Pergamon

Cement and Concrete Research, Vol. 27, No. 12, pp. 1841–1850, 1997

0008-8846/97 $17.00 + .00

PII S0008-8846(97)00196-8

THE INFLUENCE OF SULPHATES ON CHLORIDE BINDING AND PORE SOLUTION CHEMISTRY

Y. Xu[1]
Department of Civil and Environmental Engineering, University College of London,
Gower Street, London WC1E 6BT, United Kingdom

(Refereed)
(Received February 7, 1997; in final form September 11, 1997)

ABSTRACT

Ordinary Portland cement (OPC) and OPC/ground granulated blastfurnace slag (GGBS) 65% cements containing 2.0 to 9.0% sulphates derived from sodium sulphate and calcium sulphate were investigated in respect to their chloride binding properties and the concentrations of chloride and hydroxyl ions in the pore solutions. Chlorides derived from sodium and calcium chlorides were introduced at the time of mixing. The results indicate that calcium sulphate has a different effect on chloride binding and the pore solution chemistry than sodium sulphate. The slag cement has higher chloride binding capacities as a result of simple replacement for OPC, but at the same sulphate contents, the slag cement does not give the expected higher binding capacities, suggesting that the difference in sulphate content between the two cements may be the main reason for their different chloride binding behaviour. © *1997 Elsevier Science Ltd*

Introduction

Chloride-induced corrosion of reinforcing steel in concrete structures has become a widespread durability problem throughout the world. It is now clear that it is not the total quantity of chloride in concrete, but the free chloride remaining in the pore solution that is responsible for the corrosion of steel (1). Although the mechanism of depassivation by chloride ions is not yet perfectly understood, it is known that the risk of corrosion increases with a higher ratio of chloride ion to hydroxyl ion concentration in the pore solution (2,3). Factors that influence the concentrations of chloride and hydroxyl ions are therefore directly relevant in determining the corrosion risk.

The importance of C_3A content in removing chloride ions from the pore solution has long been recognised because C_3A may form an insoluble complex, calcium chloroaluminate hydrate (Friedels' salt) in hydrated cement pastes (1,4). There is increasing evidence suggesting that hydration products of C_4AF are also responsible for binding chloride (5–7). It is also realised that the interactions of C_3A, alkali, and sulphate during cement hydration

---

[1] To whom correspondence should be addressed.

TABLE 1
Composition of the Materials (% by Weight)

Material	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O	Loi	C_3S	C_2S	C_3A	C_4AF
Clinker	65.9	20.1	5.2	3.1	2.4	1.5	0.08	0.47	0.2	71.8	3.84	8.54	9.42
GGBS	42.3	33.8	11.3	0.89	8.5	—	0.35	0.42	—				
Gypsum	32.8	5.3	2.2	0.8	1.4	44.7	—	0.28	11.2				

contribute to the chloride binding capacity (8). This is because of the preferential reaction between sulphate and C_3A (4) and the competition for binding by cement hydrates between hydroxyl and chloride ions in the pore solution (9,10).

In spite of the recognition of the role of sulphate in chloride binding, the effects of sulphate salt type and the levels of sulphate ions, either as constituents of the mix materials or entering from the service environment, remain largely unknown. Several studies concerning the effect of adding sodium sulphate have been reported (11,12). It has been found that chloride ion concentrations in pore solution increase with the addition of sulphates derived from sodium sulphate (5,9). However, because the alkalinity of the pore solution is thereby increased, there is no clear cut evidence as to the sulphate effect. It is believed, therefore, that it is necessary to study directly the effects of sulphate derived from calcium sulphate, which is normally added in ordinary Portland cement (OPC), on chloride binding and corrosion-related pore solution chemistry. The aim of this paper is to investigate the effects of sulphates derived from both $CaSO_4$ and Na_2SO_4 at various concentrations on chloride binding and pore solution chemistry. The influence of the chloride salt type (NaCl or $CaCl_2$) on OPC and a blend OPC/ground granulated blastfurnace slag (GGBS) 65% has also been studied.

