Journal of Marine Science and Technology

Volume 2 | Issue 1 Article 8

A Study of Chloride Diffusion Properties of Concrete at Early Age

W.D. Yeih
Department of Harbor and River Engineering National Taiwan Ocean University Keelung 20224, Taiwan, Republic of China

R. Huang
Department of Harbor and River Engineering National Taiwan Ocean University Keelung 20224, Taiwan, Republic of China

J.J. Chang
Department of Harbor and River Engineering National Taiwan Ocean University Keelung 20224, Taiwan, Republic of China

Recommended Citation
Yeih, W.D.; Huang, R.; and Chang, J.J. (1994) "A Study of Chloride Diffusion Properties of Concrete at Early Age," *Journal of Marine Science and Technology*: Vol. 2 : Iss. 1 , Article 8.
DOI: 10.51400/2709-6998.2489
Available at: https://jmstt.ntou.edu.tw/journal/vol2/iss1/8

A Study of Chloride Diffusion Properties of Concrete at Early Age

Acknowledgements

The authors wish to express sincere thanks to finacial support of this study by Taiwan Area National Expressway Engineering Bureau (TANEEB).

A STUDY OF CHLORIDE DIFFUSION PROPERTIES OF CONCRETE AT EARLY AGE

W.D. Yeih, R. Huang and J.J. Chang

Department of Harbor and River Engineering
National Taiwan Ocean University
Keelung 20224, Taiwan, Republic of China

Key words: concrete, mortar, chloride diffusion.

ABSTRACT

Existence of chloride ions in concrete may accelerate reinforcement corrosion. Chloride ions can penetrate into the concrete by the diffusion process even if no major cracks exist. It is well known that properties of concrete will change with time since the hydration reaction continues for a long time, which implies that the diffusion coefficient of concrete is a time-dependent function. In this research, the diffusion behavior is focused on early-age mortar and concrete. It is shown that the diffusion coefficient changes dramatically at early age; and the control of interface property is significantly important to chloride diffusion. The effect by adding silica fume in concrete and mortar is also examined.

INTRODUCTION

Corrosion problem of RC structure is very serious in marine environment since penetration of chloride ions can locally destroy the passive oxide layer of reinforcements. Various critical chloride ion contents are reported by different authors and found in Funahashi's paper [1]. Even though different viewpoints are proposed in current date, they all agree that the chloride ion is a key factor affecting corrosion of rebars in marine environment. The penetration of chloride ions can be categorized into two main domains according to the driving force. One is due to pressure difference where Darcy's law is concerned, a typical example is the penetration of chloride ions in concrete in the submerged zone. The other is due to the difference of concentration where diffusion effect is concerned [2]. Usually the penetration mechanism of chloride ions dominated by pressure difference is not significant in most cases. Two types of chloride ions in concrete can be distinguished, one is free chloride ions which can be transferred in concrete freely and another type of chloride ions can react with C_3A and C-S-H paste to yield friedel salt, i.e. $C_3A{\bullet}CaCl_2{\bullet}10H_2O$ or physically absorbed by C-S-H paste so that they would not affect reinforcement corrosion.

Several conditions will affect the diffusivity of chloride ions. Tikalsky *et al* [3] and Maslehuddin *et al* [4] found that adding fly ash or silica fume can reduce the pore size of concrete, thus decrease the diffusivity of chloride ions. Page, Short and Tarras [5] found that the diffusivity would increase while temperature increased. They also found that the diffusion rate of chloride ions became 4 to 6 times larger while w/c ratio was increased from 0.4 to 0.6. Gjørv and Vennesland [6] reported that while penetration depth is greater than 20 mm, not much difference of chloride ions' content in mortar specimen no matter what water - cement ratio was. Clear and Hay [7] published a report to describe the effect of cement type on the diffusivity of chloride ions, they evidently found that the type of cement can cause different diffusivity, which is due to different C_3A content in cement. Page, Short and Holden [8] reported that pulverized fly ash concrete and blast furnace slag concrete can reduce diffusivity and the use of type II cement has higher diffusivity comparing with OPC.

