



Diffusion of Chloride Ions in Limestone Powder Concrete

Han-Young Moon¹⁾, Ho-Seop Jung^{1)*}, and Jong-Pil Kim¹⁾

¹⁾Dept. of Civil Engineering, Hanyang University, Korea

(Received February 5, 2004; Accepted November 19, 2004)

Abstract

In this study, the diffusion of chloride ions in cement concrete made with and without the limestone powder was investigated. In order to study the effect of the limestone powder, all mixtures were prepared at a fixed water-cementitious ratio (0.45). From the experimental results, the setting time of limestone powder concrete is faster than that of control concrete, and compressive strength of all specimens decreased with increasing replacement ratio of limestone powders. The diffusion properties of limestone powder concretes indicated a trend increasing with curing period. LSA10 and LSA20 concretes, the diffusion coefficient was smaller than that of control concrete. The addition of 10-20% limestone powder reduces the diffusion coefficient of chloride ions, irrespective of fineness levels of limestone powder.

Keywords: limestone powder, setting time, diffusion coefficient, chloride ion, total passed charge

1. Introduction

In recent years, the chloride-induced corrosion of reinforcing bars and the deicing salt scaling deterioration of concrete surfaces have largely contributed to increase maintenance and repair costs of highway networks and marine structures. The problem of chloride attack arises usually when chloride ions ingress from outside. Particularly important, source of chloride ions is from sea water in contact with concrete structures. Chlorides can also be deposited on the surface of concrete in the form of air-borne very fine droplets of sea water or air-borne dust which subsequently becomes wetted by dew.¹⁾ In order to solve these problems, the diffusion of chloride ion in hydrated cement paste has recently been the subject of numerous.²⁻⁵⁾ Chloride diffusivity is one of the important properties of concrete affecting the durability of a structure. The diffusivity of porous materials is determined conventionally by diffusion cells or immersion in a solution.³⁾

The ability of concrete to resist the penetration of chloride ions is a critical parameter in determining the service life of steel reinforced concrete structures exposed to

deicing salts or marine environments. Blending cement with fly ash is known to produce concrete with a dense microstructure and hence an improvement in the physical protection of any embedded bars. The effect of fly ash and ground granulated blast furnace slag on the mass transfer properties of concrete have been well documented.^{6,7)}

Several reports also indicate that the diffusion of chloride ions is directly influenced by the microstructure of the hydrated cement paste. The diffusion coefficient of chlorides has been found to decrease with a reduction of the water binder ratio,^{8,9)} and supplementary cementitious materials, such as silica fume, fly ash and ground granulated blast furnace slag, are reported to enhance, at various degrees, the resistance of concrete to chloride ion penetration.¹⁰⁾ Despite the fact that limestone powder are now increasingly used in Europe and North America, very few data are available regarding the effect of these material additions on the diffusion of chloride ion in hydrated cement pastes. This paper investigates the permeability resistance of chloride ions in cement concrete made with and without the limestone powder. Performance was evaluated through measurement of rapid chloride permeability test, penetration depth of chloride ions, passed current charge.

* Corresponding author

Tel.: +82-2-2290-0323 Fax.: +82-2-2293-9977

E-mail address: hsnjsj97@hotmail.com

2. Experimental details

2.1 Materials

2.1.1 Cement

The cement, ordinary portland cement (hereinafter OPC), was provided by S-company cement Ltd. The blaine fineness of this cement was 328m²/kg. The physical properties and chemical composition of the cement are given in Table 1.

2.1.2 Aggregates

The fine aggregate, river sand, which is a fine aggregate immune to most chemical agent and has little organic compounds, is employed for manufacturing cement matrix specimens. The coarse aggregate was crushed stone with nominal maximum size of 20mm. The physical properties of aggregates are given in Table 2.

2.1.3 Admixtures

(1) As superplasticizer a polycarbonic acid based chemical admixture is used. It was added to the mixing water as 1.8% of weight of cementitious materials.