Experimental Program

Materials

The composition of the cement clinker, ground granulated blastfurnace slag (GGBS), and gypsum used in experimentation are given in Table 1. Gypsum was introduced to obtain OPC cements with sulphate levels of 2%, 3%, 5%, 7%, and 9% by weight of cement. Sodium sulphate was added to the OPC cement with 2% sulphate to obtain total sulphate levels of 3%, 5%, and 7%. Slag cements with different sulphate contents were made by 65% replacement of GGBS for all the OPC cements. Chloride (1.0% by weight of cement) derived from calcium chloride and sodium chloride was introduced at the time of mixing. The details of the mixes studied are included in Table 2.

Specimen Preparation and Pore Solution Expression

Paste specimens were prepared at a constant 0.5 w/c ratio and with 1.0% chloride derived from calcium chloride or sodium chloride. The cement pastes were mixed using a Hobart mixer at low speed (central shaft: 60 rpm). The mixing procedure is 2.5 min by the mixer and then 0.5 min by hand. After mixing, the specimens were cast in plastic cylinders and

TABLE 2
Mix Details and Results (w/c 0.5, 1.0% Chloride by Weight of Cement)

	SO_3 content (% by wt. of cement)		Pore water composition				
			$[Cl^-]$ (mol/l)		$[OH^-]$ (mol/l)		
Cement	as $CaSO_4$	as Na_2SO_4	with $CaCl_2$	with NaCl	with $CaCl_2$	with Nacl	Evaporable water (% by wt. of cement)
	2.0	0.088		0.282		30.4	
	3.0		0.144		0.260		31.6
OPC	5.0			0.359		0.140	34.1
	7.0			0.465		0.045	36.5
	9.0		0.451		0.045		37.4
	2.0			0.271		0.632	32.2
	3.0			0.359		0.592	33.2
OPC	5.0			0.652		0.450	34.8
	7.0			0.697		0.100	36.9
	9.0			0.694		0.095	37.7
	2.0	1.0		0.479		0.901	33.9
OPC	2.0	3.0		0.860		1.340	32.8
	2.0	5.0		1.015		1.460	27.8
	0.70		0.035		0.175		36.0
OPC/	1.05		0.049		0.140		36.2
GGBS 65%	1.75		0.063		0.130		36.5
	2.45				0.120		36.9
	3.15		0.105		0.100		37.2
	0.70			0.141		0.445	37.6
OPC/	1.05			0.144		0.442	37.3
GGBS 65%	1.75			0.172		0.430	37.6
	2.45			0.240		0.380	38.0
	3.15			0.313		0.335	38.5

compacted by vibration. The moulds were sealed and stored in a fog room at a temperature of 20 ± 1°C for 6 months to ensure that an equilibrium state of hydration had been achieved.

At the end of the curing period, the pore solution was expressed from two specimens using a device similar to that described by Barneyback and Diamond (13). The load was increased at a rate of about 1 kN per second up to a maximum pressure of 350 MPa, where the load was sustained for about 2 min: depending on the cement type, 3 to 7 mL pore solutions were obtained. Chloride ion concentrations in the pore solution were analysed by potentiometric titration with silver nitrate solution using a chloride ion selective electrode. The hydroxyl ion concentrations were determined by direct titration against hydrochloric acid (HCl) using a phenolphthalein indicator. Evaporable and nonevaporable water contents were determined on parallel specimens at 105°C and 1000°C, respectively, based on which bound proportion of total chloride contents is estimated.

