CHLORIDE DIFFUSIVITY IN HIGH STRENGTH CONCRETE AT DIFFERENT AGES

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ABSTRACT

The chloride diffusivity in high strength concrete blended with and without silica fume was determined at different ages by using a rapid method recently developed by the authors of this paper. The quantitative relations between diffusivity and curing age were obtained and expressed by regression equation $D = a \cdot t^{-b}$. The chloride penetration was evaluated and discussed by applying Fick's law taking diffusivity as the age dependent variable.

Key words: chloride, concrete, curing age, diffusivity, high strength concrete, silica fume.

1. INTRODUCTION

The properties of concrete greatly depend on its curing history. The changes in properties with age should be taken into account when predicting the service life of a structure. One of the important properties regarding the durability of a structure is chloride diffusivity. The conventional methods for determining chloride diffusivity are rather time-consuming and can only be used for evaluating the diffusivity in relatively 'old' concrete, generally at an age of more than 90 days. In practice, only few engineering structures can wait such a long time before being put into service. It is rather difficult, however, to employ the conventional methods when evaluating the diffusivity in concrete at an early age. Recently /1/, we modified Fick's law and designed a new method for rapid determination of chloride diffusivity by applying an electric field in order to make it possible to evaluate the chloride diffusivity in high strength concrete at different ages. The purpose of the work reported here is to find the quantitative influence of curing age on the chloride diffusivity in high strength concrete, which is of great importance for the prediction of chloride penetration in concrete regarding the service life of reinforced concrete structures.

2. EXPERIMENTAL

The cement used in this study was Swedish Slite OPC and the silica fume was Norwegian Elkem Microsilica. The mix proportions and 28 day strengths of concrete are listed in Table 1. Mighty 100 superplasticizer was used to provide sufficient workability.

Table 1—Mix Proportions of Concrete

Mix No. ---→	NSC	HSCSF0	HSCSF6	HSCSF12	HSCSF24
OPC (Slite)	270	522	492.5	466	421
CSF (Norway)	0	0	29.5	56	101
Sand (<4 mm)	769	0	0	0	0
Sand (<8 mm)	0	700	700	700	700
Gravel (8~12 mm)	1153	1050	1050	1050	1050
Water	189	165	165	165	165
Superplasticizer	0	5.22	6.26	6.68	7.20
CSF/OPC	0	0	6%	12%	24%
water/binder	0.7	0.32	0.32	0.32	0.32
admixture/binder	0	1%	1.2%	1.28%	1.38%
Compr. strength (at 28 days, MPa)	37.8	83.0	94.6	94.7	97.8

The materials were mixed in the same way as /2/, and the fresh concrete was cast into 150×150×150 mm cubic moulds. The top surfaces were covered with plastic film to prevent water from evaporating. The concrete cubes were cured at room temperature for one day before being demoulded, then sealed in plastic bags and stored in the laboratory for the specified age.

At the specified age, the compressive strength of different cubes was tested, and two specimens of thickness 50 mm and cross-section about 70×70 mm were cut out from an intact cube for the chloride penetration test. The positions of the cut specimens are indicated in Fig. 1.

The newly developed method for rapid determination of chloride diffusivity involves applying a D.C. potential across the specimen for a certain time (from 8 hours for young specimens up to a week for old dense specimens in this study), then measuring the chloride penetration depth by using the colorimetric method. The experimental arrangement is shown in Fig. 2.

