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The relationship between charge passed and the chloride-ion concentration in concrete using steady-state chloride migration test

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Abstract

The accelerated chloride migration test in this study is a modified version of the ASTM C1202-97 or AASHTO T277-96 (RCPT) method. The current, chloride-ion concentration and temperature were measured during the experiment. Four different concretes used for test had a water to cementitious ratio of 0.4, containing various mineral admixtures. The transport properties were investigated using the accelerated chloride migration test. At a steady-state chloride flux, a good correlation was found between the charge passed (obtained by integrating the current-time curve) and the chloride-ion concentration. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Migration; Steady-state; Chloride-ion concentration; Charge passed

1. Introduction

The resistance to chloride-ion penetration into concrete is a crucial parameter affecting the durability of reinforced concrete structures exposed to marine environment. Several researchers [1–3] have conducted conventional chloride diffusion test to evaluate the permeability of cement-based materials. The conventional diffusion method requires considerable time to obtain the steady-state chloride flow across the specimen. Since conventional chloride diffusion test for the cement-based materials is time consuming, the accelerated chloride-ions diffusion test methods were developed. An effective method is to apply an external electrical field for accelerating chloride diffusion or penetration.

In the rapid chloride penetration test, RCPT (ASTM C1202-97 [4] or AASHTO T277-96 [5]), the current passing through the cement-based materials in 6 h is measured, and the resistance of the concrete specimen to chloride-ion penetration is assessed by the total charge passed [6]. The RCPT method has been used investigate on the mineral admixture effect on the resistance of chloride-ion penetration [7,8]. Several studies have been performed to evaluate the influence of aggregate fraction [9], curing condition [10] and pore size [7,10] on the penetration of chloride-ion using RCPT method. Feldman et al. [11,12] correlated the initial current with charge passed. The Norwegian test [13,14], an accelerated steady-state migration test, is a modified version of RCPT. A potential of 12 V is applied in Norwegian test instead of 60 V in RCPT, and the passing chloride-ion concentration is measured in Norwegian test. Several studies [13,15] have used the Norwegian test to study the influence of different curing condition on concrete permeability. Luping and Nilsson [16,17] introduced an accelerated nonsteady-state migration test method, and a colorimetric method was also used to measure the penetration depth of chlorides. The accelerated testing method has been used to determine the chloride diffusivity in cement-based materials. The chloride diffusivity in concrete based on the nonsteady-state and steady-state chloride-ion migration tests have been carried out by Tang and Nilsson [16] and several other researchers [17,18]. Dhir et al. [19] proposed an approach to predicate the total chloride content profile of specimen under the nonsteady-state and the steady-state conditions. Garboczi and Bentz [20] developed a digital image-based model to derive the diffusivity of cement paste.

Detwiler and Fapohunda [21] pointed out that the practical difficulty is the need to measure low concentrations of chlorides in the NaOH solution when conducting the Norwegian test. In this study, the accelerated chloride migration

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test is modified from RCPT by reducing the temperature effect and providing enough samples for measuring the chloride-ion concentration during the experiment. The current, chloride-ion concentration and temperature were recorded during the test. The charge passed and chloride-ion concentration were compared and correlated.

2. Experimental program

2.1. Materials and specimen preparation

ASTM Type I Portland cement (specific gravity: 3.15), slag (specific gravity: 2.2) and fly ash (specific gravity: 1.66) were used as binders and mix proportions are shown in Table 1. Forty percent of cement was replaced by slag in Mix S and by fly ash in Mix F, respectively. In Mix M, 40% of cement was replaced by fly ash (12%) and slag (28%). River sand was used as fine aggregate and crushed limestone with a maximum size of 10 mm was used as coarse aggregate. The volume fraction (percentage of total mix volume) of fine aggregate and coarse aggregate were 0.32 and 0.29, respectively. For all mixes, superplasticizer was adjusted to keep required slump and slump flow.

