Pergamon

Cement and Concrete Research, Vol. 27, No. 6, pp. 937-945, 1997

0008-8846/97 $17.00 + .00

PII S0008-8846(97)00064-1

INFLUENCE OF SLAG BLENDED CEMENT CONCRETE ON CHLORIDE DIFFUSION RATE

Changiz Dehghanian and Mosieb Arjemandi
University of Technology in Isfahan
P.O. Box 111
Department of Chemical Engineering
Isfahan, Iran

(Refereed)
(Received September 10, 1996; in final form April 1, 1997)

ABSTRACT

This research was conducted to investigate the effect of 0 to 30% partial replacement of cement by slag on chloride diffusion rate in concrete. Concretes with 0 to 30% slag were used and exposed to 2 to 5% NaCl solutions. The effect of different external salt concentration solutions and the influence of water-cement ratios ranging from 0.45 to 0.75 was also studied. In this research, different curing methods such as 9 to 18 days exposure to 100% humidity and 9 to 18 days submersion in distilled water were selected. The results indicated that after 90 days of exposure to salt solutions and 108 days of concrete age, chloride diffusivity for concretes containing slag almost remained the same. This effect was more pronounced for water-cement ratio of 0.45 and curing condition of 18 days submersion in water. An increase in water-cement ratio beyond 0.55 indicated a higher chloride diffusion rate. Curing condition for slag blended cement concrete also indicated a different behavior in chloride diffusivity. The best curing method obtained for this type of concrete was 18 days submersion in water. © *1997 Elsevier Science Ltd*

Introduction

Cracking and spalling of concrete structures due to embedded metal corrosion has been projected to be a serious problem, both nationally and internationally (1). The damage has been apparent in many types of applications, including bridges, pilings, buildings and various other coastal and offshore structures (2,3,4,5). The magnitude of the problem is evidenced by the increasing scientific and engineering research activity which has been devoted to this problem in recent years and also by the number of structures affected and the economics of repair.

In many situations the corrosion rate of steel in concrete is low, and decades of maintenance-free service are realized. This is primarily a consequence of the relatively alkaline nature of soluble components in concrete, which results in a pH near 12.4 or above for the pore water (6), and the fact that steel is normally passive for such a situation (7). However, penetration of chlorides through concrete cover, due to pressure differentials, capillary action or diffusion may destroy the passivity and lead to active corrosion of steel. Therefore, preventing the ingress of chlorides to the reinforcement is one approach to improve the durability of a concrete structure. This can be done with concrete highly impermeable to chloride ions.

The main mechanism for transport of chloride ions through crack-free concrete is diffusion. This has been demonstrated by several researchers (8,9,10,11,12,13). This explains the need for test that can be used in the field to measure the permeability of concretes to chloride ions (14).

The main objective of the present paper is to provide information on the diffusion rates of chloride into slag blended cement concretes. The effect of water-cement ratio and curing condition on chloride diffusivity was also investigated.

Experimental Investigation

Sample Preparation. A number of concrete disks were cast. These disks had a diameter of 46 mm and a thickness of 10 mm. These disks were made of different slag blended cement concrete. The concrete disks were formulated for different percentages of cement replacement by slag. Three concrete disks of each kind were made in order to check the reproducibility of data. The slag composition used in this investigation is shown in Table 1.

The concrete mix was made of 15.3% by weight Type I portland cement, 37.4% coarse aggregate and 35.4% fine aggregate with water-cement ratio of 0.45. Concrete disks with different water-cement ratios were cast. These disks were also made with different curing methods. One of the curing techniques was to submerse the concrete in water with no salt for 9 or 18 days. The other curing method was to place the concrete in 100% humidity chamber for 9 or 18 days. The concrete disks were placed between two compartments as shown in Figure 1. The corner of disks and compartments was completely sealed with epoxy glue in order to prevent the solution leakage. This assembly was called a diffusion cell.