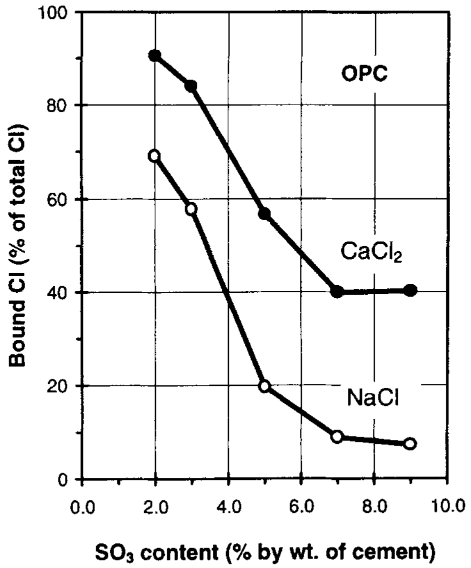

FIG. 1.

The effect of sulphate added as $CaSO_4$ on chloride binding (OPC, 1.0% chloride derived from NaCl and $CaCl_2$).

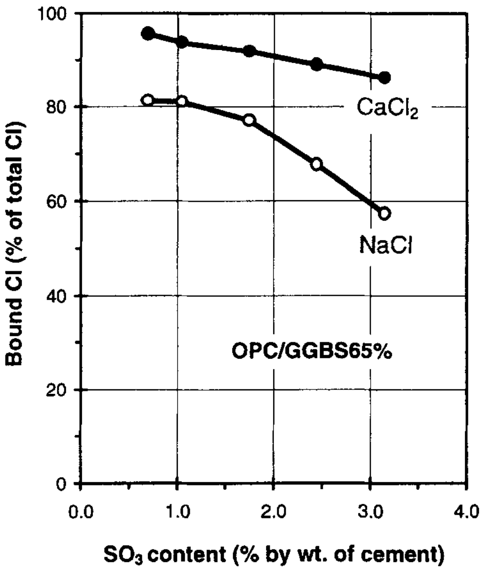

FIG. 2.

The effect of sulphate added as $CaSO_4$ on chloride binding (OPC/GGBS 65%, 1.0% chloride derived from NaCl and $CaCl_2$).

Results and Discussion

Chloride Binding Capacity

Table 2 shows the pore solution compositions and the evaporable water contents of the specimens studied. From the results shown in Figure 1, it is apparent that bound chloride drops rapidly as sulphate content increases from 2% to 7%. Above 7%, however, no sensible further reduction in bound chloride is observed. It is also clear that more chloride derived from $CaCl_2$ is bound than chloride from NaCl over the range of sulphate contents studied, and that the difference in bound chloride increases with increasing sulphate content.

As can be seen from Figure 2, similar trends are observed for slag cement OPC/GGBS 65%. Note that the five levels of sulphate content in OPC/GGBS 65% from 0.7 to 3.15% correspond to the five levels of sulphate content in OPC from 2 to 9%, respectively, as a result of simple replacement of 65% GGBS for OPC. Figures 1 and 2 confirm both this and other author's previous observations that the replacement of GGBS for OPC significantly increases the percentage of bound chloride (5,14–16). However, comparison of Figures 1 and 2 shows that at the same sulphate levels, the slag cement has almost the same binding power as the OPC cement. This implies that the higher binding capacity of the slag cement compared to the parent OPC may mainly result from the reduced sulphate content. This finding strongly suggests that the decreased sulphate content may be a main contributor to the increased chloride binding capacity of the slag cement.

Figure 3 presents the results of the associated cation effect on chloride binding. At the same sulphate content, calcium sulphate gives a higher chloride binding capacity than

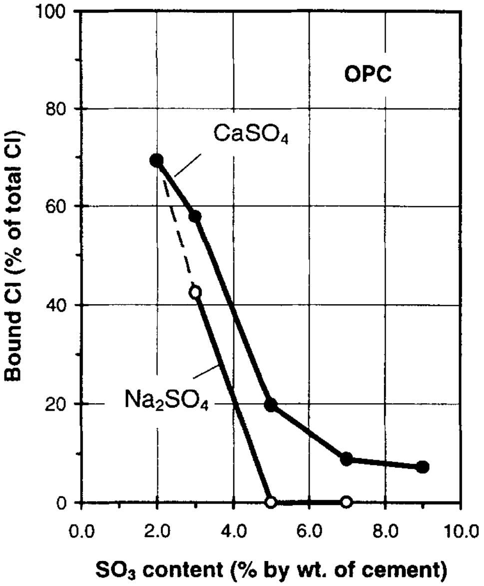

FIG. 3.