Diffusion equation is usually used to describe mass transfer of chloride ions in concrete. Solutions for submerged zone can be expressed by error function [9], and solutions for splash zone and atmospheric zone can be found in reference [2]. A basic assumption for above-mentioned solutions is that the diffusion coefficient is not time-dependent, i.e. concrete is considered as a steady-state material. However, concrete properties change with time especially at early age. Based on 1,200-day data, Magnet and Gurusamy [10] [11] reported that the diffusion coefficient of chloride ions can be expressed as $D(t)$= $[2.81 + 7 \cdot \exp(-0.005t)]\times10^{-8}$(cm^2/sec) for ordinary portland cement concrete and $D(t)=(10.54-0.0168t-1.181\times 10^{-5}t^2 + 2.148\times10^{-8}t^3)\times10^{-8}$(cm^2/sec) for fly ash concrete. When the property is a function of time, by assigning $D(t) = D_0f(t)$ and employing a transformation $T = \int_0^t f(t)\,dt$ the diffusion equation $\frac{\partial C}{\partial t} = D(t)\frac{\partial^2 C}{\partial x^2}$ can be transformed into a standard type diffusion equation, $\frac{\partial C}{\partial T} = D_0\frac{\partial^2 C}{\partial x^2}$.

In this paper, the diffusion coefficients of chloride ions in mortar and concrete specimen at early age were studied and effect of adding silica fume on chloride diffusion was also examined. Diffusion coefficients for mortar and concrete were compared and analyzed. Best-fit curves were developped to describe diffusion coefficients and predict diffusion behavior of chloride ions.

EXPERIMENTAL APPARATUS AND PROCEDURES

Specimens

Both mortar and concrete specimens were prepared. Three different w/c ratios were used for mortar specimens and one w/c ratio was used for concrete. Details of mix design are listed as the following table.

In the mix design, w/c ratio is calculated by water divided by cementitious material. Compressive strength specimen were ϕ100mm x 200mm cylinders for concrete and 50mm x 50mm x 50mm cubes for mortar.

Diffusion Cell

Diffusion cell was designed as a 100mm x 200 mm x 120 mm rectangular container, a 4mm-thick plate with two 25mm x 25 mm square holes was placed between two cells. The detail of diffusion cell is illustrated in Figure 1. After 7 days or 28 days curing, concrete or mortar were cut into a 25mm x 25 mm square thin plate with a thickness of 4mm. After placing specimens, four sides of the plate were sealed with silicon to prevent leakage.

Chloride measurement

Several testing methods are available for chloride measurement. Traditionally, the chemical titration method is the most popular method employed by the researchers. In this study, chloride contents were monitored by chloride-selective eletrodes. One of the diffusion cell was filled with 3.5% NaCl solution and the other one was filled with distilled water. As diffusion last, chloride contents was continuously monitored.

RESULTS AND DISCUSSION

Diffusion coefficient and compressive strength

Mortar specimens can be divided into two groups according to the age of curing: 7-day curing and 28-day curing. After curing, specimens were cut into thin plates to place into diffusion cells and chloride contents were monitored. Changes of diffusion coefficients with time are illustrated in Figure 2 to Figure 3. Concrete specimens were water-cured for 7 days and similar procedures were repeated as for mortar specimens. Results are illustrated in Figure 4. The compressive strengths for mortar and concrete specimens are listed in Table 2.

Effect of w/c ratio on diffusion coefficient

As we know, w/c ratio is a key factor to control the property of concrete. General speaking, concrete is more