Chloride Diffusivity Measurement. Chloride diffusion coefficient in concrete was measured by a technique proposed by Page et al. (15). In this method, a diffusion cell shown in Figure 1 was used. One compartment of diffusion cell was filled with NaCl solution and the other

TABLE 1

Composition of Slag Used in this Study

Slag components	weight%
SiO_2	34.31
Al_2O_3	9.55
CaO	35.19
MgO	9.89
TiO_2	4.19
K_2O+NaO_2	1.03
MnO	1.34
P_2O_5	0.25
FeO	0.65
S	1.3

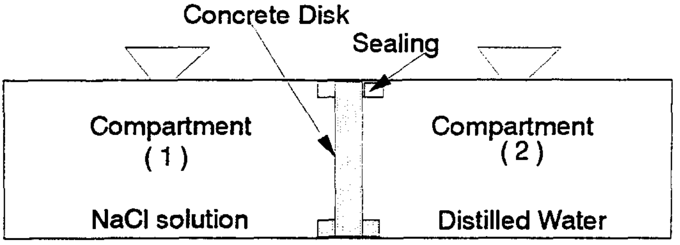

FIG. 1.
Schematic diagram of diffusion cell.

compartment with distilled water. Chloride ions diffused through the cement disk from compartment 1 into compartment 2 with time. The variation in chloride concentration in compartment 2 containing distilled water was monitored as a function of time. The initial NaCl concentration in compartment 1 was 3% by weight and kept constant at all times. After an initial delay time for chloride diffusion in concrete disk layer to be stabilized, chloride concentration in compartment 2 increased linearly with time. This condition is similar to quasi-steady-state diffusion through a disk. This means that the mass flux in all regions perpendicular to diffusion direction are constant.

The chloride concentration in compartment 2 was measured as a function of time by Mohr (16) method.

Results and Discussion

The diffusion cell designed in this study as described in the experimental section was such that we could write the following equation:

$$J = \frac{V}{A} \times \frac{dC_2}{dt} = \frac{D}{L} \times (C_1 - C_2) \qquad (1)$$

where J is the flux of chloride in moles/cm^2-sec that entered into compartment 2 (see Figure 1), D is the chloride diffusivity in cm^2/sec, V is the solution volume in compartment 2 in cm^3, L is the concrete disk thickness in cm, C_1 is the chloride concentration in compartment 1 in moles/cm^3 and C_2 is the chloride concentration in the compartment 2 in mole/cm^3. If we assume that the chloride concentration in the solution is equal to the chloride concentration on the concrete disk surface, then we have:

$$\ln[1 + \frac{C_2}{C_1 - C_2}] = \frac{D \times A}{V \times L} \times (t - t_0) \qquad (2)$$

and from that we have,

$$C_2 = \frac{D \times A \times C_1}{V \times L} \times (t - t_0) \qquad (3)$$

TABLE 2

Concentration of Chloride Ions as a Function of Time for Cell No. 71*

	DIFFUSION CELL NO.					
	71A		71B		71C	
Row No.	Time/sec	[C] ppm	Time/sec	[C] ppm	Time/sec	[C] ppm
1	684000	2140	684720	1540	684960	1820
2	1036560	2760	1036920	2020	1037280	2120
3	1792740	3718	1792800	2252	1792980	3917
4	2370660	4433	2371140	2760	2371980	4697
5	2891640	5148	2891280	2836	2892120	4760
6	4018920	6380	4018380	3580	4019340	6140
7	4361820	6475	4361400	3586	4362300	6393
8	5224020	6450	52246620	3744	7056000	8788
9	7055580	8035	7055880	4316	7056000	8788
10						
11	Slope (M)	0.001264	0.00065		0.00182	
12	D [CL$^-$]	2.46E-07	1.26E-07		3.5E-07	
13	Mean Chloride Diffusivity = 2.42E-07 cm^2/sec.					

*- In this table, the cells 71A, 71B and 71C are similar and their configuration and conditions were the same as the one described in the experimental section.

for $t > t_0$ and $C_1 \gg C_2$ for which t_0 is the initial delay time. Therefore, the effective diffusivity can be obtained from the slope of concentration vs time curve. If M stands for the slope, then we have:

$$D = \frac{V \times L \times M}{A \times C_1} \tag{4}$$

The chloride diffusivity used in this study is an average of three diffusion cells of the same kind (see Table 2). In this table, the cells 71A, 71B and 71C are similar. A typical plot of chloride concentration as a function of time for the cell 71A in Table 2 is shown in Figure 2.