The effect of sulphate added as Na_2SO_4 and $CaSO_4$ on chloride binding (OPC, 1.0% Cl^- derived from NaCl).

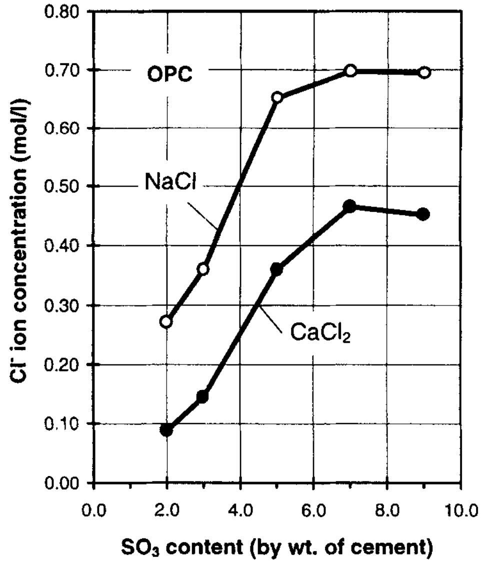

FIG. 4.

The influence of sulphate added as $CaSO_4$ on the chloride ion concentration of the pore solution (OPC, 1.0% Cl^- derived from NaCl and $CaCl_2$).

Na_2SO_4. It is also clear that the chloride binding capacity decreases faster in specimens containing Na_2SO_4 than those containing $CaSO_4$. At 5% sulphate, of which 3% is derived from Na_2SO_4, bound chloride has been reduced to zero, whereas $CaSO_4$ leaves 20% bound chloride at 5% sulphate content. The sulphide content of the slag has not been measured; possible oxidation of the sulphide (S^{2-}) of the slag may lead to a systematic error in available sulphate content, although our previous data shows that the sulphide content in slag from the same source is about 0.5% by mass as SO_3.

The findings indicate the importance of sulphate content and the associated cation type in chloride binding. A major mechanism for the increased chloride binding power of the slag cement may be attributable to the reduced sulphate content, as a result of the slag replacement. $CaSO_4$ has a less significant effect on chloride binding than Na_2SO_4. Differences in sulphate content may also be an important factor influencing the chloride binding capacity of other blended cements. Furthermore, differences between OPC and SRPC in sulphate content may also be a reason why some workers found that the chloride binding capacity of SRPC is lower than that of OPC (7,17) while others found the opposite (18).

Chloride Ion Concentration in Pore Solution

The effects of sulphate content on chloride pore solution concentrations are shown in Figures 4 through 6. Figure 4 shows the effect of sulphate as $CaSO_4$ in OPC specimens containing NaCl or $CaCl_2$. The results clearly demonstrate that the chloride ion concentrations significantly increase with increasing sulphate content up to 7%, above which little change occurs.

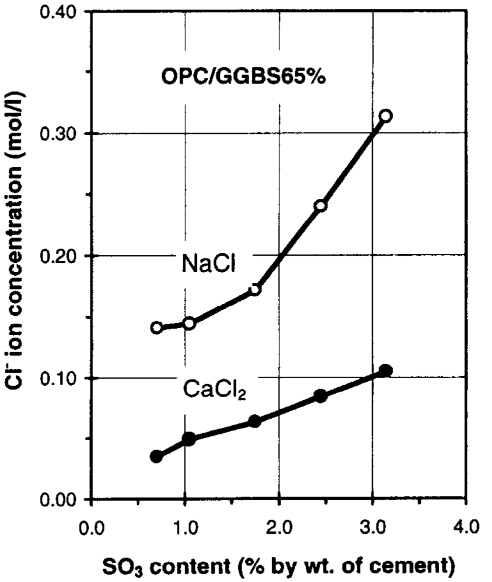

FIG. 5.
The influence of sulphate added as $CaSO_4$ on the chloride ion concentration of the pore solution (OPC/GGBS 65%, 1.0% chloride derived from NaCl and $CaCl_2$).

