH of the pore solution, due to the incorporation of NaCl or Na_2SO_4 may affect the concrete durability indirectly. For example, the change in the alkalinity may affect the chloride- and sulfate-binding capacity of cement, as will be discussed in the later part of this paper. Another concern is to the acceleration of alkali-aggregate reaction if reactive aggregates are present. Contamination of concrete by sodium chloride and/or sodium sulfate is a possibility from the aggregates, mix water or admixtures. Due to this possibility, specifications for allowable chloride and sulfate content should be strictly adhered to.

A comparison of data in Figs. 1 and 2 indicate that 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

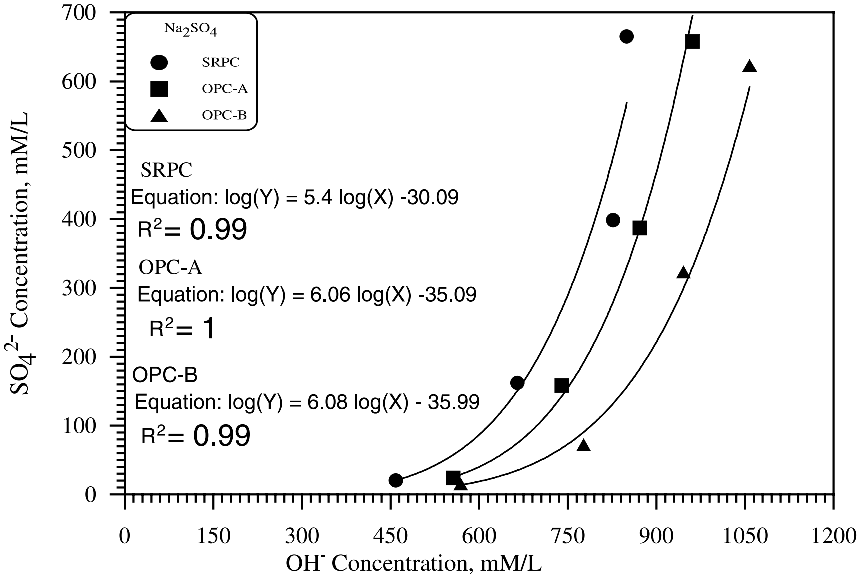

Fig. 9. Variation of SO_4^{2-} concentration with OH^- concentration in the plain cement paste specimens admixed with NaCl plus Na_2SO_4.

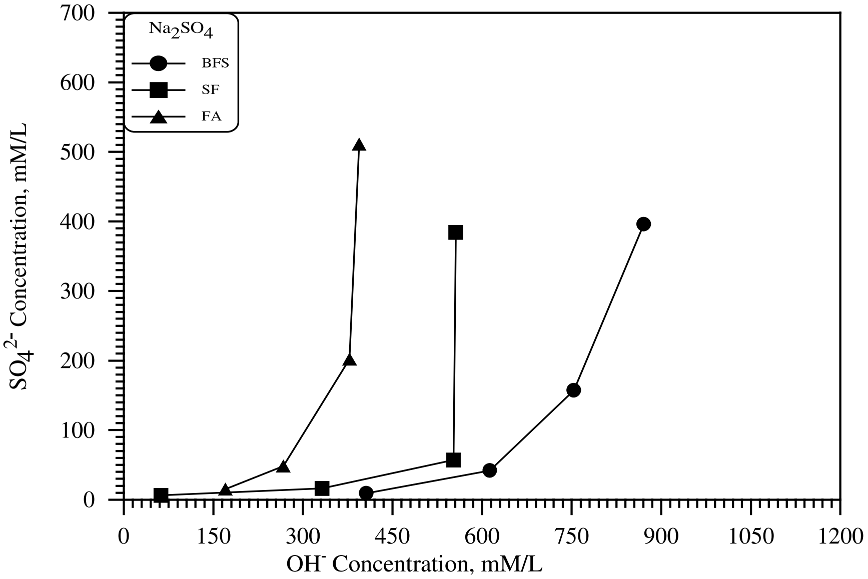

Fig. 10. Variation of SO_4^{2-} concentration with OH^- concentration in the blended cement paste specimens admixed with NaCl plus Na_2SO_4.

chloride plus magnesium sulfate was more or less similar to that in the specimens admixed with only sodium chloride. In fact, the OH^- concentration generally decreased when the sulfate concentration was 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 acidic nature of magnesium hydroxide formed as a byproduct of the reaction between magnesium sulfate and the calcium hydroxide in the cement.

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.

The insignificant change in the alkalinity when magnesium sulfate was incorporated may not significantly affect both the chloride- and sulfate-binding capacity of cements as will be discussed in the later part of this paper.