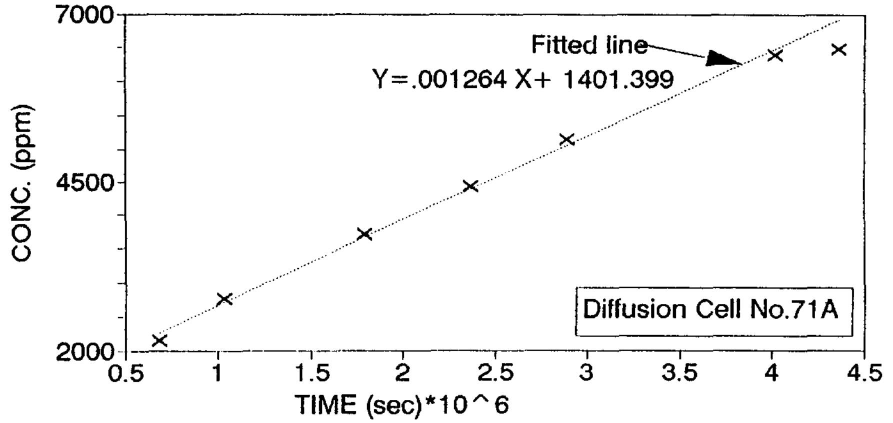

FIG. 2.
Concentration of chloride ions as a function of time for cell 71A.

The best line equation which fits the data are also shown in the graph. The chloride diffusivity was determined by using the slopes of these lines into Equation 4.

For all concrete samples with different conditions, the above technique was used to determine the chloride diffusivity. The average chloride diffusivity obtained for the concrete with no slag addition was about $1.06 \times 10^{-8} cm^2/sec$ which was the same as the value reported by Jang (17) for the sound concrete. He estimated the chloride diffusivity by using Fick's second law of diffusion:

$$\frac{dC}{dt} = D \times \frac{d^2C}{dx^2} \tag{5}$$

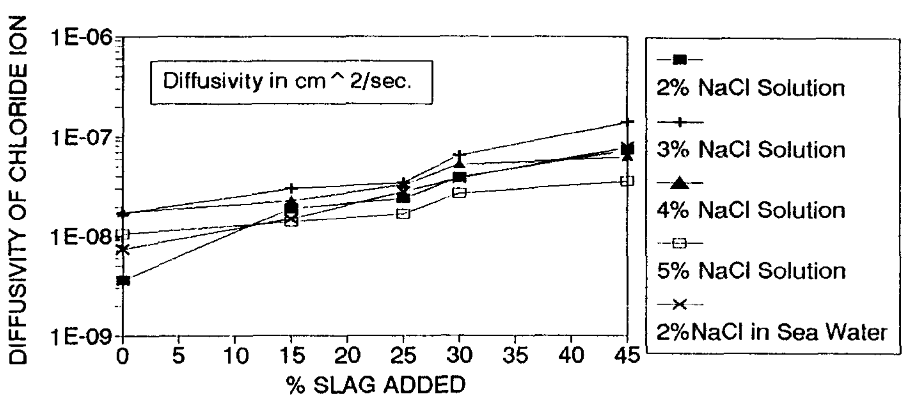

FIG. 3.
Diffusivity of chloride ions as a function of percent slag added at various external salt concentration after 90 days of exposure. The concrete samples were 108 days old.

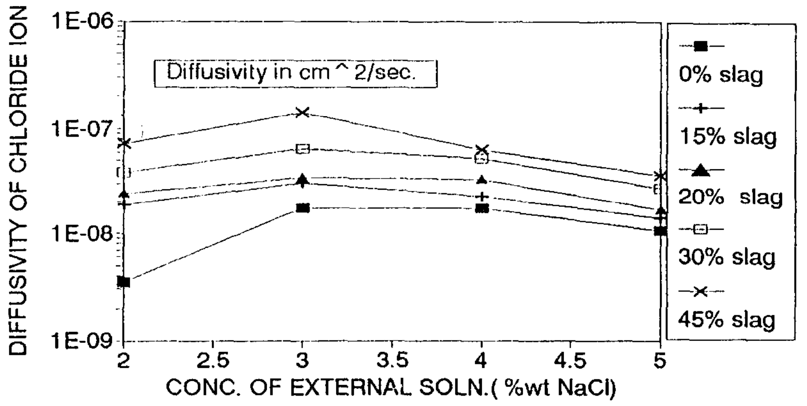

FIG. 4.
Diffusivity of chloride ions as a function of external salt concentration at various slag contents. The concrete samples were 108 days old.

for boundary concentration of C = 0 at t = 0 for (0 ⟨x⟨∞) and C = C_0 at x = 0 for (0⟨t⟨∞), where the solution for Eq.5 is

$$\frac{C}{C_0} = 1 - erf\left(\frac{x}{2 \times \sqrt{D \times t}}\right) \tag{6}$$

where C is the concentration of chloride ion in concrete at a distance x from the surface at a time t, and C_0 is the concentration at equilibrium (10%). Therefore, a method used for determining chloride diffusion coefficient in this work was in good agreement with the method used by Jang and Iwasaki (17).