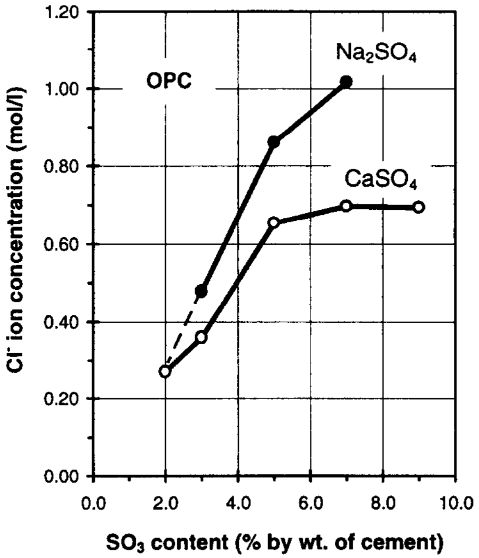

FIG. 6.
The effect of sulphate added as Na_2SO_4 and $CaSO_4$ on the chloride ion concentration of the pore solution (OPC, 1.0% chloride derived from NaCl).

There is also a clear difference between the chloride ion concentrations in NaCl- and $CaCl_2$-containing pastes.

The same behaviour is observed in slag cement specimens within the similar range of sulphate content (Fig. 5). By comparing the results in Figure 4 and 5, it can be found that the chloride ion concentration in OPC specimens is higher than in OPC/GGBS 65% specimens at the same sulphate content, e.g., at 3%. This may be due to the difference in their evaporable water contents. As can be seen from Table 2, OPC has less evaporable water content than the slag cement. In this case, the lower chloride ion concentrations in slag cement does not necessarily mean higher chloride binding. It might be worth noting that the slag cement is presumably still undergoing reaction, although any extrapolation of the data presented here is uncertain.

Figure 6 shows the effect of associated cations on chloride ion concentration in the pore solution. In contrast to $CaSO_4$, Na_2SO_4 is seen to produce a significantly higher chloride ion concentration. The difference in the chloride ion concentration between the two sulphate salts increases as the sulphate content increases.

Hydroxyl Ion Concentration in Pore Solution

The influence of $CaSO_4$ on hydroxyl ion concentration in the pore solution of OPC specimens is presented in Figure 7. $CaSO_4$ reduces the alkalinity of the pore solution; the hydroxyl ion concentration rapidly drops as the sulphate content increases from 2% to 7% in both NaCl-

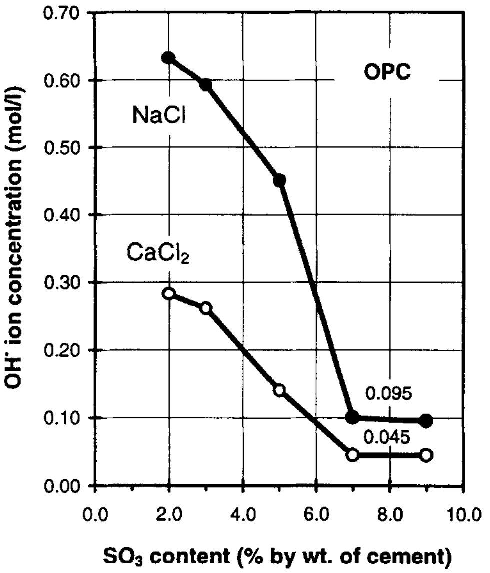

FIG. 7.

The effect of sulphate derived from $CaSO_4$ on the hydroxyl ion concentration of the pore solution (OPC, 1.0% Cl^- derived from NaCl and $CaCl_2$).

