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ROLE OF PERMEABILITY IN SULPHATE ATTACK

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ABSTRACT

The role of permeability in sulphate attack was evaluated in this study. Resistance to sulphate attack was measured by determining the expansion caused in concrete specimens with exposure to 5% Na_2SO_4 solution. Concrete specimens were prepared from five binders, namely: ordinary Portland cement (OPC), high slag cement (HSC), sulphate-resistant cement (SRC), OPC with 7% silica fume (SF) and HSC with 7% SF. Concrete of grades 35 and 40 were used. The expansions of concrete samples were compared to their permeabilities to establish the role of permeability in controlling the expansion due to sulphate attack. It was found that the relative performance of concretes cannot be explained by either their permeability only or by only the chemical resistance of the binder. However, by combining the information on permeability and the chemical resistance of binder, the relative performance of concretes can be estimated. Thus, both permeability and the type of binder play an important role in sulphate attack. © *1997 Elsevier Science Ltd*

Introduction

Permeability is considered to be the key to the durability of concretes in various aggressive environments. In a critical review on sulphate attack on concrete, Mehta had concluded that for the prevention of sulphate attack "control of the permeability of concrete is more important than control of the chemistry of cement" (1). Several other studies have also concluded that permeability plays an important role in providing resistance to chloride environments (2–5). This study was carried out to study the importance of permeability in governing sulphate resistance of concretes.

Sulphate resistance of concrete can be broadly classified into two aspects: physical and chemical. The sulphate ions must first diffuse into the concrete and subsequently react with the cement portion of the concrete, leading to disintegration. The physical resistance of the concrete can be correlated to its permeability, and the chemical resistance of the concrete is dependent on the type of binder.

Sulphate attack is usually exhibited in terms of concrete expansion and reduction in strength. Expansion leads to cracking and spalling. The resistance to sulphate environments was evaluated in this study by measuring the expansion of concrete specimens exposed to 5% Na_2SO_4 solution. Expansion values were compared to the permeability values to establish the role of permeability in sulphate attack.

The sulphate resistance was determined by measuring the expansion of mortar samples. The procedure of ASTM C1012–89 was followed (6), in which expansion was measured on mortar samples of 25 × 25 × 285 mm. Expansions of concrete samples of size 75 × 75 × 285 mm were also determined. Mortar samples were of significantly smaller cross-section than the concrete samples and hence the influence of permeability is expected to be significantly less for mortar samples than concrete samples. Thus, for mortar samples the sulphate resistance is expected to be accentuated by the type of the binder, whereas in concrete the sulphate resistance is expected to be controlled by both the permeability of the concrete and the type of binder. By establishing the chemical resistance part of the sulphate resistance, the role of permeability in governing the sulphate resistance can be clearly evaluated.

The concretes studied were structural concrete of grades 35 and 40 as specified in BS 8110 (7). Concretes of grades 35 and 40 are expected to withstand "mild to moderate" conditions of exposure as per BS 8110 (7). Two grades of concrete were studied to determine the effect of strength on sulphate resistance. Furthermore, the trends observed for the expansion values and permeability values in one grade of concrete were compared to the trends observed in another grade. Thereby the consistency in the trends can be also determined.

Experimental Details

Materials. Mortar and concrete samples were prepared using ordinary Portland cement (OPC), high slag cement (HSC), sulphate-resistant cement (SRC), OPC with 7% silica fume

TABLE 1

Chemical Composition by Percentage of Various Binders and Hypothetical Compound Composition

Oxides	OPC	HSC	SRC	SF
CaO	64.3	50.3	65.6	0.2
SiO_2	22.1	28.2	22.3	95.4
Al_2O_3	5.4	10.0	3.2	0.2
Fe_2O_3	2.8	1.6	5.0	0.1
MgO	1.8	5.0	0.9	0.4
TiO_2	0.3	—	—	0.1
SO_3	2.3	3.2	2.1	0.1
K_2O	0.6	0.7	0.37	0.27
Loss on ignition	0.8	0.2	0.9	4.7
C_3S	47	—	63	—
C_2S	28	—	16	—
C_3A	9.4	—	0.1	—
C_4AF	9	—	15	—

TABLE 2

Mix Designs for All Concrete Mixes (All Values in kg/m^3)