For each mix, a number of cylindrical specimens (φ 100 × 200 mm) were cast and cured. After mixing, a vibrating table was used to ensure good compaction. The surface of the specimens was then smoothed, and the wet burlap was used to cover the concrete. After demolding, the specimens were cured in water (23 °C) for 6 months. The compressive strength of specimen is listed in Table 1. The accelerated chloride migration test specimen (50 mm in thickness) was obtained by sawing the midportion of cylindrical specimen.

2.2. Experimental procedure

The conventional test method for determining the chloride-ion penetration rate using the diffusion cell is time consuming, and many researchers [12,21,22] have indicated that the applied electrical potential of RCPT heats up the concrete specimen, which may affect the flow speed. The accelerated chloride migration test proposed in this study is a modified version of RCPT method. In this test, the solution volume of each acrylic cell is 4750 ml, instead of 250 ml suggested by ASTM C1202. The increasing volume may minimize the temperature effect on the test result. Fig. 1 shows that the measured temperature change is lower than that in the standard rapid chloride penetration test.

Table 1
Mix proportions and strength of concrete

Mix	C	S	F	M
Cement (kg/m^3)	524	292	271	286
Fly ash (kg/m^3)	0	0	181	57
Slag (kg/m^3)	0	195	0	133
Water (kg/m^3)	203	189	174	185
SP (kg/m^3)	6.3	5.8	6.8	5.7
Coarse aggregate (kg/m^3)	753	753	753	753
Fine aggregate (kg/m^3)	842	842	842	842
180-day strength (MPa)	58.6	65.3	58.3	43.0

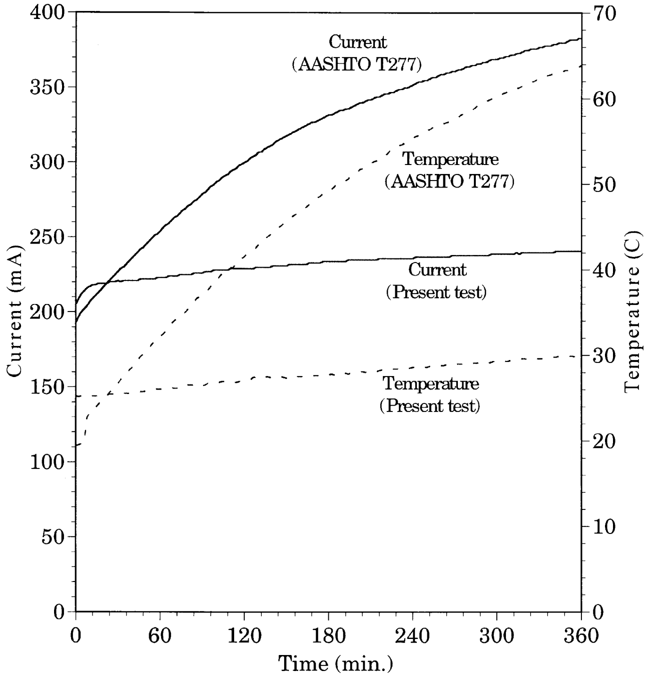

Fig. 1. Influence of test method on current and temperature from the same batch (Mix C).

The specimen was placed between two cells and the edge was sealed with an epoxy resin and vacuum-saturated by the procedures as described in ASTM C1202-97. One of the cells was filled with 0.30 N NaOH solution and another was with 3.0% NaCl solution. The cells were connected to a 60-V power source so that the NaOH electrode becomes the anode and the NaCl electrode becomes the cathode. The experimental arrangement of the accelerated chloride migration test is shown in Fig. 2. The quantity of chloride-ions passing through the concrete specimen was measured periodically. The solution in the anode was taken and chloride concentration was determined by potentiometric titration with 0.01 N silver nitrate ($AgNO_3$) solution. This measurement was performed with the 702 SM Titrino titrator and chloride-ion concentration was the average of three individual results. A data logger was used to record the current and the temperature of NaOH solution during the experiment.