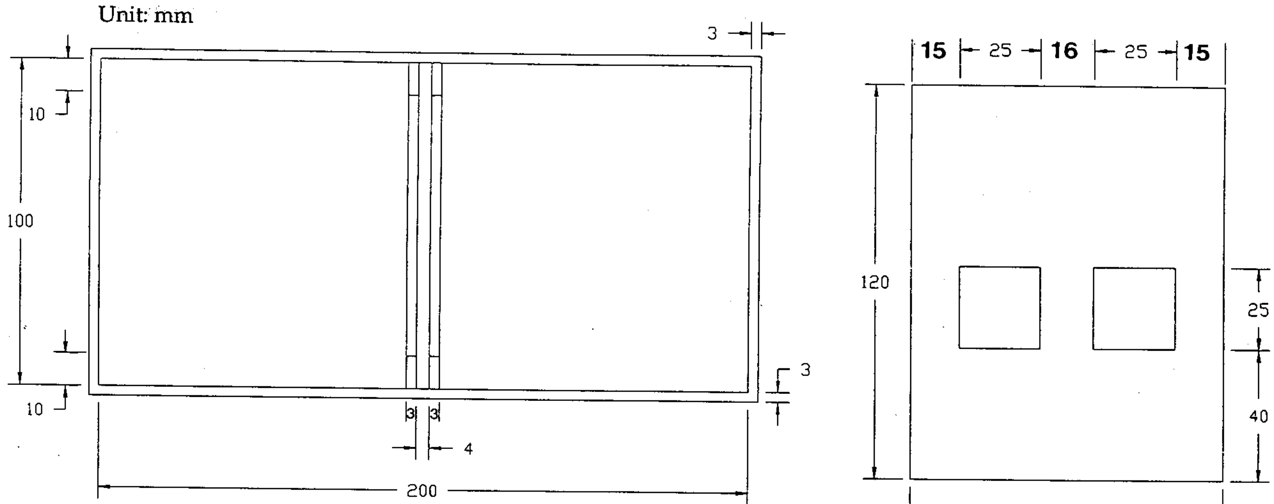

Fig. 1. Diffusion cell setup.

Table 1. Mix design for OPC and aortar specimen

	label no.	w/c	cement	water	aggregate	sand	silica fume
mortar	M5	0.5	536	268	0	1475	0
	M6		500	300	0	1375	0
	M6S1	0.6	463	300	0	1375	38
	M6S2		425	300	0	1375	76
	M7	0.7	480	36	0	1320	0
OPC	C6		318	191	1193	636	0
	C6S1	0.6	294	191	1193	636	24
	C6S2		270	191	1193	636	48

Unit: Kg/m^3

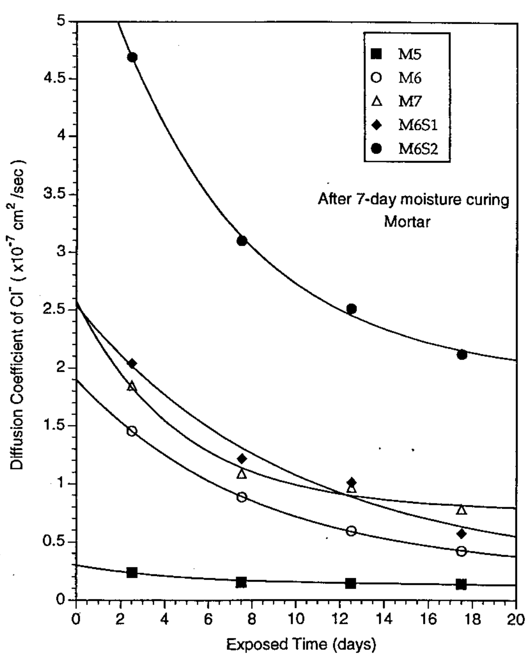

Fig. 2. Diffusion coefficients vs. exposed time for 7-day curing mortar specimens.

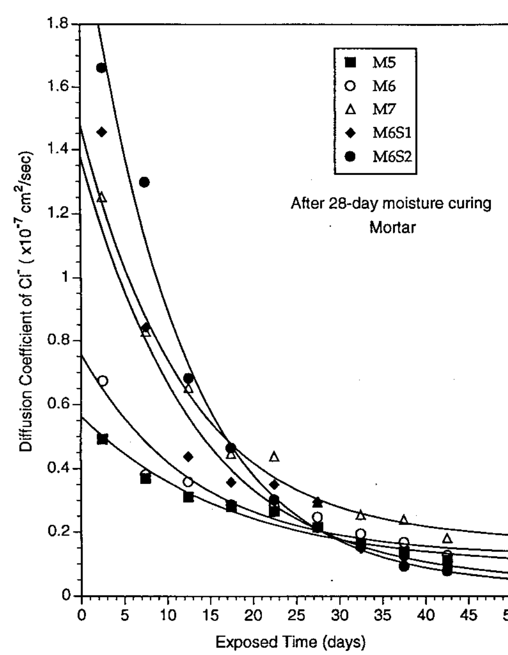

Fig. 3. Diffusion coefficients vs. exposed time for 28-day curing mortar specimens.