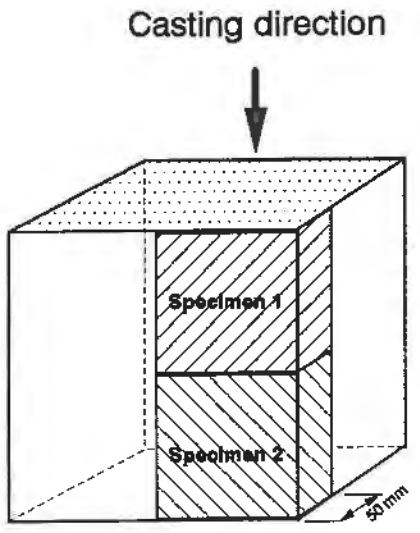

Fig. 1.—Positions of the cut specimens

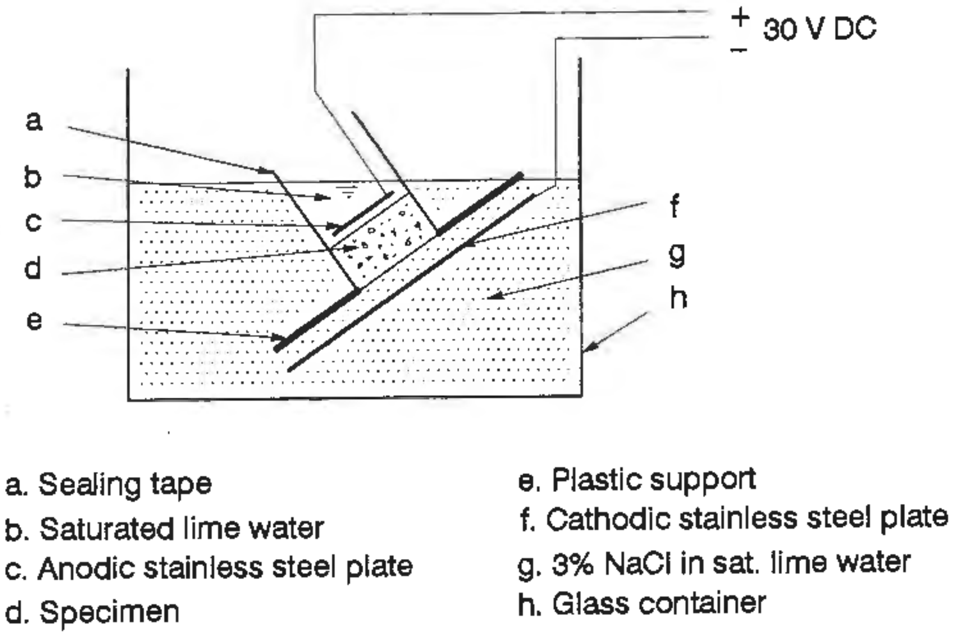

Fig. 2.—Experimental arrangement for rapid penetration of chloride.

The details of the experimental procedures for rapid determination of the chloride diffusivity were previously reported in /1/. In this study, if not otherwise stated, the intact surface of the specimen was exposed to chloride solution. The specimens of early age (1 and 3 days) were vacuum saturated with lime water (i.e. immersed in lime water and vacuum-pumped) for 8 hours and those of older age (>7 days) for 24 hours. Since concrete has less capillary pore volume than paste and mortar, the concentration of NaCl solution was increased to 6% instead of 3% used in /1/, so that the penetration depth could be more easily observed. In order to shorten the testing time, the voltage for some specimens was increased to 40 V D.C. In this case, the following equation was used to calculate the effective diffusion coefficient:

$$D = \frac{RTL}{zFU} \cdot \frac{x_d - \alpha x_d^{\beta}}{3.6 \times 10^9 \cdot t} \qquad (1)$$

where D: effective diffusion coefficient, m^2/s;
R: gas constant, $R = 8.314$ J/(K·mol);
T: solution temperature, K;
L: thickness of the specimen, mm;
z: absolute value of ion valency, for chloride, $z = 1$;
F: Faraday constant, $F = 9.648 \times 10^4$ J/(V·mol);
U: absolute value of potential, V;
x_d: chloride penetration depth; mm;
t: testing time, hr;
α, β: constants from a numerical solution of Fick's second law, for $T = 298$ K (25 °C), $L = 50$ mm, when $U = 30$ V, $\alpha = 1.061$ and $\beta = 0.589$, and when $U = 40$ V, $\alpha = 1.010$ and $\beta = 0.570$.