(2) Limestone powder: The limestone powders were provided by W-chemical Ltd. There are three kinds of limestone powders which is used in this study; their mean diameters are 3.11 μ m (hereinafter LSA), 7.53 μ m (hereinafter LSB) and 18.62 μ m (hereinafter LSC), respectively. There are physical properties and chemical composition of limestone powders given in Table 1.

2.2 Mixture proportion

The physical properties of concrete containing limestone powders were investigated. The experiment is performed for concrete specimen using the limestone powders to following conditions. Sand percentage and air content are 39% and 4.5%, respectively. The mixture proportion of concrete is given in Table 3.

2.3 Methodologies

2.3.1 Setting time of concrete

Setting time of concrete, after fresh concrete was passed through a sieve of 5 mm, was conducted on accordance with KS F 2436. There were defined the initial and final setting time of the time from when cement grains come in contact with water up to 3.4MPa and 27.4MPa of penetration resistance, respectively.

2.3.2 Rapid chloride permeability test (RCPT)

The additions of chemical and mineral admixtures affect

Table 1 Physical properties and chemical composition of OPC and limestone powder

Items	OPC	LSA	LSB	LSC
Silicon dioxide	21.7	0.51	0.82	0.92
Aluminum dioxide	5.7	0.22	0.24	0.28
Ferric oxide	3.2	0.09	0.13	0.15
Calcium oxide	63.1	54.4	54.5	53.1
Magnesium oxide	2.8	0.62	0.65	0.88
Sulfur trioxide	2.2	-	-	-
I.g loss	1.3	43.44	43.41	43.35
Specific gravity	3.15	2.71	2.71	2.71
Fineness (m ² /kg)	328	2,650	1,730	1,010

Table 2 Physical properties of aggregates

	Fine agg.	Coarse agg.
Specific gravity	2.60	2.62
Absorption (%)	1.20	0.80
F.M.	2.80	7.30

Table 3 Mixture proportion of concrete

Symbol	W/Cm (%)	W (kg)	C (kg)	S (kg)	G (kg)	Limestone powder(kg)
Control	45	165	367	675	1,076	0
LSA10	45	165	330	662	1,055	36.7
LSA20	45	165	293	648	1,033	73.3
LSA30	45	165	257	635	1,012	110.0
LSB10	45	165	330	662	1,055	36.7
LSB20	45	165	293	648	1,033	73.3
LSB30	45	165	257	635	1,012	110.0
LSC10	45	165	330	662	1,055	36.7
LSC20	45	165	293	648	1,033	73.3
LSC30	45	165	257	635	1,012	110.0

the concrete pore size distribution and also the concrete pore solution chemistry.^{11,12)} The concrete specimens for diffusion test are cylindrical, ϕ 100 \times 50mm (Fig. 1). These were de-molded after 1 day of being cast and cured for additional each days in tap water. The temperature of tap water was kept at 20 \pm 1 $^{\circ}$ C during the curing period. Diffusion test using electrochemical technique was carried out using the classical two compartment cell, as schematically shown in Fig. 2.¹³⁾ To supply chloride ions, 0.5M NaCl solution was used in cathode chamber. Saturated Ca(OH)₂ solution was introduced into the anode chamber. This test was performed by applying a potential difference of 30V DC and the real voltage drop was also measured.

2.3.3 Penetration depth of chloride ions

After the voltage had been applied for 8 hours, the concrete specimens used were splitted into two parts. And then, according to colorimetric method, 0.1N AgNO₃ solution was sprayed on the surface of the splitted specimens. The discolored part was measured as penetration depth of chloride ions.