Table 2. Compressive Strength (MPa)

days\label	M5	M6	M6S1	M6S2	M7	C6	C6S1	C6S2
3	-----	-----	-----	-----	-----	8.7	10.8	12.9
7	26.9	20.4	22.9	19.2	13.5	10.2	11.2	16.7
28	39.8 (0.472)*	31.2 (0.674)	36.7 (1.456)	28.2 (1.661)	27.1 (1.253)	14.7 (0.575)	19.3 (0.575)	24.7 (0.444)
60	40.5 (0.164)	33.3 (0.195)	42.1 (0.149)	42.8 (0.154)	31.1 (0.256)	-----	-----	-----

*:value ( )$\times 10^{-7}$ (cm^2/sec) is diffusion coefficient.

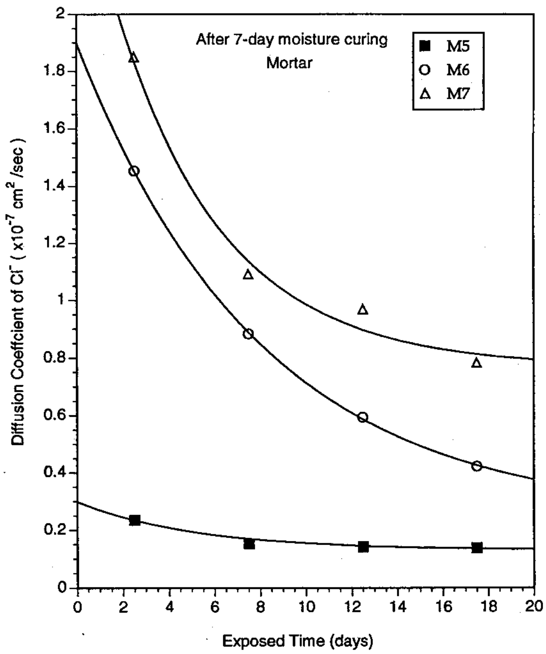

Fig. 4. Diffusion coefficients vs. exposed time for 7-day curing concrete specimens.

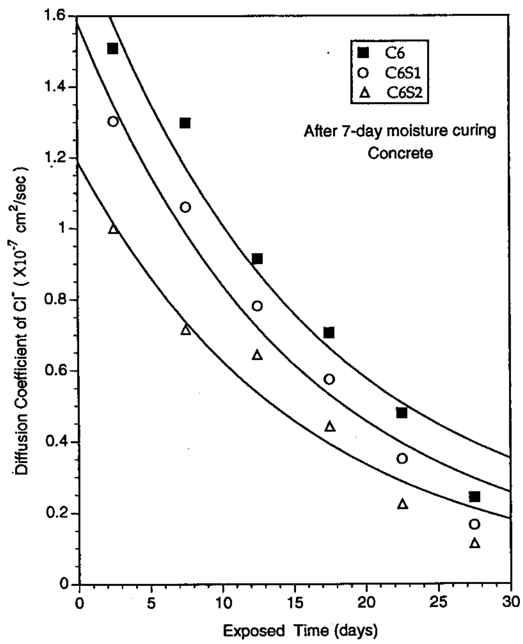

Fig. 5. Effect of w/c ratio on the chloride diffusion for 7-day curing mortar specimens.

dense if w/c ratio is lower. This imply the diffusion coefficient will increase as w/c ratio increases. Gjørv and Vennesland [6] reported that the diffusion coefficient did not change significantly with w/c ratio after long-term exposure. Figures 5 and 6 show the diffusion coefficient of 7-day and 28-day curing mortar specimens with respect to exposed time respectively. From this study, it can be found that the diffusion coefficient is dependent on w/c ratio for specimens at early age. As exposed time increases, the difference between specimens with various w/c ratios decreases.