The data in Fig. 1 also show that the OH^- concentration in the OPC-B (C_3A: 9.65%), was more than that in OPC-A (C_3A: 8.5%) which was more than that in SRPC (C_3A: 3.6%). The increase in the OH^- concentration with increasing C_3A may be attributed to the

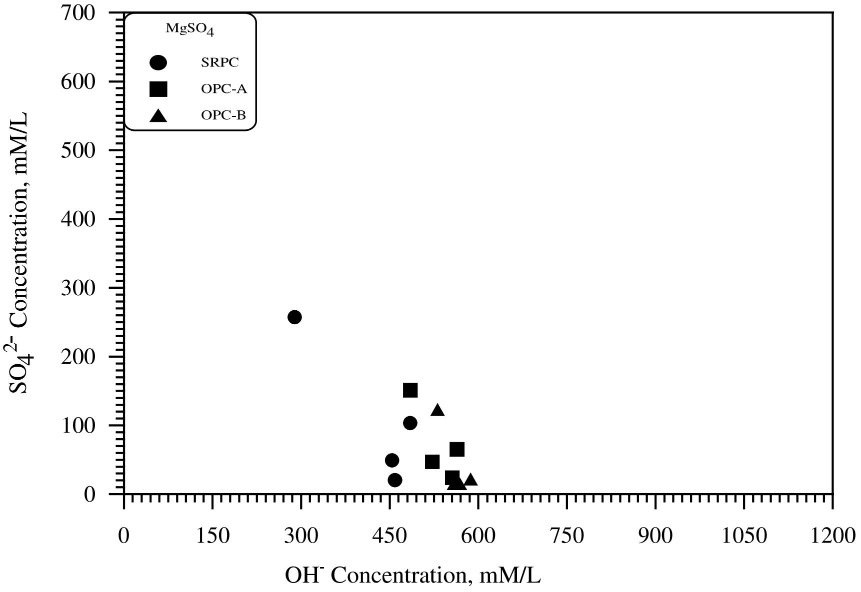

Fig. 11. Variation of SO_4^{2-} concentration with OH^- concentration in the plain cement paste specimens admixed with NaCl plus $MgSO_4$.

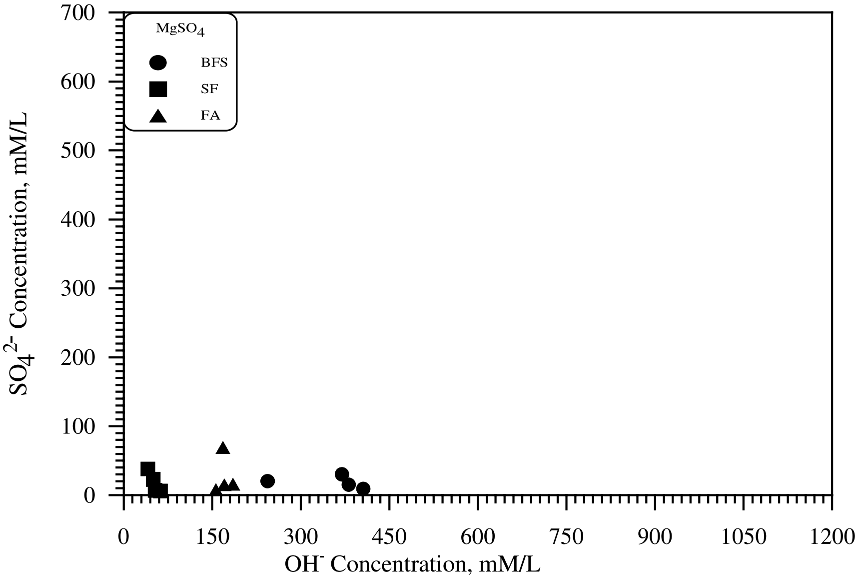

Fig. 12. Variation of SO_4^{2-} concentration with OH^- concentration in the blended cement paste specimens admixed with NaCl plus $MgSO_4$.

chloride/or sulfate binding. When chloride and sulfate ions are bound by C_3A, sodium ions are liberated in the pore solution which leads to an increase in the OH^- concentration.

4.2. Chloride concentration

As shown in Fig. 5, the chloride concentration in the plain cements, admixed with sodium chloride plus sodium sulfate, increased with increasing quantity of sulfate contamination. The chloride concentration in the plain cement paste specimens admixed with sodium chloride plus magnesium sulfate increased with increasing quantity of magnesium sulfate of 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 concentration in the blended cements admixed with sodium chloride plus sodium sulfate or magnesium sulfate exhibited a trend similar to that noted in plain cement with similar contamination as is evident in Fig. 6. However, the chloride concentration in the blended cements was less than that in the plain cement specimens. This indicates the superior performance of blended cements, compared to plain cements, in binding admixed chlorides.

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 of both plain and blended cements decreased with increasing sodium sulfate concentration. In the specimens admixed with sodium chloride plus magnesium sulfate, the chloride binding was reduced up to SO_4^{2-} content of 1%. Thereafter, the chloride binding capacity of both plain and blended cements was restored.

4.3. SO_4^{2-} concentration

The data in Figs. 7 and 8 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 quantity of 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 difference in sulfate binding 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.