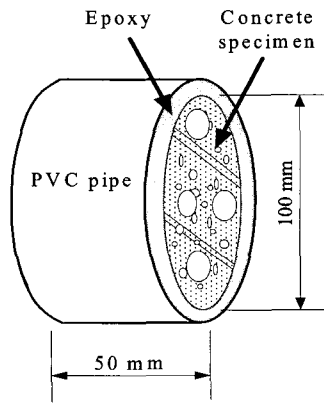


Fig. 1 RCPT specimen

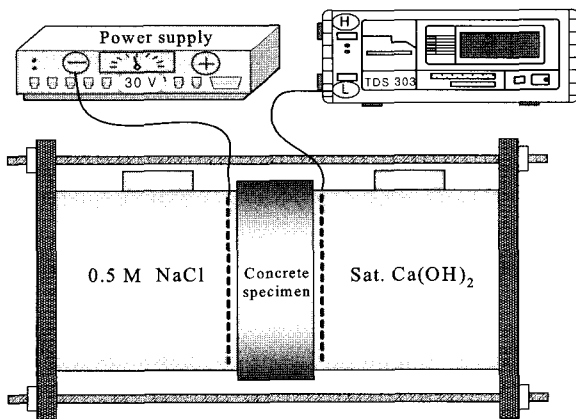


Fig. 2 Schematics of RCPT

2.3.4 Passed current charge

Passed current was measured every half an hour for 8 hours using a data logger, total passed charge was calculated by Eq. (1) (ASTM C 1202).

$$Q_{\text{total}} = 900(I_0 + 2I_{30} + 2I_{60} + \dots + 2I_{450} + I_{480}) \quad (1)$$

where, Q_{total} : charge passed (coulomb)

I_0 : current (A) immediately after voltage is applied

I_t : current (A) at t min after voltage is applied

2.3.5 Determination of diffusion coefficient

The diffusion coefficient of chloride ions in concrete was determined on the basis of the Eq. (2) and Eq. (3) proposed by Andrade¹⁴⁾ and Tang⁴⁾, respectively. Equation (2) takes account of the transference number of chloride ions, t_{Cl} , which represents the proportion of the total current transported by every ion. The transference number of chloride ions was reported in the literature.¹⁵⁾

$$D_A = \frac{RT}{nF^2} \frac{it_{\text{Cl}}}{\Delta E} \frac{l}{A} \frac{1}{C_{\text{Cl}}Z} \quad (2)$$

where, D : diffusion coefficient (m^2/sec)
 R : gas constant, F : faraday's constant,
 T : absolute temperature, A : cross section,
 E : potential difference, Z : balance ion,
 l : thickness of specimen, i : total passed current,
 t_{Cl} : transference number,
 C_{Cl} : concentration of chloride ion

$$D_T = 1.189 \times 10^{-11} \left(\frac{x_d - 1.061x_d^{0.589}}{t} \right) \quad (3)$$

where, D : diffusion coefficient (m^2/sec)
 x_d : penetration depth (cm), t : time (hour)

3. Results and discussion

3.1 Physical properties of concrete

3.1.1 Setting time

Setting time is defined as the onset of rigidity in fresh concrete. It is distinct from hardening, which describes the development of useful and measurable strength. It can view setting as a transitional period between states of true fluidity and true rigidity. In order to determine the setting time of concrete containing limestone, the penetration tests used to measure the times of setting are purely arbitrary measurements. The variable is replacement ratio of the limestone powder such as 10, 20 and 30%. The water cementitious ratio and experimental temperature are 0.45 and 25°C , respectively. Initial setting times of all mixtures were measured around 4.5 hours. However, the mixtures with increased replacement ratio of all kind of limestone powder, regardless of its fineness levels, appear to be fast. Fig. 3 shows setting time of concrete containing limestone powder in case of the substitute of limestone powder for cement.

This figure indicates that the initial and final setting times of LSA concrete is faster than that of control concrete, regardless of replacement ratios. It should be remembered that the cement hydration begins as soon as water is added at the mixer. Setting is controlled primarily by the hydration of alite. The setting time of concrete containing limestone is faster than that of control concrete, because limestone powder makes filling in pore of mortar specimen and to accelerate the hydration reaction of alite and aluminate at early ages.¹⁶⁾ These results also correspond to the study of Brookbanks.¹⁷⁾ In case of LSB and LSC concrete, the trend show similar to LSA concrete.

3.1.2 Compressive strength

The compressive strength of concrete with the 0.45 water-cementitious ratio at 3, 7 and 28 days is illustrated in Fig. 4.