3. RESULTS AND DISCUSSION

The strength development of high strength concrete at different ages is shown in Fig. 3. At the early age, the strength of high strength concrete blended with a great amount of silica fume (e.g. HSCSF24) increases slowly, but after 7 days, it increases quickly and becomes higher than that of concrete without silica fume (e.g. HSCSF0). This corresponds with the conclusion from /3/. However, replacing OPC with silica fume in concrete could only increase the strength by about 15% ~ 20%.

The experimental results of chloride diffusivity in various specimens are listed in Table 2, and their average values are shown in Fig. 4. In the experiment, the cut surfaces of the specimens of HSCSF24 at an age of 90 and 180 days were exposed to chloride solution, as no visible penetration depth was observed from the test with intact surface exposing.

It can be seen from the results that the chloride diffusivity in high strength concrete is very low compared with that in normal strength concrete, even at very early age, but the decreasing tendency of diffusivity in high strength concrete without silica fume seams similar to that in normal concrete. The influence of silica fume on diffusivity becomes noticeable after only 3 days. The greater the amount of silica fume the concrete contains, the lower the diffusivity becomes. At an age of 180 days, the diffusivity in concrete blended with silica fume is 1 to 2 magnitude orders lower than that without silica fume.

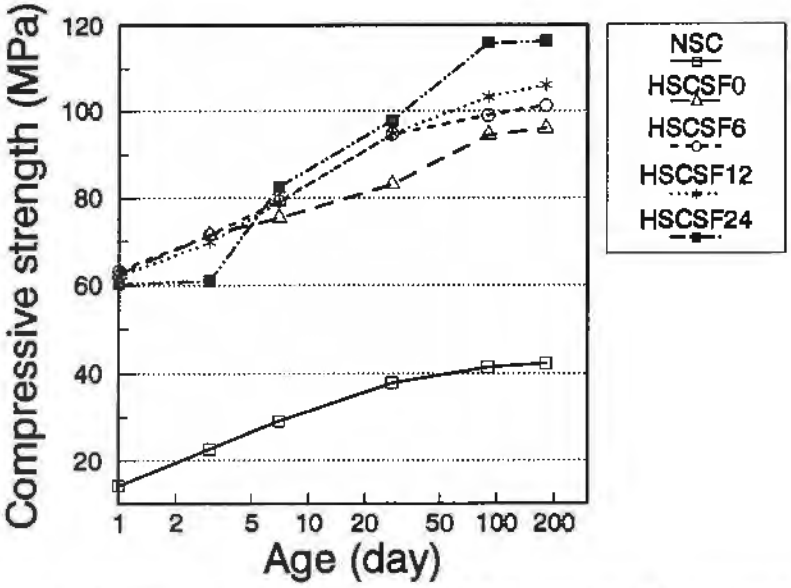

Fig. 3.—Strength development of high strength concretes.

Table 2—Chloride Diffusivity in Various Concretes

Age (day)	Specimen—> No.	NSC	HSCSF0	HSCSF6	HSCSF12	HSCSF24
			Diffusivity, x10^{-12} m^2/s			
1	1	46.9	7.41	9.09	6.83	8.24
1	2	44.3	7.37	7.39	6.50	7.67
3	1	27.9	5.97	4.69	3.32	1.01
3	2	26.0	6.47	5.58	3.76	1.17
7	1	20.5	4.96	2.64	1.55	0.56
7	2	21.7	4.89	2.94	1.65	0.39
28	1	13.9	3.33	1.05	0.48	0.26
28	2	15.1	3.10	0.76	0.39	0.11
90	1	15.2	1.84	0.53	0.31	0.08*
90	2	15.4	1.74	0.44	0.36	0.12*
180	1	n.d.	1.80	0.36	0.24	n.d.
180	2	n.d.	1.67	0.40	0.20	0.04*

n.d.—not determined;
*—cut surface exposed.