3. Results and discussion

3.1. Rate of chloride migration

The chloride-ion concentrations vs. time curves are shown in Fig. 3, and the curves become quite linear after the chloride flux reaches steady-state. It is found that the

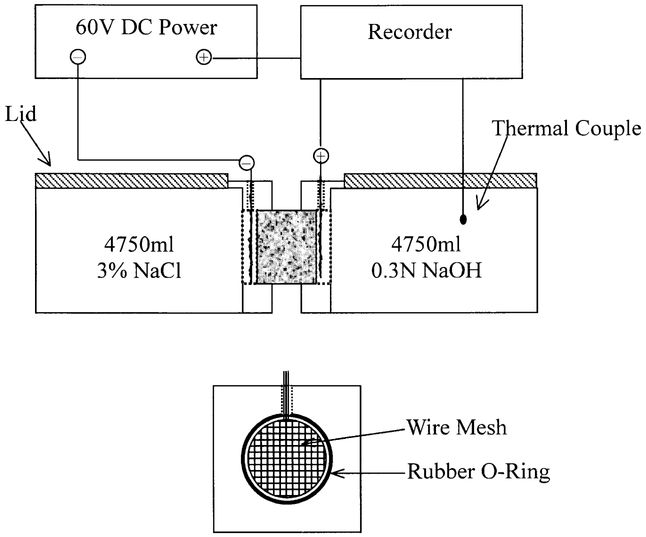

Fig. 2. Schematic diagram of accelerated chloride migration test cell.

Table 2
Rate of chloride migration

Mix	t_p (day)	k (mmol/l/day)	k, average (mmol/l/day)	r
C				
C-1	1.6	19.47		.996
C-2	1.8	18.14	18.48	.998
C-3	1.7	17.84		.938
S				
S-1	3.3	10.61		.998
S-2	4.5	8.89	9.68	.974
S-3	4.0	9.55		.993
F				
F-1	5.2	6.01		.996
F-2	4.9	6.98	6.48	.996
F-3	4.5	6.44		.993
M				
M-1	3.8	10.37		.996
M-2	3.7	11.68	10.80	.995
M-3	3.7	10.35		.993

chloride diffusion of all mixes reaches a steady-state after chloride-ions pass through the specimen. The time-span (t_p) for chloride-ion penetration is listed in Table 2 and t_p of fly ash and slag concretes is longer than that of control concrete (Mix C). As shown in Fig. 3, for Mix F, the chloride-ion concentrations at all ages are lower than those of other three mixes. Linear regression is carried out for the steady-state portion of the curve to obtain the chloride migration rate k, which is the slope of the chloride-ion concentration versus time curve. Both of the chloride migration rate and the correlation coefficient r are listed in Table 2. From the results of chloride migration rate, it appears that the resistances to chloride-ion migration of concrete containing either slag or fly ash is higher than that of plain Portland cement concrete. In this investigation, it also shows that the resistance to chloride-ion migration in fly ash concrete is higher than that in slag concrete. This may be related to the refined pore structure of the mixes containing pozzolans.

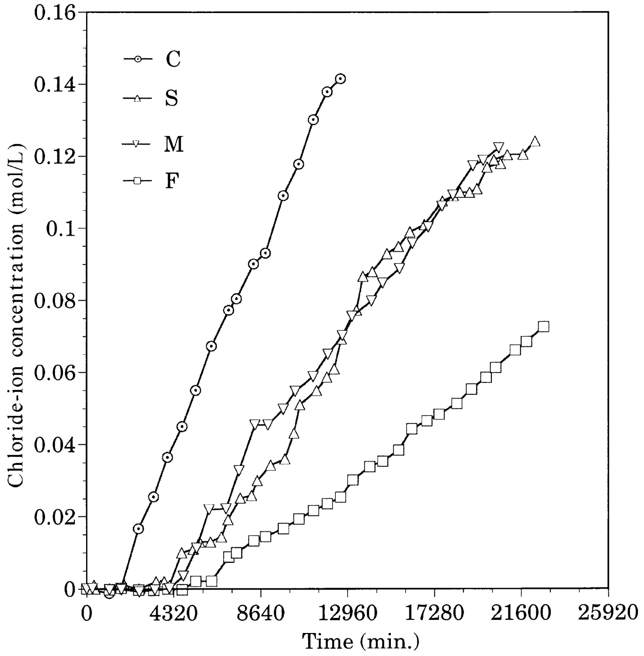

Fig. 3. Variations of chloride-ion concentration in anode cell.