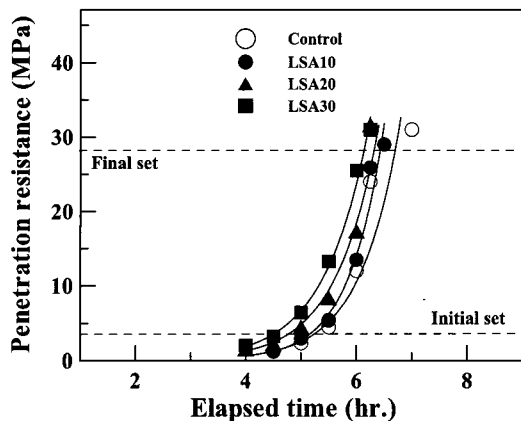


Fig. 3 Setting time of LSA concrete

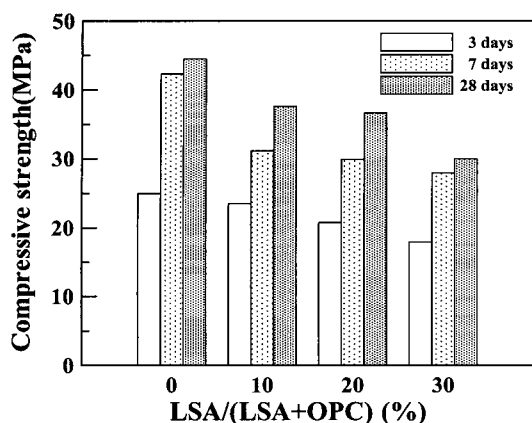


Fig. 4 Compressive strength of LSA concrete

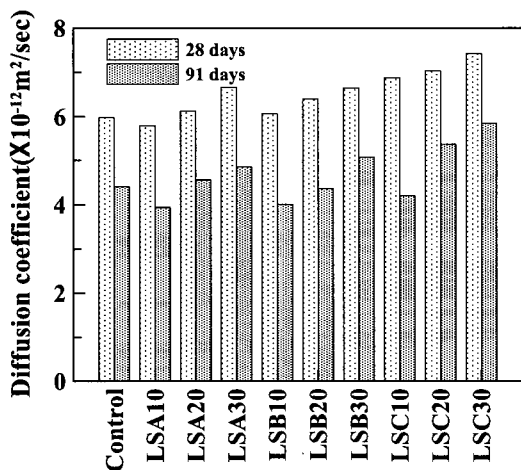


Fig. 5 Diffusion coefficient of hardened concrete with limestone powder

The compressive strengths of concrete specimens containing limestone powder of concrete mixtures decreased with increasing replacement ratio of limestone powders irrespective of fineness levels. The compressive strength decreased, because the unit cement content decreased due to the replacement ratio. The other concretes, LSB, LSC concrete, are presented in similar to LSA concrete.

Table 4 Chloride ion diffusion coefficients of concrete

Types	Tang	Andrade
	Diffusion coefficient, ($\times 10^{-11}$, m^2/s)	Diffusion coefficient, ($\times 10^{-12}$, m^2/s)
control	1.57	4.41
LSA10	1.39	3.94
LSA20	1.45	4.57
LSA30	1.67	4.85
LSB10	1.55	4.01
LSB20	1.63	4.36
LSB30	1.67	5.07
LSC10	1.68	4.20
LSC20	1.78	5.37
LSC30	1.80	5.85

Therefore, the effectiveness of the containing limestone powder is not fineness levels but replacement ratio.

3.2 Diffusion coefficient

Diffusion is the process that matter is transported from one part of a system to another due to concentration gradient. Diffusion coefficient of chloride ions in concretes was determined on Eq. (2) and Eq. (3) proposed by Andrade¹⁴ and Tang⁴. The chloride diffusion test results at 91 days are summarized in Table 4.