Materials	OPC		HSC		SRC
	Grade 35	Grade 40	Grade 35	Grade 40	Grade 35
OPC	364	393	—	—	—
HSC	—	—	384	404	—
SRC	—	—	—	—	309
Coarse aggregate	1080	1090	1083	1092	1131
Sand	661	640	635	614	664
Water	183	181	176	177	175
WRA	1.72	1.85	1.67	1.90	1.45
Water/binder	0.50	0.46	0.46	0.44	0.57
28-day strength (MPa)	41.0	46.0	40.5	45.5	40.0
Materials	**OPC+SF**		**HSC+SF**		**SRC**
	Grade 35	**Grade 40**	**Grade 35**	**Grade 40**	**Grade 40**
OPC	349	377	—	—	—
HSC	—	—	430	532	—
SRC	—	—	—	—	350
Silica fume (SF)	26	28	32	40	—
Coarse aggregate	1049	1058	1010	953	1154
Sand	616	599	593	536	649
Water	202	199	197	203	173
WRA	1.77	1.87	2.16	2.70	1.62
Water/binder	0.54	0.49	0.43	0.36	0.49
28-day strength (MPa)	43.5	49.0	42.0	48.5	48.0

(SF) and HSC with 7% SF. HSC consisted of about 60% slag and 40% OPC. The chemical composition of the various binders are given in Table 1.

Concrete Mix Proportions. Concrete mixes of grades 35 and 40 were prepared, and the mix proportions are given in Table 2. The coarse aggregate was a crushed granite with maximum aggregate size of 20 mm. The fine aggregate was a river sand. A water-reducing agent (WRA) was added to all mixes at the dosage recommended by the manufacturer, which was 400 mL per 100 kg of binder. The WRA was a modified sodium salt lignosulphonic acid. It can be seen from Table 2 that concretes prepared from all the five binders achieved similar 28-day strengths for their respective grade.

Experimental Set-up for Evaluation of Resistance to Sulphate Environments. Expansion due to exposure to sulphate environments were measured on three prismatic concrete specimens measuring 75 × 75 × 285 mm, and the average values have been reported. The prisms were cured in saturated lime water for 3 days and were subsequently stored in standard laboratory conditions at 23 ± 2°C and 50 ± 5% RH. At 28 days, the samples were immersed in 5% sodium sulphate solution maintained at pH 7. On immersion of the concrete samples, the pH of the solution increases due to leaching of $Ca(OH)_2$ from concrete samples. To counteract the increase in pH, diluted sulphuric acid was added to maintain the solution at the desired pH of 7.5–8 (8). This set-up is fully automated by a computer and the procedure of Cao *et al.* (9) was followed.

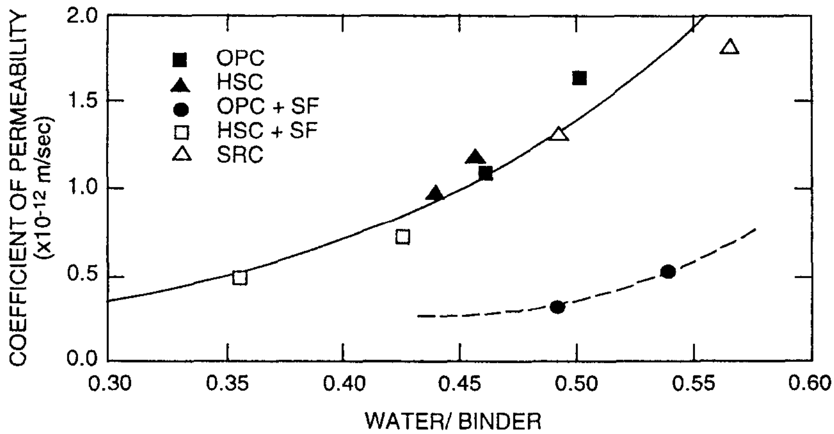

FIG. 1.
Variation in coefficient of permeability with water/binder ratio.

Expansions of mortar bars exposed to sulphate environments were determined by following the procedure outlined in ASTM C1012–89 (6).

<u>Experimental Set-up for the Evaluation of Coefficient of Permeability</u>. The specimens for the measurement of coefficient of water permeability were subjected to similar curing as the concrete specimens exposed to sulphate solution. Coefficient of permeability was measured between the age of three and four weeks. The details of the experimental procedure has been given elsewhere (10).