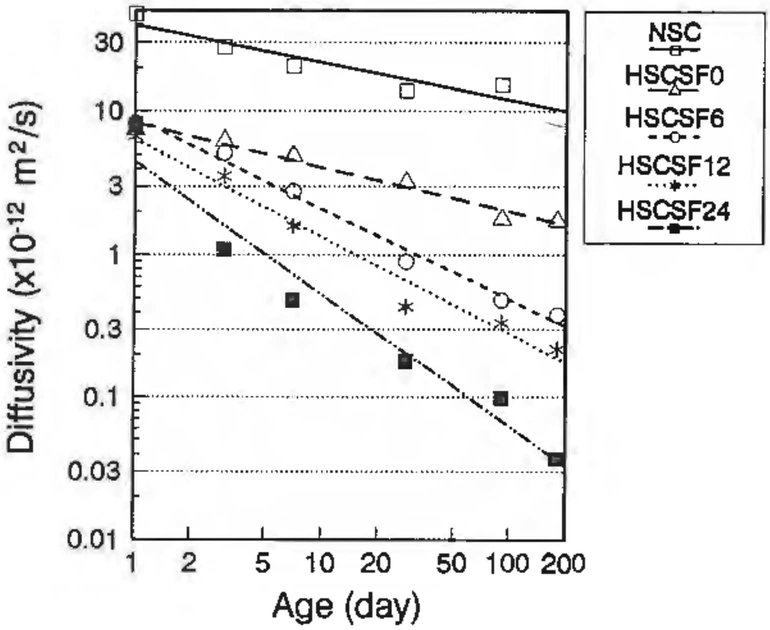

Fig. 4.—Relations between diffusivity and curing age.

There seems to be no apparent quantitative relationship between the strength development and the diffusivity decrement.

Analyzing the data in Table 2, we can obtain the following regression equation to express the relation between diffusivity and curing age:

$$D = a \cdot t^{-b} \tag{2}$$

where D: effective diffusion coefficient, m^2/s;
t: curing age, day;
a, b: regressive constants.

The values of a and b for various concretes are listed in Table 3. It is apparent that the concrete blended with silica fume reveals a larger b value which reflects the decreasing tendency of diffusivity with the increment of curing age.

Table 3—The Values of a and b

Specimen—>	NSC	HSCSF0	HSCSF6	HSCSF12	HSCSF24
a, $\times 10^{-12}$	38.4	8.22	8.90	6.36	4.47
b	0.246	0.306	0.631	0.679	0.926
Relative Coef.	0.936	0.987	0.994	0.987	0.977

As observed above, the chloride diffusivity in concrete is strongly dependent on the curing age. Therefore, Fick's law can be expressed as

$$\frac{\partial C}{\partial t} = D(t)\frac{\partial^2 C}{\partial x^2} \tag{3}$$

where C is ion concentration, and x the distance from the surface. According to Crank /4/, the above equation can be reduced to

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial x^2} \tag{4}$$

where

$$T = \int_0^t D(t')\,dt' \tag{5}$$

Inserting Eq. (2) into Eq. (5), we get

$$T = \int_{t_0}^{t_i+t_0} a t^{-b} dt = \frac{a}{1-b}\left[(t_i + t_0)^{1-b} - t_0^{1-b}\right] \tag{6}$$

where t_i is immersion time and t_0 the age before immersion. For semi-infinite diffusion, the solution of Eq. (4) is

$$\frac{C}{C_0} = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{T}}\right) \tag{7}$$

where C_0 is the concentration at the surface, and erf refers to error function.

Fig. 5 shows the calculated chloride penetration profiles of various concretes when $t_0 = 7$ days and $t_i = 1$ year. It can be seen that high strength concrete, especially when blended with silica fume, reveals a much better resistance to chloride penetration.