Both the measured diffusion coefficient of all concrete specimens, except for 10% replacement ratio, were significantly smaller than that of the control concrete specimen. The diffusion coefficient of chloride ions of Tang and Andrade tests had a good interrelationship in all concrete mixtures. The diffusion coefficient of concretes of 10% replacement ratio were significantly smaller compared with the concretes of 20 and 30% replacement ratio irrespective of fineness level.

Fig. 5 shows the relationship between replacement ratio and diffusion coefficient of hardened concrete containing limestone powders at 28 and 91 days. The measured diffusion coefficient is the average of two specimens.

The diffusion coefficient of LSA10 and LSA20 concrete specimen was smaller than that of control concrete specimens. However, LSB and LSC concrete specimens are relatively larger value than that of control concrete specimen except 10% replacement ratio. According to the results shown in Fig. 5 and Table 4, the measured diffusion coefficient at 28 days is significantly higher than that of the measured at 91 days. However, when the comparison is the experimental result of Hornain et al.¹⁸, the opposite trend is observed. They have reported the addition of a limestone powder reduces the diffusion coefficient of chloride ions. This reduction is attributed to the effect of the limestone powder particles on the tortuosity of the system.

The diffusion coefficient of LSA10 concrete specimen at both days was the lowest, and the coefficients increased with increase of the blended ratio of limestone powder. However, at 91 days, the results of diffusion coefficient of blended cement concretes with 10% limestone powder were presented the lower than that of control concrete. The diffusion coefficients measured in this investigation are similar to those previously reported in the literature.^{8,18)}

Figs. 6 and 7 show the relationship between compressive strength and diffusion coefficient by Tang and Andrade method, respectively. According to the results shown in these Figures, the diffusion coefficient decreases proportionally and the coefficients by both Tang and Andrade equation are inversely proportional to the compressive strength of concrete.

The diffusion coefficient calculated by Tang equation differs from Andrade equation in unit as one order. The coefficient of determinations of Tang and Andrade are 0.84 and 0.56, respectively. Thus, diffusion coefficient calculated by Tang equation is significantly better than that of calculated Andrade equation. Tang equation is harmonize with those relationship better than Andrade equation.

3.3 Total passed charge and penetration depth

The penetration of chloride ions into hardened cement matrices has been measured by chemical analysis. In general, the penetration depth of chloride ions depends on the permeability. Thus, the greater the water binder ratio, the greater the penetration property.⁹⁾

Fig. 8 shows the relationship between compressive strengths of concrete specimen with or without limestone powder and total passed charge.

According to the results shown in this Figure, the total passed charge were found inversely proportional to compressive strength with relatively high interrelationship. Similarly, relationships between compressive strengths and total passed charge of concrete specimens are similar to those between compressive strength and diffusion coefficient. The diffusion coefficient of chloride ions of blended cement concrete specimens were greatly reduced with curing periods due to the lower concrete porosity and permeability.¹⁹⁾

Furthermore, Fig. 9 and Fig. 10 show the relationship between penetration depth of chloride ion and diffusion coefficient calculated by Tang and Andrade. As the coefficients of determination of Tang and Andrade are 0.99 and 0.97, respectively, penetration depths of chloride ions have also very close relation with the diffusion coefficient.