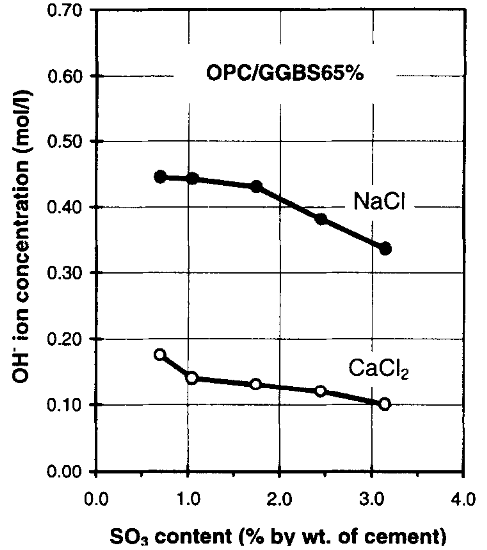

FIG. 8.

The effect of sulphate derived from $CaSO_4$ on the hydroxyl ion concentration of the pore solution (OPC/GGBS 65%, 1.0% Cl^- derived from NaCl and $CaCl_2$).

and $CaCl_2$-containing OPC specimens. At 7% sulphate content, the hydroxyl ion concentration is reduced to 0.095 mol/L and 0.045 mol/L for NaCl and $CaCl_2$, respectively. There is a clear limit of sulphate content above which there is little effect on the hydroxyl ion concentration. In this instance, the limit of the sulphate content seems to be 7%.

Similarly, the hydroxyl ion concentration in the slag cement specimens is found to decrease with increasing sulphate content derived from $CaSO_4$ (Fig. 8). It appears that the effect of sulphate on the alkalinity of the pore solution is small when sulphate content is lower than 2%.

As expected, Na_2SO_4 has different effects on the alkalinity of the pore solution compared to $CaSO_4$ (Fig. 9). The hydroxyl ion concentration significantly increases with sulphate content from 3% to 7%. It should be noted here that the higher chloride ion concentrations in Na_2SO_4-containing specimens may not purely result from the increased sulphate content; the increased hydroxyl ion concentration may have played a part (9).

The [Cl^-] / [OH^-] Ratio

From the corrosion point of view, the ratio of [Cl^-]/[OH^-] has been used as a criteria for determining the threshold value for corrosion initiation (2,3). The relationships between the ratio and the sulphate content for the various cements, chlorides, and sulphates are displayed in Figures 10 through 12. Figure 10 shows that the increases in the [Cl^-]/[OH^-] ratio are relatively slight up to 5% sulphate derived from $CaSO_4$ but very significant between 5% to 7%. Further increase of the sulphate content does not produce apparent change in the ratio.

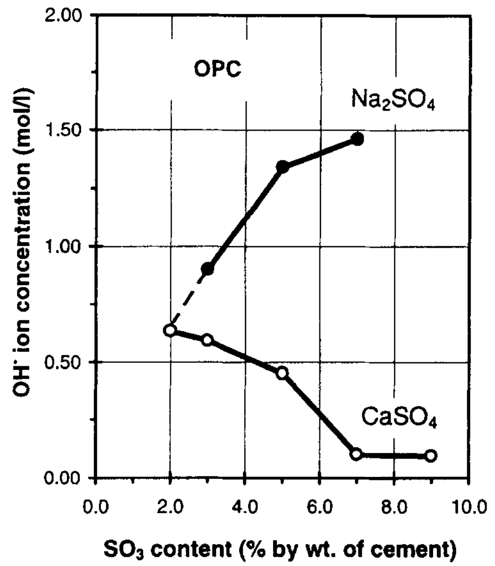

FIG. 9.
The effect of sulphate added as Na_2SO_4 and $CaSO_4$ on the hydroxyl ion concentration of the pore solution (OPC, 1.0% Cl^- derived from NaCl).

