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EFFECT OF SULFATE AND CARBON DIOXIDE ON CHLORIDE DIFFUSIVITY

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ABSTRACT

The effects of sulfate and CO_2 on chloride penetration fronts and diffusivities were determined at 60 months exposure for ordinary Portland cement concrete and concrete incorporating the partial replacement of the cement with slag. It was found that sulfate and CO_2 decrease the chloride penetration and diffusivity in the ordinary Portland cement concrete whereas the opposite behavior is observed for the slag concrete. However, chloride ingress is always considerably less in the slag concrete.

Introduction

Despite obvious practical implications, there is a paucity of information available on the synergistic effects of more than one aggressive agent on the ingress of ions into concrete. Feldman and co-workers (1) reported that the concurrent presence of sulfate and chloride ions in solution decreased the chloride ion ingress rate into ordinary Portland cement concrete and concrete incorporating the partial replacement of the cement with slag and silica fume. However, the experimental data was limited to 12 months, and the chloride and chloride-sulfate baths were not maintained at the same temperature. Further, the presence of CO_2 in solution was not considered. It was recently reported that CO_2 in solution increases ionic ingress (2). Therefore, this paper reports on the synergistic effects over 60 months due to the combined actions of chloride, sulfate and CO_2 on the ingress of chloride ion into ordinary Portland cement concrete and concrete incorporating the partial replacement of the cement with slag.

Experimental

- Binders: Portland cement CSA types 10 and 50, silica fume and ground granulated blast furnace slag were used for the two concretes. The oxide analysis is given in Table 1.
- Aggregates: The fine aggregate was an unblended quartz/feldspar sand. A crushed pelitic pemicrite limestone of 19 *mm* maximum size was the coarse aggregate. All aggregate was previously tested for alkali reactivity, freeze-thaw durability and defects detectable by petrographic examination. The results were satisfactory.

TABLE 1

Oxide Analysis (%) of the Cements, Slag, and Silica Fume

	Type 10 Cement	Type 50 Cement	Slag	Silica Fume
SiO_2	19.43	20.71	35.30	95.17
Al_2O_3	4.18	3.77	10.62	0.21
Fe_2O_3	3.20	4.36	0.58	0.13
CaO	61.21	62.46	36.94	0.23
MgO	4.09	3.35	13.32	0.15
Na_2O	0.45	0.35	—	0.10
K_2O	0.89	0.87	—	0.27
C	—	—	—	1.56
L-O-I*	1.53	0.88	1.16	2.30
SO_3	3.93	2.46	1.41	0.12
Free Lime	1.15	0.70	—	—

*L-O-I: loss on ignition.

- Concrete: The concrete mix designs are summarized in Table 2. Beams of dimension 75 *mm* × 75 *mm* × 280 *mm* were cast and cured at 100% *rh* for the time indicated in Table 2. Subsequently, the beams were waxed on five sides for unidirectional chloride ingress. Chloride penetrated the concrete through the unwaxed 75 *mm* × 280 *mm* side.
- Solution Baths: Specimens were exposed to three solutions maintained at 25°C. The compositions are summarized in Table 3.
- Chloride Front: After certain periods of exposure to the baths, the beams were removed. The chloride contents were gravimetrically determined (ASTM C114) at various penetration depths using 1-2 *mm* slices dry-cut from the beam. A value of 0.3% chloride was used to

TABLE 2

Concrete Mix Designs ($kg\ m^{-3}$)

	Concrete 1	Concrete 2
Type 10 Cement	369.96	—
Type 50 Cement	—	81.38
Slag	—	277.43
Silica Fume	—	11.15
Water	155.40	155.40
Coarse Aggregate	1117.27	1107.01
Fine Aggregate	744.60	737.95
Air Agent (Darex)	0.23	0.43
Superplasticizer (40% Disal)	4.32	2.16
Slump (*mm*)	1.31	156
Air (%)	5.9	5.3
Curing Time (*days*)	14	28

TABLE 3

Composition of Baths

	Na_2SO_4 ($g\ l^{-1}$)	NaCl ($g\ l^{-2}$)	CO_2
Bath 1	22.19	4.95	No
Bath 2	22.19	4.95	Yes
Bath 3	—	4.95	No

determine the position of the chloride front. The concentration is considered a practical limit for maintaining passivity of steel in concrete.

Results and Discussion

The data for the chloride penetration front of 0.3% chloride are presented in Table 4. Comparing concretes 1 and 2, there is a marked improvement for resisting chloride penetration with concrete 2 regardless of the bath composition. The relatively high resistance of the concrete 2 (i.e. partial replacement of the cement with slag) to chloride ion ingress can be partly explained by its expected lower median pore diameter and porosity values. Furthermore, concrete 1 will have a higher $Ca(OH)_2$ content in the hydrated structure (3). Therefore, chloride ion diffusion may be increased in concrete 1 due to enhanced $Ca(OH)_2$ solubility, $Ca(OH)_2$-chloride complex formation, or a $Ca(OH)_2$-CSH interface effect (1, 3). For concrete 1, the penetration front of chloride ions into the concrete is reduced when sulfate is present in the bath, and is reduced further when CO_2 is bubbled through the bath. For concrete 2, the opposite

TABLE 4

Chloride Penetration Front (*cm*)