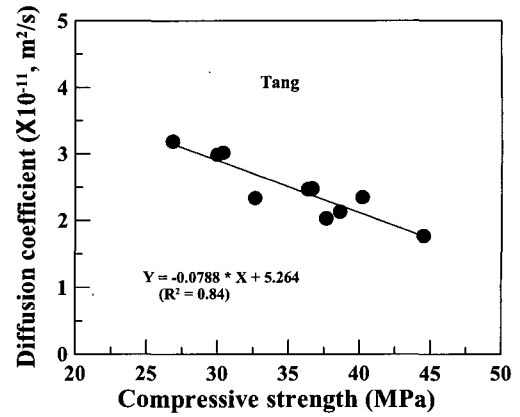


Fig. 6 Relationship between compressive strength and diffusion coefficient

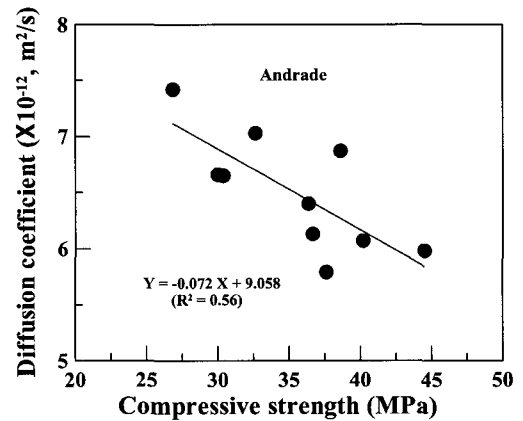


Fig. 7 Relationship between compressive strength and diffusion coefficient

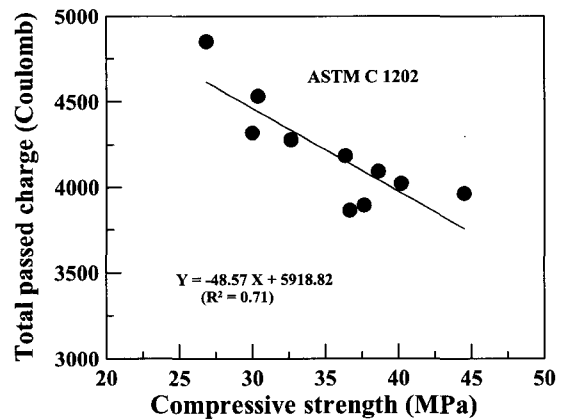


Fig. 8 Relationship between compressive strength and total passed charge

Figs. 11 and 12 present the relationship between replacement ratio and chloride penetration depth and total passed charge of limestone powder concretes with various fineness levels at 28 and 91 days. Penetration depth and diffusion coefficient of chloride ions had a good relationship in all concrete mixtures.

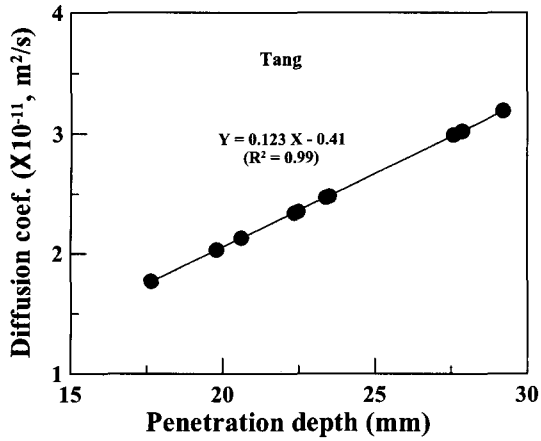


Fig. 9 Relationship between penetration depth and diffusion coefficient

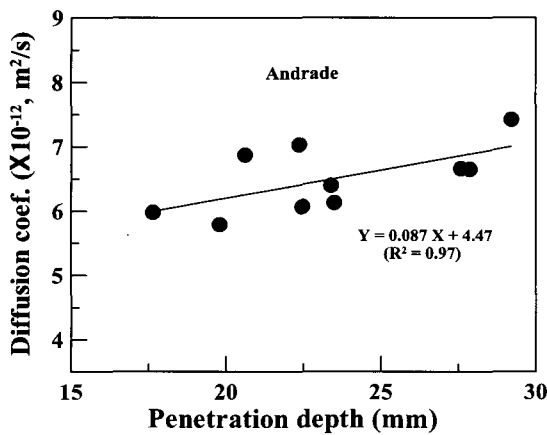


Fig. 10 Relationship between penetration depth and diffusion coefficient

The concrete specimens containing the limestone powder indicate a clear increase of the total passed charge, compared to control concrete specimen. In case of 28 days, only LSA10 and LSA20 concrete specimens were located less than 4,000 coulombs, however, at 91 days, all of the mixtures were located in medium range of chloride ion penetrability. The chloride ion penetrability of almost all of mixtures was higher than that of control concrete specimen at 28 and 91 days. When compared to experimental results of Hassan et al.²⁰⁾ and Tsivilis et al.²¹⁾, the identical trend is observed.