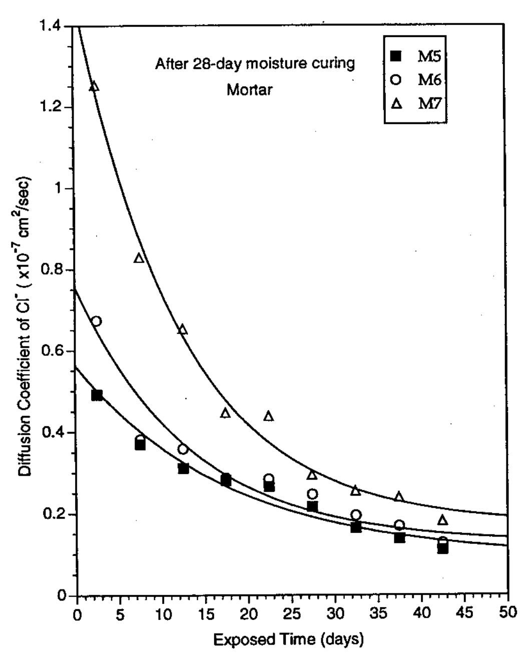

Fig. 6. Effect of w/c ratio on the chloride diffusion for 28-day curing mortar specimens.

Effect of silica fume on compressive strength and diffusion coefficient

Mortar

Silica fume is one of the pozzolan materials which can yield extra C-S-H paste through the pozzolan reaction. Figure 7 shows that adding silica fume as partial substitution of cement has higher diffusion coefficients than the control group before exposed 28 days. However, after 28 days silica-fume mortar has lower diffusion coefficient. The reasons and several mechanisms are listed as below:

1. When silica fume is used as partial substitution for cement, the amount of C_3A will decrease (under same w/c ratio). C_3A reacts with chloride ions so that free chloride ions decrease, and the diffusion coefficient will decrease.
2. Before pozzolan reaction happens, silica fume can be considered as fine aggregate . It can fill the micropores between C-S-H paste to reduce diffusion rate, however it is not benefit for compressive strength because of increasing weak interface areas.
3. At the early age, silica fume substitution will reduce the hydration reaction rate such that the compressive strength becomes lower and diffusion coefficient is higher. As pozzolan reaction continues, the compressive strength will increase if appropriate substitution

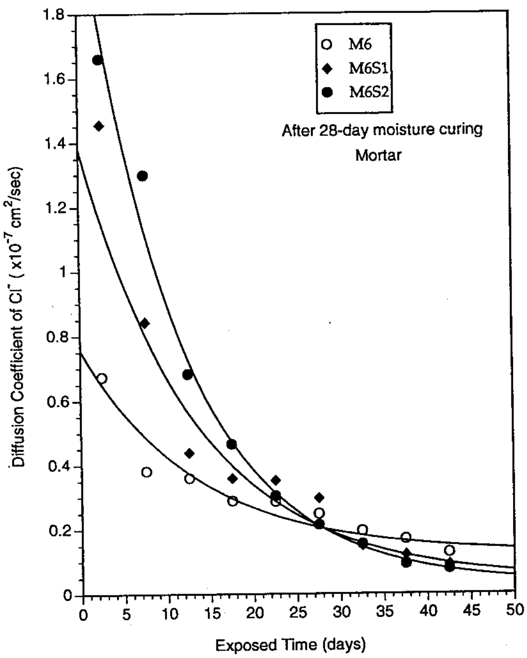

Fig. 7. Effect of silica fume on the chloride diffusion behavior in mortar.

is applied. At the same time, diffusion coefficient will decrease.

At the early age, even silica fume can fill micropores, the diffusion behavior is still controlled by low hydration rate and C_3A effect. Thus, no matter what substitution amount, a higher diffusivity is shown compared with control specimens. From Table 2, it can be found the compressive strengths at age of 7 days and 28 days have M6S1>M6>M6S2 order. This shows pozzolan effect already develops before 28 days, however 15% substitution is too large so that part of silica fume particles still remain as fine aggregate. It is also observed that 7.5% silica fume substituition group has higher compressive strength than control group and the diffusion coefficient is higher. The reason was previously explained. At the age of 60 days (exposed for 32 days), diffusion coefficient of control group became highest and 15 % silica fume substitution group showed lowest diffusion coefficient. Also from Table 2, 15% silica fume substitution group has the highest compressive strength and control group has the lowest strength at age of 60 days. It can be concluded that pozzolan effect may be fulfilled by that time and the properties of concrete is dominated mainly by pozzolan effect.