In practice, the concrete structures are often put into service after being cast for only 1 to 7 days. It is very important, therefore, to evaluate the influence of the age before immersion, or service, t_0, on chloride penetration. From Eq. (7) we can obtain

$$1 - \mathrm{erf}\left(\frac{x_d}{2\sqrt{T}}\right) = 1 - \mathrm{erf}\left(\frac{x_{d1}}{2\sqrt{T_1}}\right) \tag{8}$$

which results in

$$T = \gamma^2 \cdot T_1 \tag{9}$$

where γ: relative penetration depth, $\gamma = x_d/x_{d1}$.

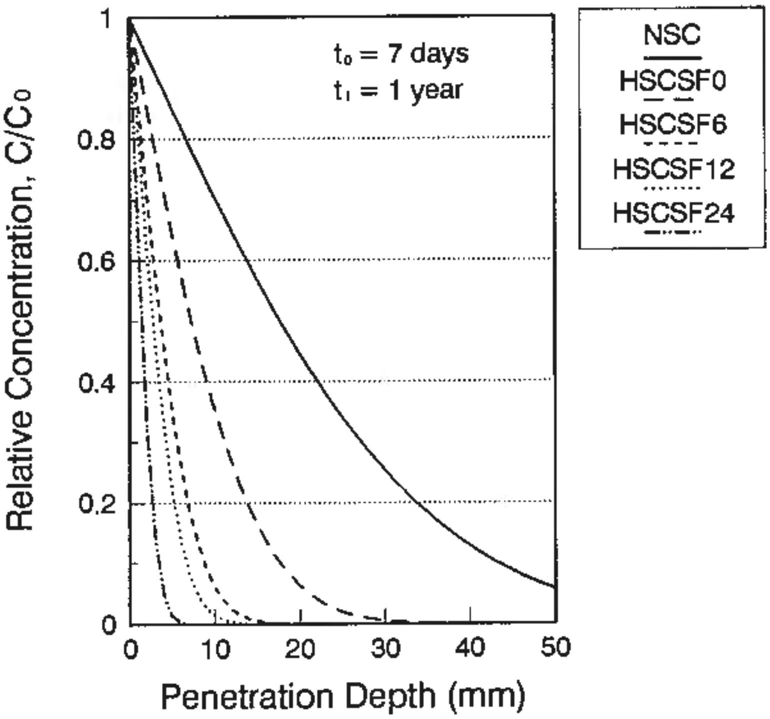

Fig. 5.—Calculated chloride penetration profiles.

Combining Eq. (9) with Eq. (6), and assuming t_{01} and t_{i1} in T_1 to be 7 days and 1 year respectively, for different curing age t_0, we can calculate the immersion time t_i, which is needed for chloride to reach a different relative penetration depth γ. The calculated results are shown in Fig. 6. The general tendency is that shortening the curing age t_0 results in a fast chloride penetration. It can be seen from Fig. 6 that the influence of t_0 on chloride penetration in concrete blended with silica fume is more noticeable than that without silica fume, but this influence in normal strength concrete seems similar to that in high strength concrete.