As shown in Fig. 12, the concrete specimens containing the limestone powder indicate a clear increase of the penetration depth of chloride ions, compared to control concrete specimen. Although these results are similar to the total passed charge, the results at 28 days significantly differ from those at 91 days. Since the limestone powder is relatively non-reactive materials, the behavior of cement matrices with silica fume and fly ash which have pozzolanic properties differ from limestone powder cement matrix.

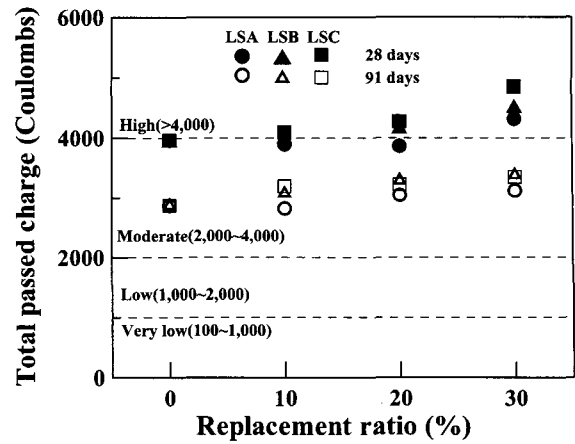


Fig. 11 Total passed charge of concrete

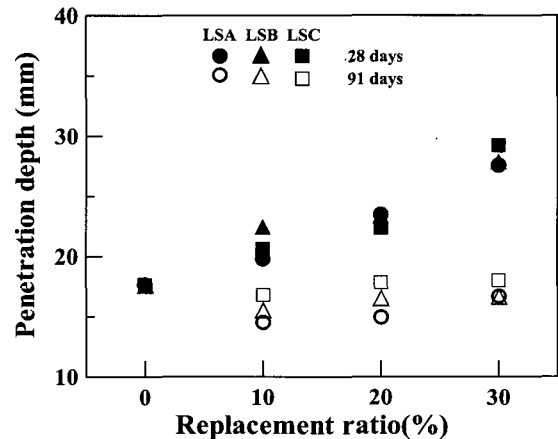


Fig. 12 Penetration depth of concrete

According to Hassan et al.²⁰⁾, silica fume and fly ash reduced the transport characteristics at early age, and the reduction was more prominent in the long term. The addition of mineral admixtures provides additional improvement to the porosity.

4. Conclusions

- 1) The setting time of concrete containing limestone is faster than that of control concrete, because limestone powder makes filling in pore of mortar specimen and to accelerate the hydration reaction of alite and aluminate at early ages
- 2) The diffusion properties of concrete specimens with limestone powder indicated a trend increasing with curing period. Furthermore, the diffusion coefficient of concrete specimens increased with enlargement of replacement and fineness levels.
- 3) The diffusion coefficient of LSA10 and LSA20 concrete specimen was smaller than that of control concrete.

However, LSB and LSC concrete specimens have relatively larger value than that of control concrete except at 10% replacement ratio.

- 4) From the relationship between compressive strength and diffusion coefficient calculated by Tang and penetration depth of chloride ions, the interrelationship was in good agreement with each others.