	Bath 1		Bath 2		Bath 3	
Time (*Months*)	Concrete 1	Concrete 2	Concrete 1	Concrete 2	Concrete 1	Concrete 2
3	0.18	0.34	0.65	0.29	1.50	0.32
6	0.81	0.26	0.69	0.33	1.75	0.18
9	—	0.37	0.84	0.38	1.67	0.19
12	1.02	0.42	0.79	0.28	1.42	0.15
16	1.15	0.65	1.06	0.47	1.62	0.17
20	0.95	0.44	1.08	0.54	1.32	0.15
24	1.10	0.40	1.70	0.58	1.62	0.15
28	1.45	0.50	1.98	0.77	1.94	0.11
34	1.53	0.63	1.36	0.55	1.98	0.21
46	2.05	0.54	1.67	0.66	2.10	0.42
60	2.03	0.64	1.76	0.70	2.30	0.52

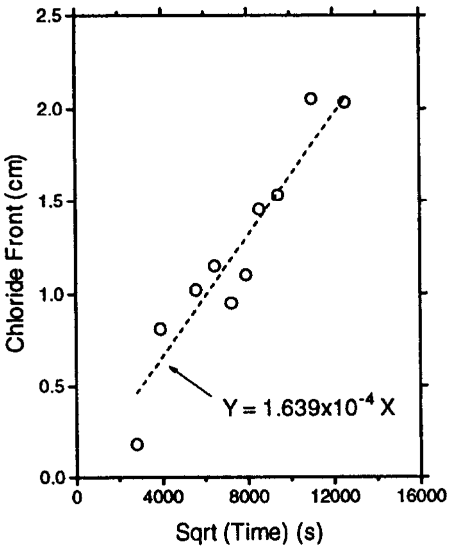

FIG. 1.
Chloride penetration front versus the square root of time for concrete 1 exposed to bath 1.

is observed. That is, the chloride penetration front is increased when sulfate ion is present, and the front extends further into the concrete when CO_2 is present in the bath. The latter observation confirms the earlier work in this laboratory (4, 5).

The dominant mechanism for chloride ingress into these saturated specimens is diffusion which leads to an inward spreading front of the chloride. The situation can be represented as a semi-infinite block of concrete whose surface is exposed to the bath at fixed concentration C_o starting at time zero. The simple non-steady state diffusion equation is then (6),

$$C(x,t) = C_0 \mathrm{erfc}\left(\frac{x}{\sqrt{4Dt}}\right) \tag{1}$$

where, C(x,t) is the concentration at a depth x within the concrete at a time t, erfc is the statistical complimentary error function, and D is the diffusivity. It should be noted that the chloride diffusivities reported in this paper have been calculated using the acid soluble chloride. Strictly, it is the free chloride concentration gradient which is the thermodynamic driving force for diffusion. However, recently Mangat and co-workers (7) determined that chloride diffusivities based on total acid soluble chloride and the free chloride were approximately equal. It is expected from the form of the solution for Eq. [1] that the 0.3% chloride front increases progressively in proportion to the square root of the time. Therefore, it is reasonable to fit the chloride front data to a linear function of the form,

$$x(t) = A\sqrt{t} \tag{2}$$

where, x(t) is the chloride front, t is the time, and A is a constant. The constant A is related to the chloride diffusivity by,

$$A = 2 \cdot \mathrm{erfc}^{-1}\left(\frac{c(x,t)}{C_o}\right) \cdot \sqrt{D} \tag{3}$$

The chloride penetration front data in Table 4 have been plotted against the square root of time as indicated in Eq. [2]. Figure 1 is an example plot for concrete 1 exposed to bath 1. It can be seen in Figure 1 that the data are well represented by the indicated least squares line. In all other cases, there are similar observations. The results have been summarized in Table 5 together with the diffusivity calculated from Eq. [3].

As expected, the chloride diffusivities reflect the same trends as those of the raw data for the chloride fronts. That is, concrete 2 incorporating slag is more impermeable to chloride ingress than the concrete 1 control irrespective of the composition of the baths. Further, the ingress of chloride is accelerated when sulfate is present for concrete 2 but the opposite behavior is observed in concrete 1. Lastly, when CO_2 is bubbled into the solution, the chloride diffusivity for concrete 2 is increased while for concrete 1 there is only a minor effect because CO_2 coarsens the concrete pore structure when slag is present (4, 5, 8, 9).

Conclusions

- Concrete incorporating partial replacement of Portland cement by slag is markedly better at preventing the ingress of chloride than Portland cement concrete.
- The synergistic effect of sulfate ion on chloride ingress is different in Portland cement concrete and concrete incorporating partial replacement of Portland cement by slag. In the former, the presence of sulfate ions in the solution bath decreased chloride penetration and diffusivity. But, in the latter, sulfate ions in the solution bath increased chloride penetration and diffusivity.
- When CO_2 is bubbled through the sulfate-chloride bath, the chloride penetration is decreased for Portland cement concrete but increased for concrete incorporating partial replacement of Portland cement by slag. For Portland cement concrete, there is a minor effect on the chloride diffusivity when CO_2 is present. But CO_2 in the sulfate-chloride bath appreciably increases the chloride diffusivity for concrete incorporating partial replacement of Portland cement by slag.

TABLE 5

Linear Regression Constants and Chloride Diffusivities

	Bath 1		Bath 2		Bath3	
Constant	Concrete 1	Concrete 2	Concrete 1	Concrete 2	Concrete 1	Concrete2
A ($cm\ s^{-05}$)	1.639×10^{-4}	6.028×10^{-5}	1.643×10^{-4}	6.620×10^{-5}	2.172×10^{-4}	3.068×10^{-5}
D ($cm^2\ s^{-1}$)	2.85×10^{-7}	3.85×10^{-8}	2.86×10^{-7}	4.65×10^{-8}	5.00×10^{-7}	9.99×10^{-9}

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