Results and Discussion

<u>Expansion of Mortars Due to Sulphate Attack (ASTM C1012–89)</u>. The cross-sections of mortar samples were significantly smaller than the concrete samples and it can be assumed that permeability plays a significantly less important role in mortar samples. Thus, the sulphate resistance of mortars can be expected to be derived mainly from the "chemical resistance" of the binder, whereas in concrete samples the sulphate resistance is due to both physical (permeability) and chemical (binder) resistance.

TABLE 3

Water to Binder Ratio of Mortar and Concrete Mixes

Binder	Mortar		Concrete	
	W/B ratio	Number of days to achieve 20 MPa	W/B ratio of grade 35	W/B ratio of grade 40
OPC	0.485	7	0.502	0.462
HSC	0.465	20	0.457	0.439
SRC	0.473	9	0.566	0.493
OPC+SF	0.510	7	0.539	0.492
HSC+SF	0.483	17	0.425	0.355

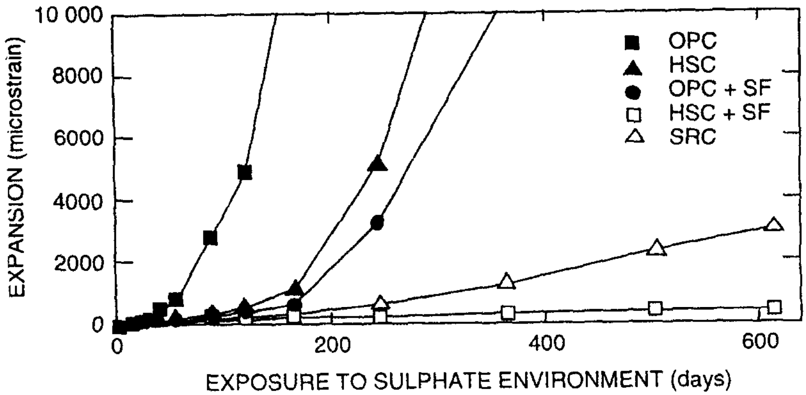

FIG. 2.
Expansion in mortar bars after immersion in 5% Na_2SO_4.

Figure 1 shows the variation of coefficient of permeability with water/binder ratio of various concretes. For all binders except the OPC+SF, the variation of coefficient of permeability with water/binder ratio falls on the same plot. For similar water/binder ratios, the coefficients of permeability of the OPC+SF concretes are significantly less than the concrete mixes prepared from other binders. Table 3 shows the water/binder ratios of the various mortars and concrete mixes. The water/binder ratio of various mortar mixes are similar and thus it can be expected that the OPC+SF mortar will have significantly lower permeability than other mortars. In the ASTM C1012 test, all mortar samples were immersed at the same strength of 20 MPa and the assumption was that the mortar would have similar permeability and thus the expansion values on exposure to sulphate solution would reflect the "chemical resistance" of the binder. This assumption appears to be correct except for the OPC+SF binder, as the mortar prepared from this binder is expected to have significantly lower permeability. Thus in this study the ranking of binder OPC+SF based on the expansion values of mortars was ignored.

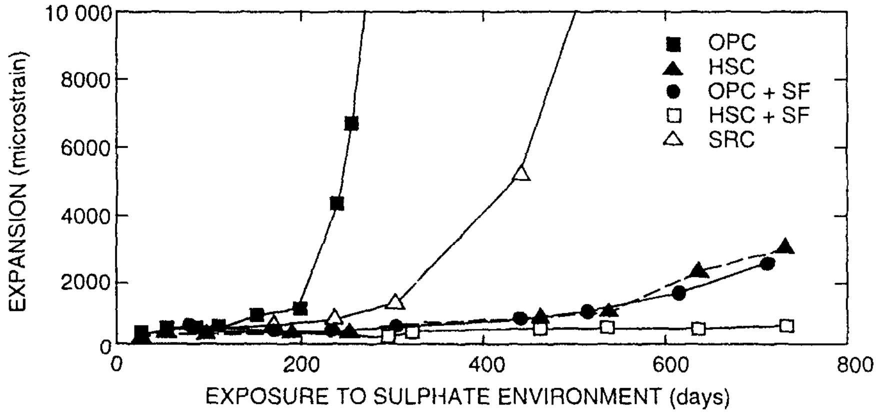

FIG. 3.
Expansion in Grade 35 concrete prisms on immersion in 5% Na_2SO_4. Solution maintained at pH 7.