References

1. Neville, A. M., "Properties of Concrete," 4th and final edition, Addison Wesley Longman Limited, 1996, pp.482~576.
2. Hisada, M., Nagataki, S., and Otsuki, N., "Evaluation of mineral admixtures on the viewpoint of chloride ion migration through mortar," *Cement and Concrete Composites*, Vol.21, 1999, pp.443 ~ 448.
3. Tang, Luping, and Lars-Olof, Nilsson, "Rapid determination of the chloride diffusivity in concrete by applying an electrical field," *ACI Materials Journal*, No.89-M6, 1992, pp.49 ~ 53.
4. Tang, Luping, "Concentration dependence of diffusion and migration of chloride ions, Part 1. Theoretical consideration," *Cement and Concrete Research*, Vol.29, 1999, pp.1463 ~ 1468.
5. Mejlhede, O., Jensen, P., Freiesleben, Hansen, Coats, A. M., and Glasser, F. P., "Chloride ingress in cement paste and mortar," *Cement and Concrete Research*, Vol.29, 1999, pp.1497 ~ 1504.
6. Ampadu, K. O., Torii, K., and Kawamura, M., "Beneficial effect of fly ash on chloride diffusivity of hardened cement paste," *Cement and Concrete Research*, Vol.29, 1999, pp.585 ~ 590.
7. Michael, D. A., Thomas and Phil, B. Bamforth, "Modelling chloride diffusion in concrete effect of fly ash and slag," *Cement and Concrete Research*, Vol.29, 1999, pp.487 ~ 495.
8. Page, C. L., Short, N. R., and El Tarras, A., "Diffusion of chloride ions in hardened cement pastes," *Cement and Concrete Research*, Vol.11, 1981, pp.395 ~ 406.
9. Midgley, H. G. and Illston, J. M., "The penetration of chlorides into hardened cement paste," *Cement and Concrete Research*, Vol.14, 1984, pp.546 ~ 558.
10. Li, S., and Roy, D. M., "Investigation of relations between porosity, pore structure, and Cl⁻ diffusion of fly ash and blended cement pastes," *Cement and Concrete Research*, Vol. 16, 1986, pp.749 ~ 759.
11. Berke, N. S. and Roberts, L. R., "Use of concrete admixtures to provide long term durability from steel corrosion," *Proceedings of 3rd International Conference on Superplasticizers and Other Chemical Admixtures in Concrete*, ACI SP-119, Ottawa, Canada, 1989, pp.383 ~ 404.
12. Shi, C., Stegemann, J. A., and Caldwell, R. J., "Effect of supplementary cementing materials on the specific conductivity of pore solution and its implications on the rapid chloride permeability test results," *ACI Materials Journal*, Vol.95, No.4, July-August, 1998, pp.389 ~ 394.
13. Kim, H. S., "Assessment of chloride ions diffusion and prediction of initiation time of reinforcing steel corrosion in concrete by electrochemical techniques," Ph. D. Dissertation, Hanyang Univ., Korea, 2001.
14. Andrade, C., "Calculation of chloride diffusion coefficients in concrete from ionic migration measurements," *Cement and Concrete Research*, Vol. 23, No. 3, 1993, pp.724 ~ 742.
15. Castellote, M., Andrade, C., and Alonso, C., "Chloride transfer number in steady-state migration tests," *Magazine of Concrete Research*, Vol.51, No.2, 2000, pp.93 ~ 100.
16. Walter, A. Gutteridge and John, A. Dalziel, "Filler cement : The effect of the secondary component on the hydration of portland cement," *Cement and Concrete Research*, Vol.20, 1990, pp.853 ~ 861.
17. Brookbanks, P., "Properties of fresh concrete, performance of limestone filled cements," *Proceedings BRE/BCA seminar*, Garston, 1989, pp.4.1 ~ 4.15.
18. Hornain, H., Marchand, J., Duhot, V., and Moranville, R. M., "Diffusion of chloride ions in limestone filler blended cement pastes and mortars," *Cement and Concrete Research*, Vol.25, No.8, 1995, pp.1667 ~ 1678.
19. Dehghanian, C. and Arjemandi, M., "Influence of slag blended cement concrete on chloride diffusion rate," *Cement and Concrete Research*, Vol.27, No.6, 1997, pp.937 ~ 945.
20. Hassan, K. E., Cabrera, J. G. and Maliehe, R. S., "The effect of mineral admixtures on the properties of high-performance concrete," *Cement and Concrete Composites*, Vol.22, 2000, pp.267 ~ 271.
21. Tsvivilis, S., Gatis, G., Chaniotakis, E., Grigoriadis, Gr., and Theodossis, D., "Properties and behavior of limestone cement concrete and mortar," *Cement and Concrete Research*, Vol.30, 2000, pp.1679 ~ 1683.