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 by the following reactions:

$$\begin{aligned}&MgSO_4 + Ca(OH)_2 + 2H_2O\\&\quad \rightarrow CaSO_4 \cdot 2H_2O + Mg(OH)_2\end{aligned} \tag{5}$$

The magnesium hydroxide so formed is insoluble and its alkalinity is low ($pH < 10.5$). In the absence of $Ca(OH)_2$, such as in the blended cements, the magnesium sulfate reacts with calcium silicate hydrate to form calcium sulfate, magnesium hydroxide and silica gel.

The data in Figs. 7 and 8 indicate that for similar level of sulfate contamination, the sulfate concentration in the specimens admixed with sodium chloride plus sodium sulfate was more than that in the specimens admixed with sodium chloride plus magnesium sulfate. Since the OH^- concentration in the latter cement paste specimens was less than that in the former specimens, it is possible that this alkalinity influences the sulfate binding of cements. To evaluate this contention, the sulfate concentration is plotted against OH^- concentration in Figs. 9–12. As depicted in Figs. 9 and 10 sulfate concentration in the specimens admixed with sodium chloride plus sodium sulfate, increased exponentially with the OH^- concentration while such a relationship was not noted in the specimens admixed with sodium chloride plus magnesium sulfate as shown in Figs. 11 and 12. It may not be out of place to state that the OH^- concentration in the specimens admixed with sodium chloride plus sodium sulfate was in the range of 60–100 mM/l, while it was in the range of 60–400 M/l in the specimens admixed with sodium chloride plus magnesium sulfate. The high pH of the pore solution, in the specimens admixed with sodium chloride plus sodium sulfate probably leads to destabilization of gypsum and/or calcium sulphoaluminate hydrate.

The influence of pH on the reaction between SO_4^{2-} ions and, $Ca(OH)_2$, C_3A and C–S–H can therefore, be expressed as follows:

$$\begin{aligned}&(Mg, Na_2)SO_4 + Ca(OH)_2 \overset{pH}{\leftrightarrow} CaSO_4 \cdot 2H_2O\\&\quad + (Mg, Na_2)(OH)_2\end{aligned} \tag{6}$$

$$3(CaSO_4 \cdot 2H_2O) + C_3AH_{12} \overset{pH}{\leftrightarrow} C_3A \cdot 3CaSO_4 \cdot H_{32} \tag{7}$$

$$\begin{aligned}&(Mg, Na_2)SO_4 + C\text{–}S\text{–}H \overset{pH}{\leftrightarrow} CaSO_4 + (Mg, Na_2)(OH)_2\\&\quad + SiO_2\end{aligned} \tag{8}$$

The data on free sulfate concentration in the pore solution of the 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 a decrease in the electrical resistivity of concrete [18], thus increasing the rate of reinforcement corrosion. The decrease in the sulfate concentration, due to the addition of $MgSO_4$, is indicative of the reaction of sulfate ions with the cement hydration products and the formation of gypsum and ettringite, leading to concrete degradation in the form of cracking or softening of the matrix. Sodium chloride, sodium sulfate and magnesium sulfate are commonly contributed to concrete by the mixture ingredients, such as admixtures, dregged aggregate and saline mixing and curing water. These salts may compromise concrete durability in terms of reinforcement corrosion and sulfate as elucidated earlier. To improve durability of concrete, chloride and sulfate contamination should be controlled through guidelines provided by relevant standards.

5. Conclusions

The OH^- concentration of the pore solution in the plain and blended cements increased with increasing concentration of sodium sulfate, while no increase was noted in the specimens admixed with magnesium sulfate. The OH^- concentration in the specimens 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 of up to 2.5% SO_4^{2-}, beyond, which it increased marginally. The OH^- concentration of the pore solution in the 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.

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 the plain cements with similar contamination. The decrease in the OH^- concentration in the blended cements may be attributed to the reaction of pozzolans with $Ca(OH)_2$. The increase in the pH of the pore solution due to the incorporation of NaCl or Na_2SO_4 may affect concrete durability. The change in the alkalinity may affect the chloride- and sulfate-binding of cements. Another concern regarding the increase in the alkalinity of the pore solution is the acceleration of alkali-aggregate reaction if reactive aggregates are used.

The chloride concentration of the pore solution in plain and blended cements increased with increasing sodium sulfate contamination. In the specimens admixed with magnesium sulfate, the increase was noted up to 1% SO_4^{2-}, thereafter a decrease in the chloride concentration was noted.

The SO_4^{2-} 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 with increasing sulfate contamination. The SO_4^{2-} concentration in the cements admixed with sodium chloride plus sodium sulfate was more than that in the cements admixed with sodium chloride plus magnesium sulfate. The SO_4^{2-} concentration in the blended cements was less than that in the plain cements, particularly in those cements admixed with sodium chloride plus magnesium sulfate. The SO_4^{2-} concentration of the pore solution in plain and blended cements increased significantly with increasing OH^- concentration of the pore solution, particularly in the blended cements.

The data developed in this study indicate that the chloride and sulfate binding of cements is influenced by the alkalinity of the pore solution. The increase in the chloride and sulfate concentration, in cements admixed with chloride and sulfate ions, enhances the chances of reinforcement corrosion. Therefore, chloride and sulfate contamination should be controlled to improve durability of concrete.

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