The mortars prepared from the remaining four binders are expected to have similar permeability, and hence the four binders under study were ranked for their chemical resistance to sulphate attack based on the expansion of mortar samples. Figure 2 shows the expansion of mortar bars prepared from various binders and exposed to 5% Na_2SO_4 solution. Some of the expansion values of OPC, HSC and OPC+SF mortars were higher than 10,000 microstrains, however the expansion values in the plot have been restricted to 10,000 microstrains to clearly show the expansions observed in SRC and HSC+SF mortars. It is clearly evident from the results that HSC+SF is the best binder. SRC has marginally higher expansion than HSC+SF and has significantly less expansion than HSC. OPC has maximum expansion and is significantly higher than the expansion observed for HSC. Thus, based on mortar expansion data, it can be concluded that HSC+SF is the best binder and is marginally better than SRC. Both HSC+SF and SRC are significantly better than HSC, and HSC is significantly better than OPC.

Expansion in Concretes Due to Sulphate Attack. Figures 3 and 4 show the expansion obtained in prismatic samples prepared from concretes of grades 35 and 40 after immersion in 5% Na_2SO_4. In both plots, the expansion values have been restricted to 4,000 and 10,000 microstrains to clearly show the low expansion values observed in other concrete samples. It can be seen that the expansion observed in HSC+SF concrete prisms is minimum. Expansions observed in HSC and OPC+SF concrete prisms are similar and are marginally higher than the expansion observed in HSC+SF concrete prisms. SRC concrete prisms had significantly higher expansion than those observed in HSC or OPC+SF concrete prisms. Maximum expansion was observed for OPC concrete prisms and was significantly higher than that observed for SRC concrete prisms.

Figure 4 shows the expansion values of concrete prisms of grade 40. It can be seen from the figure that the trend remains the same for concretes of both grades 35 and 40.

Water Permeability Values. Figure 5 shows the coefficient of permeability of concretes of grades 35 and 40 (w/c ratios are shown in Table 2). It is clearly evident from the figure that

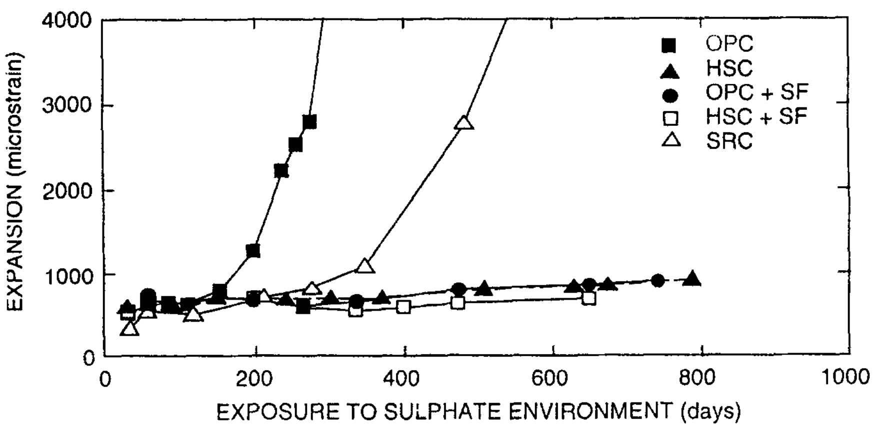

FIG. 4.

Expansion in Grade 40 concrete prisms on immersion in 5% Na_2SO_4. Solution maintained at pH 7.

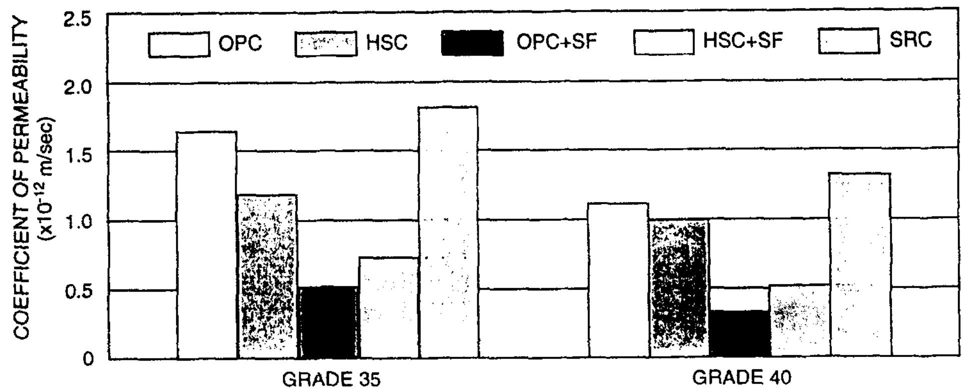

FIG. 5.
Coefficient of permeability of concretes of Grades 35 and 40.

permeability of the OPC+SF concretes is the lowest, followed by HSC+SF concretes. The permeability of HSC concretes is higher than those of HSC+SF concretes. OPC concretes have higher permeability than HSC concretes, and SRC concretes have the maximum permeability.