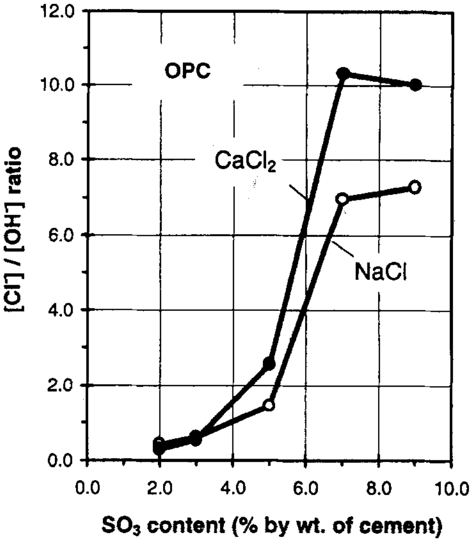

FIG. 10.
The effect of sulphate derived from $CaSO_4$ on the ratio of $[Cl^-]/[OH^-]$ of the pore solution (OPC, 1.0% Cl^- derived from NaCl and $CaCl_2$).

Another feature which can be seen from Figure 10 is that NaCl and $CaCl_2$ have different effects on the $[Cl^-]/[OH^-]$ ratio, although the overall tendency is similar. Above 3% sulphate, calcium chloride produces higher values of the $[Cl^-]/[OH^-]$ ratio than sodium chloride, and the difference becomes more profound as the sulphate content increases. This suggests that the pore solution in $CaCl_2$-containing specimens is more aggressive than in NaCl-containing specimens at the higher sulphate contents. Furthermore, the changes in the ratio are small when sulphate content is less than 3%. Similar behaviour is also observed in the slag cement specimens (Fig. 11).

In contrast to $CaSO_4$, the addition of Na_2SO_4 has little effect on the $[Cl^-]/[OH^-]$ ratio over 3 to 7% of total sulphate content. The $[Cl^-]/[OH^-]$ ratios at the higher sulphate contents are similar to that at 2% sulphate. This suggests that the extent of increase in the chloride and hydroxyl ion concentrations in the pore solution are similar.

Conclusion

The following conclusions are drawn from the present investigation:

Generally, the chloride binding capacity of cement decreases rapidly with increasing sulphate contents derived from both sodium sulphate and calcium sulphate.

At the same sulphate content, cement pastes containing calcium sulphate have a higher chloride binding capacity than those containing sodium sulphate.

Simple replacement of GGBS for OPC significantly increases the chloride binding capac-

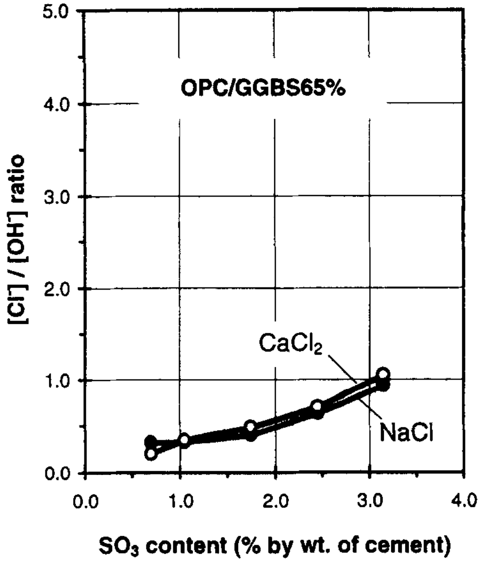

FIG. 11.

The effect of sulphate derived from $CaSO_4$ on the ratio of $[Cl^-]/[OH^-]$ of the pore solution (OPC/GGBS 65%, 1.0% Cl^- derived from NaCl and $CaCl_2$).