Concrete

The coarse aggregates and the transition zone around coarse aggregates exist in concrete. Therefore, two new mechanisms should be considered:

1* Transition zone can provide a good path for chloride penetration. While silica fume still remain as fine particles, micropores in transition zone can be filled so that diffusion coefficient will be reduced. Silica fume will increase the compressive strength since it improves the property of transition zone;

2* Coarse aggregates are more dense than C-S-H paste. Penetration of chloride ions mainly pass through transition zone and mortar. Thus, concrete has lower effective diffusion area compared with mortar.

Item 1* and 2* are much more important than items 1 to 4 in concrete. From Table 2, it can be found adding silica fume improves the compressive strength. Also from Figure 4, 15% silica fume substitution group has the lowest diffusion coefficient and control group has the highest value. It can be concluded that the compressive strength and diffusivity is dominated by transition zone property.

Best-fit curves and prediction of penetration depth

Diffusion rate of chloride ions depends on material property. The properties of concrete and mortar change with time since hydration reaction continues. In this study, it is found the diffusion coefficient changes rapidly at early age and its tendency slows down as hydration reaction rate becomes lower. From experimental data, best-fitting curves can be found. Theoretical speaking, best-fitting curve can be chosen in many ways. However, experience and physical judgement are needed to determine which curve is suitable. According to test data, the diffusion coefficient decreases with time, and finally reaches a stable value. In addition, the time derivative of diffusion coefficient is negative. In this study, the model of best-fitting curves can be chosen as $D(t; a, b, c) = a+b \exp(-ct)$. The equations of best-fit curves in this study are tabulated in Table 3.

Chloride ion penetrations can be caculated using best-fit curves. The prediction of chloride ion concentration vs. penetration depth is shown in Figure 8 for concrete in the submerged zone.

CONCLUSIONS

In this study, the diffusion behaviors of chloride ions in mortar and concrete at early age are evaluated. It is found that the diffusion coefficients change rapidly with time at early age and the change rate decreases with time. Adding silica fume in mortar increases the diffusion coefficient at early age. However, diffusion coefficients of silica fume mortar areless than those of ordinary portland cement mortar after pozzolanic reaction fulfills. According to this study, the use of silica fume in concrete decreases the diffusion coefficient and the more silica fume results in the less diffusion coefficient. The difference of diffusion coefficient between mortar and concrete mainly can be explained by the transition zone around

Table 3. Coefficients of best-fit curves

Label No	Curring age	Best-fit curve (Uit: cm^2/sec)
M5	7 days	$D(t^*)=2.38\times10^{-8}+1.66\times10^{-7}\exp(-1.25\times10^{-1}t)$
M6	7 days	$D(t^*)=1.29\times10^{-8}+0.17\times10^{-7}\exp(-1.921\times10^{-1}t)$
M6S1	7 days	$D(t)=2.59\times10^{-8}+2.28\times10^{-7}\exp(-1.035\times10^{-1}t)$
M6S2	7 days	$D(t)=1.91\times10^{-8}+4.17\times10^{-7}\exp(-1.642\times10^{-1}t)$
M7	7 days	$D(t)=7.67\times10^{-8}+1.80\times10^{-7}\exp(-2.114\times10^{-1}t)$
M5	28 days	$D(t)=8.69\times10^{-9}+0.47\times10^{-7}\exp(-5.552\times10^{-2}t)$
M6	28 days	$D(t)=1.24\times10^{-8}+0.63\times10^{-7}\exp(-7.482\times10^{-2}t)$
M6S1	28 days	$D(t)=4.02\times10^{-9}+1.34\times10^{-7}\exp(-7.552\times10^{-2}t)$
M6S2	28 days	$D(t)=2.85\times10^{-9}+2.14\times10^{-7}\exp(-8.882\times10^{-2}t)$
M7	28 days	$D(t)=1.70\times10^{-9}+1.30\times10^{-7}\exp(-8.261\times10^{-2}t)$
C6	7 days	$D(t)=9.71\times10^{-9}+1.74\times10^{-7}\exp(-6.407\times10^{-2}t)$
C6S1	7 days	$D(t)=3.72\times10^{-9}+1.54\times10^{-7}\exp(-6.509\times10^{-2}t)$
C6S2	7 days	$D(t)=1.10\times10^{-9}+1.18\times10^{-7}\exp(-6.455\times10^{-2}t)$