Role of Permeability in Sulphate Resistance of Concretes. The expansion observed in SRC mortars is significantly lower than both HSC and OPC+SF mortars. Thus, SRC concretes are expected to have significantly lower expansion than HSC and OPC+SF concretes, but HSC and OPC+SF concretes were found to have significantly lower expansion than SRC concretes. The lower expansion of HSC and OPC+SF concretes can be explained by the permeability data. Significantly lower permeability of HSC and OPC+SF concretes resulted in their lower expansion. Expansion observed in concrete prepared from HSC+SF is minimum as the permeability of the concrete is very low and the expansion observed in the mortar is minimum.

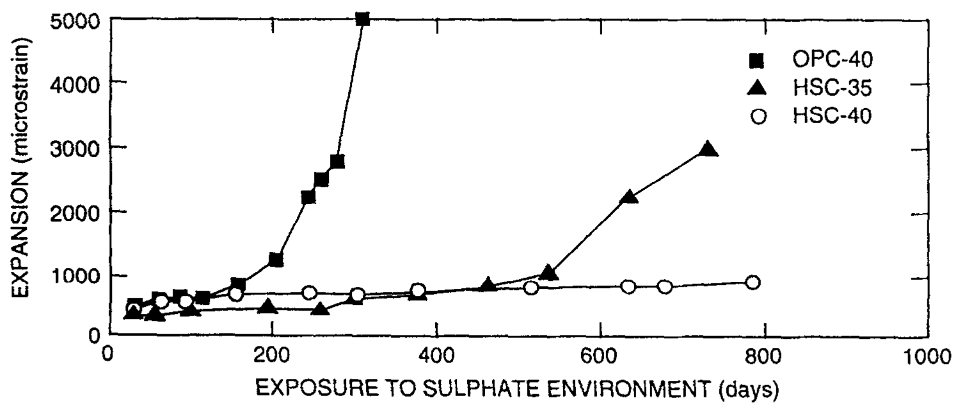

FIG. 6.
Comparison of expansions in concrete samples with similar permeability values.

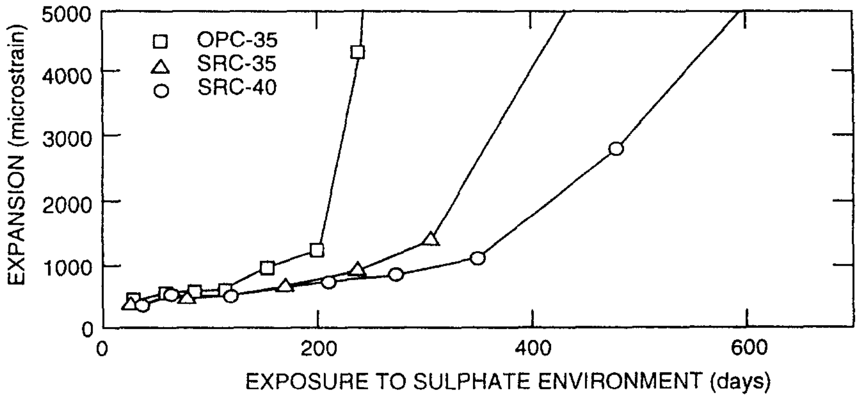

FIG. 7.
Comparison of expansions in concrete samples with similar permeability values.

Lower permeability values of HSC, OPC+SF and HSC+SF concretes resulted in lower expansion than the OPC and SRC concretes. However, the expansion values of SRC concretes are lower than OPC concretes in spite of the lower permeability values of OPC concretes. The superior chemical resistance of SRC offsets its lower permeability, resulting in better performance in the concrete.