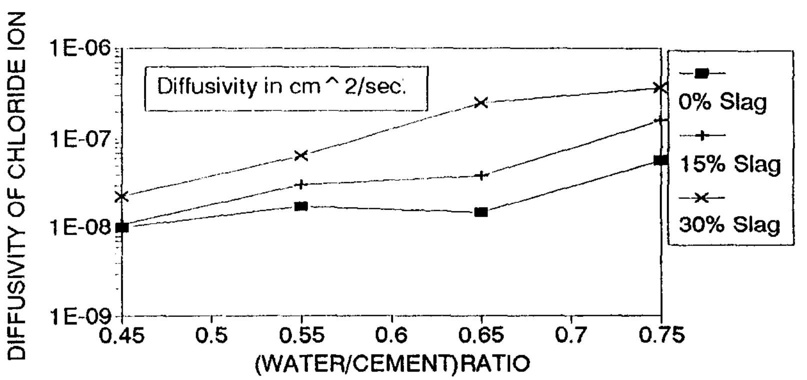

FIG. 5.
Diffusivity of chloride ions as a function of water-cement ratio at different slag concentration. The concrete samples were 108 days old.

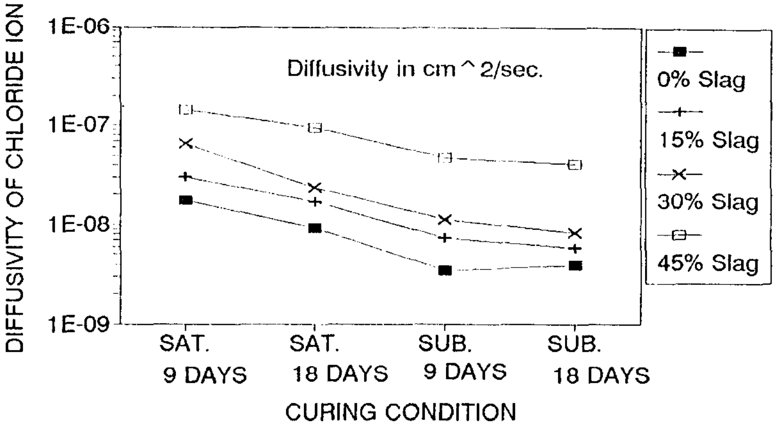

FIG. 6.
Diffusivity of chloride ions as a function of curing condition for different slag concentration. The concrete samples were 108 days old.

Figure 3 is a plot of chloride diffusivity as a function of percent slag added to concrete. The concrete disks were exposed to different salt concentration solutions. Addition of slag up to 30% indicated the same chloride diffusivity as the concrete with no slag. However, above 30% slag content, the chloride diffusivity increased compared to the concrete with no slag. This is probably due to the fact that slag blended cement concretes were at 108 days of age and have not developed sufficient age to increase their electrical resistivity large enough to lower the concrete porosity and permeability. This has been reported in the work of Hansson and Hansson (18) which indicated that for blast furnace slag cement paste with water-cement ratio of 0.55, an increase of 82% in electrical resistivity from age 20 days up to 200 days was observed. However, for the concrete with no slag he did not observe any increase in electrical resistivity. Therefore, it is likely for the concretes up to 30% slag content to increase its resistivity with age. This probably reduces its chloride permeability with age compared to concretes with no slag.

Figure 4 is a plot of chloride diffusion coefficient as a function of the external salt concentration solutions for concretes with different amount of slag. The results indicated an increase in chloride diffusivity for all concrete samples in 3% NaCl solution. However, the chloride diffusivity decreased in a solution containing more than 3% NaCl.

Figure 5 illustrates the chloride diffusion with respect to water-cement ratios (W/C). At the water cement ratio of 0.45, addition of slag to concrete up to 30% did not make any significant change in the chloride diffusivity. This trend almost continued up to water-cement ratio of 0.55. After that the increase in water-cement ratio caused a dramatic increase in chloride diffusivity for the concrete containing 30% slag. However, the chloride diffusivity for the concretes containing 0 and 15% slag with water cement ratio of 0.65 did not change with respect to the concretes with water-cement ratio of 0.45 and 0.55. At water-cement ratio more than 0.65 an increase in chloride diffusion rate was observed.