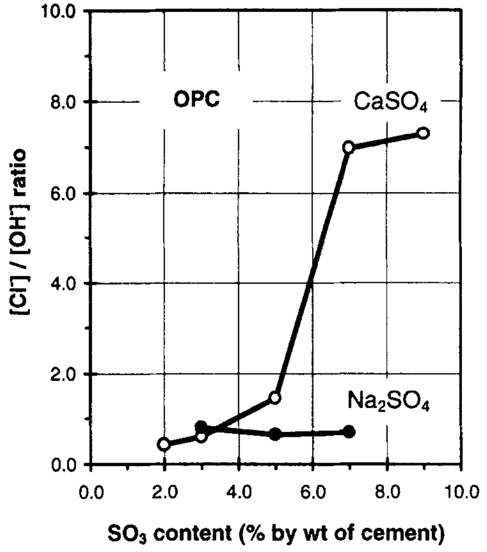

FIG. 12.

The effect of sulphate added as Na_2SO_4 and $CaSO_4$ on the ratio of $[Cl^-]/[OH^-]$ of the pore solution (OPC, 1.0% Cl^- derived from NaCl).

ity, but if the comparison is made at the same sulphate content, the chloride binding capacities of OPC and OPC/GGBS 65% are very similar.

$CaSO_4$ and Na_2SO_4 have different effects on hydroxyl ion concentrations in the pore solution. Sodium sulphate increases the alkalinity of the pore solution, whereas calcium sulphate decreases it.

Na_2SO_4 has little effect on the $[Cl^-]/[OH^-]$ ratio, whereas in $CaSO_4$-containing specimens, the ratio significantly increases with increasing sulphate content.

The maximum effective sulphate content as $CaSO_4$ was found to be 7%, above which there appears little effect on the chloride and hydroxyl ions concentration of pore solution and chloride binding.

Acknowlegement

The author is grateful to Mr. R. Yang, my collegue at China Building Materials Academy, for providing the Portland cement materials and Dr. E. Maschner for his help in writing this paper.

References

1. C.L. Page and K.W.J. Treadaway, Nature 297, 109 (1982).
2. D.A. Hausmann, Mater. Prot. 6, 19 (1967).
3. V.K. Gouda, Br. J. Corros. 5, 198 (1970).

4. W. Richartz, Zement-Kalk–Gips 22, 447 (1969).
5. G. Blunk, P. Gunkel, and H.G. Smolczyk, Proc. 8th Int. Conf. Chem. Cem. V, 5–90 (1986).
6. F.P. Glasser, K. Luke, and M.J. Angus, Cem. Concr. Res. 18, 165 (1988).
7. A.K. Suryavanshi, J.D. Scantlebury, and S.B. Lyon, Cem. Concr. Res. 25, 581 (1995).
8. P.K. Mehta, Chloride Corrosion of Steel in Concrete, STP-629, ASTM, Philadelphia, 1977, pp. 12–19.
9. J. Tritthart, Cem. Concr. Res. 19, 683 (1989).
10. H. Pollman and H.J. Kuzel, Neues. Jb. Mineral Mh. No. 193 (1988).
11. W.R. Holden, N.R. Short, and C.L. Page, Corrosion of Reinforcement in Concrete Construction, A.P. Crane (ed.), p. 143, Ellis Horwood Publishers, London, 1983.
12. S.E. Hussain, Rasheeduzzafar, and A.S. Gahtani, Cem. Concr. Res. 24, 8 (1994).
13. Jr. R.S. Barneyback and S. Diamond, Cem. Concr. Res. 11, 279 (1981).
14. Y. Xu and C. Arya, A paper presented at International Conference on Cement and Concrete Science, St.Anne's College, Oxford University, Sept. 1994.
15. C. Arya and Y. Xu, Cem. Concr. Res. 25, 279 (1995).
16. C. Arya, N.R. Buenfeld, and J.B. Newman, Cem. Concr. Res. 20, 291 (1990).
17. Rasheeduzzafar, S.S. Al-saadoun, Al-Gahtani, and F.H. Dakhil, Cem. Concr. Res. 20, 723 (1990).
18. K. Byfors, Chloride-initiated reinforcement corrosion: Chloride binding. p.6, CBI Report 1:90, 1990.