Role of Binder in Sulphate Resistance of Concretes. To examine the role of binder in sulphate attack, expansion values of concrete samples with similar permeability were studied. Figure 6 shows the expansion values of three concrete mixes with similar permeability of about 1×10^{-12} m/s. It can be seen that HSC concretes showed much lower and delayed expansion than the OPC concrete. Thus, high slag binders provide significantly better chemical resistance to sulphate attack than OPC.

Figure 7 also compares expansion due to sulphate attack of concretes with similar permeability of $1.3–1.8 \times 10^{-12}$ m/s. Grade 35 OPC concrete has permeability values between the two grades of SRC concretes, it however showed the greatest expansion on exposure to sulphate solution. The improved resistance of SRC concrete to sulphate attack is largely

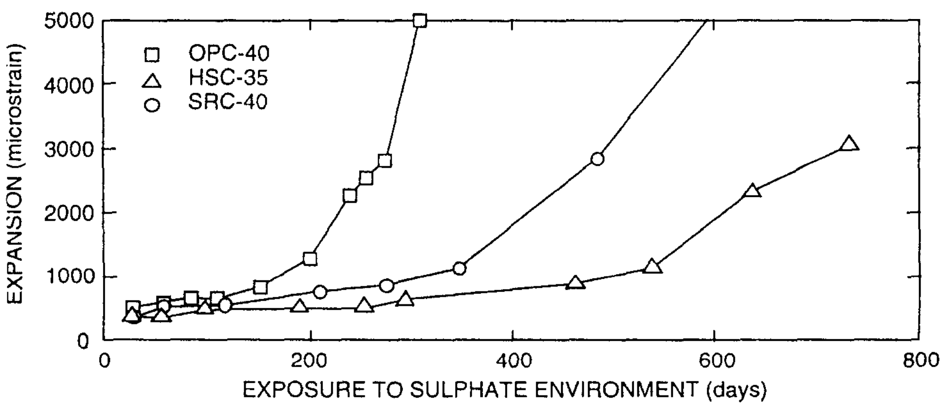

FIG. 8.
Comparison of expansions in concrete samples with similar permeability values.

derived from its chemical resistance. The effect is clearly demonstrated in the relative expansion of SRC mortar compared with the OPC mortar.

Expansion values of grade 40 OPC and SRC concretes and grade 35 HSC concretes are shown in Figure 8. These three concretes have similar permeabilities in the range of 1.1–1.3 $\times 10^{-12}$ m/s and thus the chemical resistance of the binder should be the factor which can distinguish their sulphate resistance. Both SRC and HSC binders have superior chemical resistance than OPC. As expected, grade 40 SRC concrete and grade 35 HSC concrete have better sulphate resistance than grade 40 OPC concrete. However, the superior chemical resistance of SRC compared to HSC shown in mortar results did not bring about the same relative better performance of grade 40 SRC concrete. The present study is unable to explain this anomaly and more studies need to be carried out to explain the superior resistance of grade 35 HSC concrete compared to grade 40 SRC concrete.

It can be concluded that expansion of concrete in sulphate solution is controlled by both the permeability of the concrete and the chemical resistance of the binder. The relative expansion of concretes cannot be explained by their relative permeabilities nor by the chemical resistance of the binders alone. However, by combining the information on permeability and on the chemical resistance of binders, the relative expansion of concretes can be explained.

Effect of pH of Sulphate Solution. It should be noted that concrete samples were immersed in 5% Na_2SO_4 solution maintained at pH 7, whereas the mortar samples were immersed in an uncontrolled pH 5% Na_2SO_4 solution. Concrete samples were immersed in a controlled pH 7 sulphate solution to simulate a neutral sulphate environment in which the sulphate ions are continuously replenished. Most concretes in the field are subjected to such sulphate environments (1,8). On the other hand, mortar samples were immersed in an uncontrolled pH solution to follow the procedure of a popular test (ASTM C1012) to measure sulphate resistance of binders which is followed by cement users and researchers worldwide (6). The trend in the expansion values of various binders in an uncontrolled pH sulphate solution could be different to the trend in a controlled pH sulphate solution, as it is known that pH of the sulphate solution effects the deterioration mechanisms of concrete (1,8,9,11).