3.2. Current and charge passed

The current across each cell and the temperature of NaOH solution were recorded with a data logger during the experiment. The variation over time in the current across each cell is shown in Fig. 4 for all mixes. Measurements of initial current (I_c), final current (I_f), initial temperature (T_o) and final temperature (T_f) for each specimen are presented in Table 3. The temperature variations for the specimens are from 3 to 8 °C during the experiment. The current I_p at t_p (the time-span for chloride-ion penetration) is also listed in Table 3. The percentage of current difference between I_p and I_c ranges from -3.6% to 143.9% and from -8.1% to 25.4% between I_f and I_p as listed in Table 3. The difference between current variations before and after chloride-ion passes through specimen illustrates that the effect of other ions in the pore solution on the current is not significant (or it is assumed that the ratio of chloride-ion to the other ions in the pore solution is constant) after the chloride-ion passes through specimen.

3.3. Charge passed and chloride-ion concentration

The transference number of an ion in a given electrolyte solution is the fraction of the total electrical current carried by ions [23]. According to the definition, the chloride

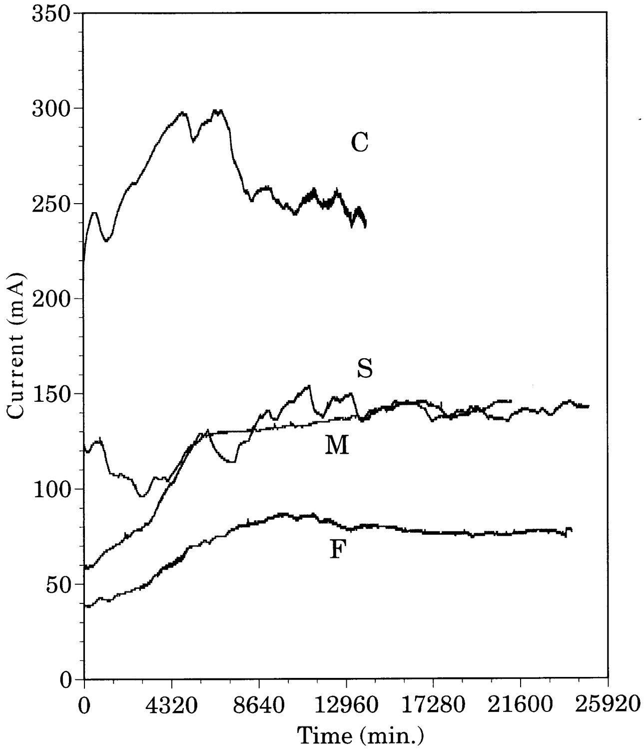

Fig. 4. The variation over time in the current across each cell.

transference number can be calculated by the following equation [22,24]

$$t_{cl} = \frac{Q_{cl}}{Q}, \tag{1}$$

where t_{cl} is the chloride transference number, Q_{cl} is the charge carried by chloride-ions (C) and Q is the total charge (C). After the chloride flux reaches steady-state, chloride-ions migrate to the anode and release electrons as (Eq. (2))

$$\mathrm{Cl}^- \rightarrow \frac{1}{2}\mathrm{Cl}_2 + \mathrm{e}^-. \tag{2}$$

Table 3
Measurement of charge passed, current and temperature

Mix	Testing duration (days)	I_c (mA)	I_p (mA)	I_f (mA)	$[(I_p-I_c)/I_c]$ 100 (%)	$[(I_f-I_p)/I_p]$ 100 (%)	T_o (°C)	T_f (°C)
C								
C-1	9.7	205	259	238	26.3	− 8.1	25.2	29.4
C-2	9.0	238	290	280	21.8	− 3.4	24.2	31.8
C-3	8.2	231	252	267	9.1	5.95	24.0	32.0
S								
S-1	17.4	117	114	143	− 2.6	25.4	23.5	26.5
S-2	15.3	92	109	134	18.5	22.9	24.3	26.9
S-3	9.2	110	106	124	− 3.6	17.0	23.8	27.0
F								
F-1	16.8	39	79	78	102.6	− 1.3	24.1	28.5
F-2	17.3	43	100	108	132.6	8.0	23.3	27.5
F-3	10.7	41	100	96	143.9	− 4.0	24.2	28.8
M								
M-1	14.7	62	125	145	101.6	16.0	24.2	27.2
M-2	11.3	75	160	188	113.3	17.5	24.1	27.0
M-3	13.7	67	144	135	114.9	− 6.2	23.7	26.9