Figure 6 demonstrated the effect of curing condition on chloride permeability in the concrete containing slag. The lowest chloride diffusion rate was obtained for the curing condition of 9 and 18 days submersion in water. The chloride diffusion coefficient at this curing condition, was approximately the same for the concretes up to 30% slag, but a sharp increase in the diffusion coefficient was observed for 45% slag content. Curing condition of 9 and 18 days exposure to 100% humidity showed more chloride diffusivity than the curing condition of 9 and 18 days submersion in water. This effect was more pronounced for the concretes with higher slag concentration.

Conclusion

From the results obtained in this investigation the following conclusion can be drawn:

1. Slag blended cement concrete containing up to 30% slag with water-cement ratio of 0.45 did not influence on chloride diffusion rate compared to concrete with no slag. This conclusion was obtained for concretes with 108 days of age. However, it is believed that with concrete age, the chloride diffusion rate for slag blended cement concrete will be reduced.
2. An increase in water-cement ratios more than 0.55 increased the chloride diffusivity of concrete. This effect was more pronounced for a higher slag contents.
3. Water-cement ratio of 0.45 provided the lowest chloride permeability for the concretes with higher slag contents.
4. Curing method had a marked effect on chloride permeability in concrete. Submersion in water for 9 and 18 days provided the best curing condition for reducing the chloride diffusion rate in concrete.

References

1. Research on the Durability of Reinforced Concrete Bridge Components, NCHRP Research Results Digest, Digest 115, Aug., 1979.
2. R.D. Brown, ACI Publication SP-65, 1980, p.169.
3. R. Kessler and R. Powers, Interim Report, Corrosion Evaluation of Substructure, Long Key Bridge, Corrosion Report No.,87-9A, Materials Office, Florida Department of Transportation, Gainesville, Florida, 1987.
4. A. Zayed, A. Sagues and R. Powers, Corrosion of Epoxy-Coated Reinforcing Steel, Paper No. 379, Corrosion/1989, NACE, Houston,1989.
5. E. Philip, Survey of Corrosion of Prestressing Steel in Concrete Water Retaining Structures, Technical Paper, No. 9, Australian Water Resources Council, Canberra, 1975.
6. O.E. Gjorv and O. Vennesland, Journal ACI, 73, 512 (1976).
7. J.R. Clifton, Materials Performance, 15, 14 (1976).
8. A. Atkinson and A.K. Nickerson, Diffusion of ions through water-saturated cement, Journal of Materials Science, 19(9), 3068-3078 (1984).
9. S. Goto and D.M. Roy, Diffusion of ions through hardened cement-paste, Cement and Concrete Research, 11(5), 751-757 (1981).
10. R. Feldman, G.W. Chan and R.J. Brousseau, Chloride ion diffusivity of blended cement mortars: A.C. impedance and pore structure parameters, Il Cemento, 90(4), 207-220 (1993).
11. S.W. Yu and C.L. Page, diffusion in cementitious materials; comparative study of chloride and oxygen diffusion in hydrated cement pastes, Cement and Concrete Research, 21, 581-588 (1991).

12. R.F. Feldman, G.W. Chan, R. Brousseau and P.J. Tumidajski, Investigation of the rapid chloride permeability test, ACI Materials J., May 1994. pp. 246-255.
13. O.E. Gjorv, K. Tan and M.H. Zhang, Diffusivity of chlorides from sea water into high-strength lightweight concrete, ACI Materials J., September, 1994, pp. 447-450.
14. D. Whiting and T. Mitchell, History of the rapid chloride permeability test, Transportation Research Record No. 1335, Jan. 1992, Preprint, pp. 55-62.
15. C.L. Page, N.R. Short and A. El Tarras, Diffusion of chloride ions in hardened cement pastes, Cement and Concrete Research, 11, 395-406 (1981).
16. D.A. Skoog, Fundamentals of analytical chemistry, 5th edition, Saunders College Publishing, New York, 1988, Chap. 7, p. 174, Chap. 31, p.764.
17. J.W. Jang and I. Iwasaki, Rebar Corrosion under simulated concrete conditions using Galvanic current measurements, Corrosion, 47(11), 875-884 (1991).
18. I.L.H. Hansson and C.M. Hansson, Electrical resistivity measurement of portland cement based materials, Cement and Concrete Research, 13, 675-683 (1983).