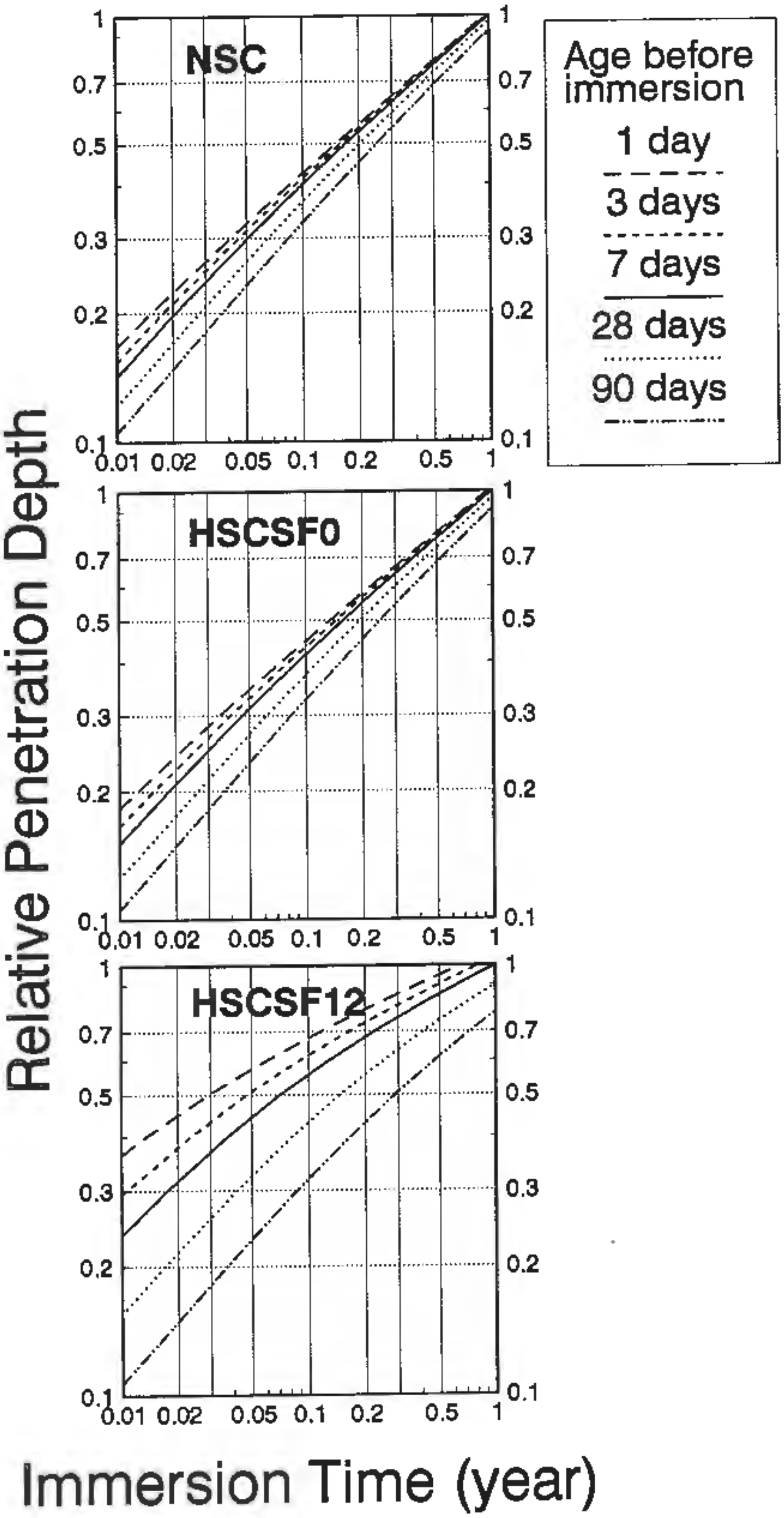

Fig. 6.—Influence of the age before immersion on relative penetration depth.

4. CONCLUSIONS

From the results the following preliminary conclusions can be drawn:

- Replacing OPC with silica fume in concrete only increases the strength by about 15% ~ 20%, but greatly decreases the chloride diffusivity. The decrement of the diffusivity in silica fume concrete becomes significant after only 3 days age. At 180 days age, the chloride diffusivity in concrete blended with silica fume becomes one to two magnitude orders lower than that without silica fume.

- The relation between chloride diffusivity and curing age can be expressed by the regression equation $D = a \cdot t^{-b}$. The constant b reflects the decreasing tendency of the diffusivity.

- By applying Fick's law, taking diffusivity as age dependent, one finds that shortening the age before service results in a fast chloride penetration. The influence of this age on chloride penetration in concrete blended with silica fume is more noticeable than that without silica fume.

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