According to Faraday's results, the charge carried by chloride-ions (Q_{cl}) is determined by the mole number of chloride that passes through the circuit. By definition

$$Q_{cl} = zFn_{cl}, \tag{3}$$

where z is the electrical charge of chlorides, F is the Faraday constant (C/mol) and n_{cl} is the mole number of chloride (mol).

From Eqs. (1) and (3), the chloride-ion concentration C_{cl} is written as

$$C_{cl} = \frac{n_{cl}}{V} = \frac{t_{cl}}{zFV}Q, \tag{4}$$

where V is the volume of solution.

The charge passed Q is determined by integrating the current-time curve. The charge passed versus time curve is presented in Fig. 5, and it appears that a linear relationship exists for each mixes. The chloride-ion concentrations versus time curves shown in Fig. 3, the curves also appear that a linear relationship exists after the chloride flux reaches steady-state for each mix. By comparing the experimental result with the theoretical result (C_{cl} from Eq. (4)), a linear relationship seems to exist between chloride-ion concentration and the charge passed after chloride flux

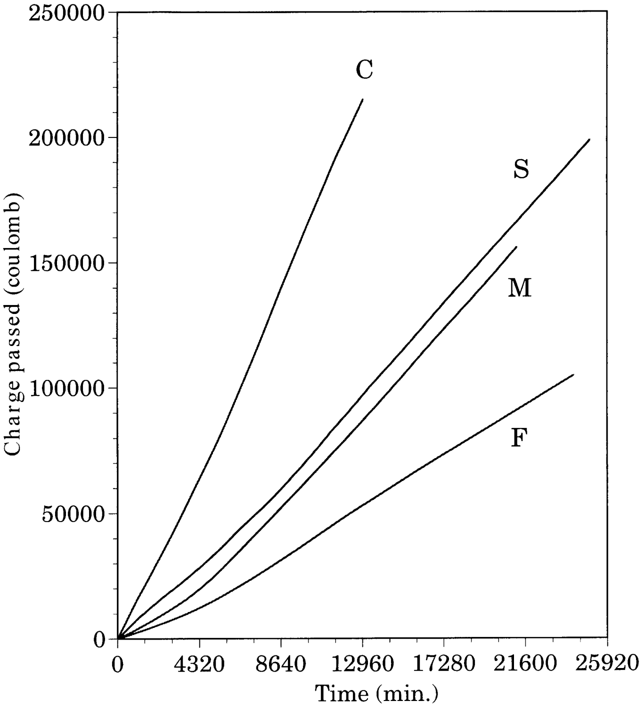

Fig. 5. The variation over time in charge passed.

reaches steady-state, which implies a constant or only small variations in t_{cl} and can be expressed as (Eq. (5))

$$C_{\mathrm{cl}} = KQ + a, \tag{5}$$

in which C_{cl} is the chloride-ion concentration in mole per liter, Q is the total charge passed in coulomb, K is the chloride-ion required to transport a coulomb of charge in mole per liter per coulomb and a is the value of the y-axis intercept. Table 4 lists the linear regression values of K, a and R (correlation coefficient) for all the specimens. The correlation coefficient R listed in Table 4 represents a fairly good linearity between the chloride-ion concentration and the charge passed. In Table 4, constants K and a show a little difference among the mixes with or without pozzolans. In order to illustrate the relationship between the chloride-ion concentration and the charge passed based on the experimental data in this study, the charge passed is graphically correlated with the chloride-ion concentration as shown in Fig. 6. The circle point represents all the test data for four mixes and the empirical relationship that relates the chloride-ion concentration to the charge passed is derived as