On immersion of mortar specimens in 5% Na_2SO_4 solution, as a result of dissolution of $Ca(OH)_2$ within a few hours the pH increases from about 7 to 12–12.5. Thus, the mortar specimens for most of the time were immersed in 5% Na_2SO_4 of pH 12–12.5, whereas the concrete samples were immersed in pH solution of 7.5–8.0. It has been established that at a pH of 12–12.5 only ettringite formation can take place and is responsible for the expansion (1). On the other hand, in the pH range of 8–11.5, gypsum formation and C-S-H decomposition are responsible for the softening of the matrix which leads to the loss of strength and expansion (1,11). At a pH lower than 8, the calcium leaching and decalcification of C-S-H is the main degradation mechanism (12).

Cao *et al.* (9) have carried out comparison of expansion of mortar bars after immersion in uncontrolled pH solution and controlled sulphate solution with pH of 3 and 7. Mortar bars prepared from various portland cements with different amounts of C_3A and C_3S were studied. In uncontrolled pH solution, the lowest expansion was observed for portland cement with low C_3A and low C_3S, followed by low C_3A and high C_3S, and portland cement with high C_3A and high C_3S had the highest expansion. On the other hand, in controlled pH solution of pH 3 and pH 7, high C_3A and high C_3S had maximum expansion and all other portland cements with low C_3A (both high and low C_3S) had lower expansion. In the present study, SRC (low C_3A of 0.1% and high C_3S of 63%) mortar had lower expansion than OPC (high C_3A of 9.4% and high C_3S of 47%) mortar in uncontrolled pH solution. Based on the study of Cao *et al.* it can be inferred that SRC mortars will have lower expansion than OPC mortars in controlled pH 7 sulphate solution also. Thus, SRC mortar is expected to have lower expansion than OPC mortar in both controlled and uncontrolled pH sulphate solution.

For 60% slag blended cement, higher expansion was observed by Cao *et al.* (9) for mortar samples immersed in controlled pH sulphate solution than those immersed in uncontrolled pH solution. It was also found that portland cement with low C_3A and high C_3S had similar expansion in controlled and in uncontrolled pH sulphate solution (9). The SRC used in this study has a low C_3A content of 0.1% and a high C_3S content of 63%. In the present study, SRC mortar was found to have lower expansion after immersion in uncontrolled pH sulphate solution than those observed for HSC mortar. Thus, based on the studies carried out by Cao *et al.* it can be concluded that the SRC mortar will have lower expansion than HSC mortar in controlled pH 7 sulphate solution.

Cao *et al.* (9) also found that for binder OPC+SF the expansion is insensitive to the pH of the sulphate solution. Thus, OPC+SF mortar is expected to have similar expansion after immersion in both uncontrolled and controlled pH sulphate solution.

Based on the studies carried out by Cao *et al.* it can be concluded that the ranking of binders in this study, based on the expansion values of mortars in uncontrolled pH sulphate solution, is expected to remain the same as the ranking obtained from the expansion values of mortars immersed in controlled pH 7 sulphate solution.

In this study, all conclusions were drawn by the comparison of expansion of mortar samples immersed in uncontrolled pH sulphate solution and expansion of concrete samples immersed in controlled pH sulphate solution. Ideally the comparison should be made between mortar and concrete samples after both are immersed in either uncontrolled or controlled pH sulphate solution. However, based on the study by Cao *et al.* (9) it can be concluded that the ranking of binders observed in the expansion values of mortars immersed in uncontrolled pH solution will remain the same as the samples immersed in controlled pH solution. This study validates the conclusions drawn earlier by the comparison of expansion values of mortar and concrete (9). In particular, the expansion values of mortars prepared from SRC is expected to be lower than those prepared from HSC and OPC+SF after immersion in both controlled and uncontrolled pH sulphate solution. Thus, only the lower permeabilities of HSC and OPC+SF concretes are responsible for their significantly lower expansion. Furthermore, lower expansion observed for SRC concrete in comparison to OPC concrete can be attributed to the significantly higher resistance to sulphate attack of SRC binder, as exhibited by the reduced expansion of mortar prepared from SRC in comparison to mortar containing OPC.

Conclusions

Trends observed in the expansion values of concrete samples were different to the trends observed in the expansion values of mortar samples. The difference in the two trends can be explained partly by their permeability values and partly by the chemical resistance of the binders. Thus, both the permeability and the type of binder (its chemical resistance) were found to play an important role in governing the sulphate resistance of the concretes. The relative expansion of concretes cannot be explained by either their permeability only or by only the chemical resistance of the binder. By combining the information on permeability and on the chemical resistance of binders, the relative expansion of concretes can be accounted for.

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