*:unit of t is day

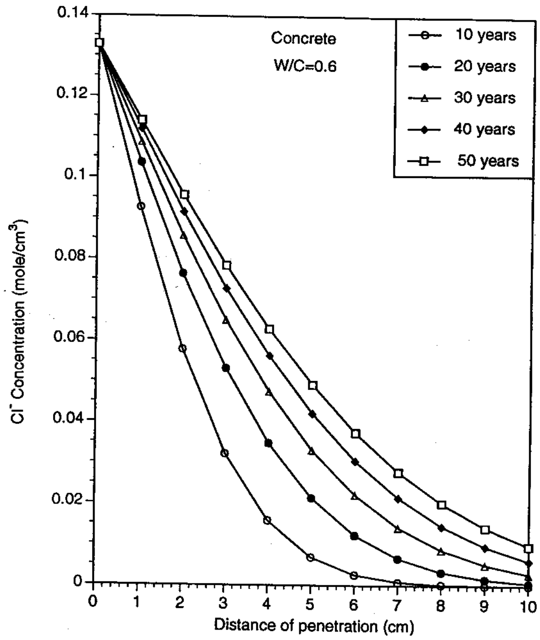

Fig. 8. Prediction of penetration depth vs. chloride ions' content diagram.

coarse aggregates. Best-fit curves can be found according to the selected mathematical model and the prediction of chloride penetration depth is possible.

ACKNOWLEDGEMENT

The authors wish to express sincere thanks to finacial support of this study by Taiwan Area National Expressway Engineering Bureau (TANEEB).

REFERENCES

1. Funahashi, M., " Predicting Corrosion-Free Service Life of a Concrete Structure in a Chloride Environment." ACI Materials Journal, Vol. 87, No. 6, pp. 581-587, November - December, 1990.
2. Nagano, H. and Takafumi, N., " Application of Diffusion Theory to Chloride Penetration into Concrete Located in Splashing Zones." Transaction of Japan Concrete Institute, Vol. 7, pp. 157-164, 1985.
3. Tikalsky, P. J., *et al*, " Strength and Durability Consideration Affecting Mix Proportioning of Concrete Containing Fly Ash." ACI Materials Journal, November - December, pp. 505-511, 1986.
4. Maslehuddin, M. *et al*, " Effect of Sand Replacement on the Early-Age Strength Gain and Long-Term Corrosion Resisting Characteristics of Fly Ash Concrete." ACI Materials Journal, January - Feburary, pp. 58-62, 1989.
5. Page, C. L., Short, N. R. and Tarras, A. el., " Diffusion of Chloride Ions in Hardened Cement Pastes." Cement and Concrete Research, Vol. 11, No. 3, pp. 395-406, 1981.
6. Gjørv, O. E. and Vennesland, Ø, " Diffusion of Chloride Ions from Seawater into Concrete." Cement and Concrete Research, Vol. 9, No. 2, pp. 229-238, 1979.
7. Clear, K. C. and Hay, R. E., " Time-to-Corrosion of Reinforcing Steel Slabs, Vol. 1: Effect of Mix Design and Construction Parameters." Interim

FHWA-RD-73-32, Fedral Highway Administration, Washington, D. C., April, pp. 103-105, 1973.
8. Page, C. L., Short, N. R. and Holden, W. R., "Influence of Different Cements on Chloride-Induced Corrosion of Reinforcing Steel." Cement and Concrete Research, Vol. 16, No. 1, pp. 79-86, 1986.
9. Subramanian, E. V. and Wheat, H. G., "Depassivation Time of Steel Reinforcement in a Chloride Enviroment - A One-Dimensional Solution." Corrosion Science, Vol. 45, No. 1, pp. 43 - 48, 1989.
10. Mangat, P. S. and Gurusamy, K., "Chloride Diffusion in Steel Fiber Reinforced Marine Concrete." Cement and Concrete Research, Vol. 17, pp. 385-389, 1987.
11. Mangat, P. S. and Gurusamy, K., "Chloride Diffusion in Steel Fiber Reinforced Concrete Containing PFA." Cement and Concrete Research, Vol. 17, pp. 640-650, 1987.