$$C_{\mathrm{cl}} = 7.344 \times 10^{-7} Q - 7.87 \times 10^{-3}. \tag{6}$$

Through linear regression, the correlation coefficient for the model (Eq. (6)) is .958. The slope of the regression line, 7.344×10^{-7} mol/l/C, is the chloride-ion concentration required to transport a coulomb of electrons. Because the chloride flux is considered at steady-state in this model, the chloride-ion concentration gradient is not a constant between the threshold chloride-ion concentration and the chloride flux at steady-state. The x-axis intercept Q_{o} calculated from Eq. (6) is 10,720 C. The Q_{o} can be used to estimate the charge at the threshold chloride-ion concentration. This relationship is verified by the experimental set-up and the electrolytes used in the present investigation. However, it may not be suitable to apply to cases under other testing condition.

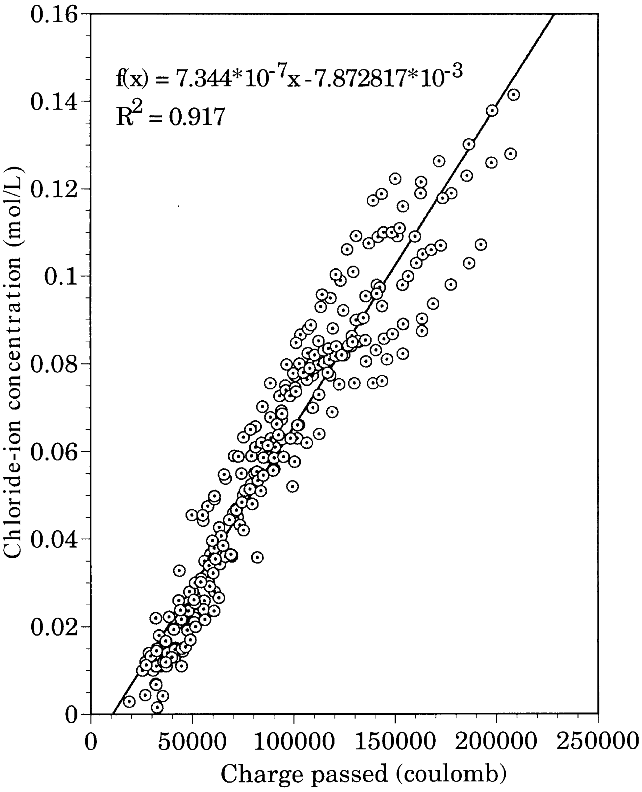

Fig. 6. Correlation between charge passed and chloride-ion concentration for different types of concrete.

Table 4
The estimated values of K, a and R

Mix	K ($\times 10^{-7}$)	a ($\times 10^{-2}$)	R
C			
C-1	8.13	−1.49	.995
C-2	7.34	−0.69	.994
C-3	7.29	−1.14	.953
S			
S-1	9.53	−2.36	.990
S-2	8.47	−1.11	.962
S-3	9.97	−2.43	.993
F			
F-1	8.87	−1.75	.996
F-2	7.51	−1.06	.965
F-3	8.11	−1.04	.993
M			
M-1	8.61	−0.35	.997
M-2	7.00	−1.02	.980
M-3	7.65	−1.67	.991

4. Conclusions

In this study, a modified accelerated chloride migration test was proposed to minimize the temperature effect. The current, chloride-ion concentration and temperature were measured during the experiment. The advantage of increasing the cell volume is not only to prevent the temperature change but also to provide more samples for measuring the chloride-ion concentration during the experiment.

Based on experimental results and the regression analysis, the following conclusions can be drawn.

(1) After the chloride flux reaches steady-state (the chloride-ion concentration change in the anodic cell becomes constant), a good correlation between the chloride-ion concentration and the charge passed is found.

(2) Measurement of charge passed provides a rapid way of predicting chloride-ion concentration without measuring the chloride-ion concentration in the anode cell.

(3) The application of fly ash or slag in concrete may increase the resistance to chloride-ion penetration.

There is still a need for more experimental results to calibrate the correlation between the charge passed and chloride-ion concentration.

Acknowledgments

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