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Evaluation of Chloride Penetration in OPC Concrete by Silver Nitrate Solution Spray Method

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Abstract: The durability of the reinforced concrete structures is greatly affected by chloride ion diffusion. The purpose of the present study is to evaluate the chloride migration coefficient under accelerated test conditions. Accelerated test methods permit migration rates to be evaluated for a specific mix design in a relatively short time. Ordinary Portland cement concretes of three different water-cement ratios 0.55, 0.45, 0.40 are used in this study. Two accelerated non-steady state test methods (i) Rapid chloride migration test (RCMT) (NT BUILD 492) and (ii) Accelerated chloride migration test (ACMT) with 24V are used. Chloride penetration depth is obtained by Colourimetric method (0.1N $AgNO_3$) and comparison is made with two accelerated test methods. It has been observed that in RCMT, the chloride migration coefficient increases with increase in water-cement ratio and is about 2.5 times less for w/c ratio 0.40 when compared to that of w/c ratio 0.55 and in ACMT, the chloride migration coefficient is 1.7 times less. The rate of Chloride penetration between two accelerated test methods showed good correlation.
Keywords: Concrete, Chlorides, Durability, Migration Coefficient, OPC Concrete, Silver Nitrate.

Introduction

Intrusion of chloride ion is one of the main causes for the corrosion of steel reinforcements in concrete structures exposed to nautical environment or de-icing salts. The penetration rate of chlorides into the concrete depends upon many factors such as pore geometry, chloride diffusivity, chemical reactions, and environmental conditions in which chloride diffusivity is the major key factor influencing the durability of the concrete. The chloride diffusion coefficient can be determined by natural diffusion methods such as salt ponding test (AASHTO T259), Immersion test (NT BUILD 443) etc. nevertheless, such tests are protracted and costly[1]. By considering those limitations, some researchers found rapid test methods such as Rapid chloride permeability test (RCPT), Rapid chloride migration test (RCMT), Acceleration chloride migration test (ACMT) etc. A quick and easy method of predicting the durability of concrete structures is RCPT, adopted as an ASTM standard method, which is originally designed by Whiting[2]. There are so many criticisms towards RCPT because of poor test results due to total charge passed through the concrete specimen and this result does not give information about the diffusion of chloride ions[3]. One of the quick methods for predicting migration coefficient in concrete, which has shown good performance in test results and linearly correlated well with natural diffusion test method is Rapid chloride migration test[4] and later these rapid test method standardized as NT BUILD 492[5]by Nordic Council Of Ministers. In order to avoid the heating of specimen as in RCPT, applied voltage and volume of salt solution may be amplified to facilitate with heat dissipation and rise in temperature does not arise in the test[6, 7]. The chloride ion penetration depth can be determined using 0.1N silver nitrate solution ($AgNO_3$) on the freshly split concrete and this method is known as Colourimetric method[8,9]. This system applied the standard where a white deposit is formed through the reaction involving silver ion (AG^+) and chloride ion (Cl^-). If colourimetric method is employed to concrete structures exposed to chloride ion, supplementary precipitation reaction happens next to white precipitation i.e. brown precipitation, occurs due to calcium hydroxide [$Ca(OH)_2$] resulting since hydration of cement[10].Another efficient technique is to apply an electric field for accelerating chloride migration or penetration is Accelerated chloride migration test (24V)[11]. With this outcome, the work has been framed to evaluate the chloride migration coefficient for concrete by two methods i.e., RCMT and ACMT. Also, Colourimetric technique (0.1 N of $AgNO_3$) is used to obtain the chloride penetration depth.

Experimental Programme

Table 1 presents the mix design for OPC concretes with three different water-cement ratios 0.55(S1), 0.45(S2), and 0.40(S3). The materials used are: commercially available 53-grade ordinary Portland cement of specific gravity 3.14, river sand of fineness modulus 3.0 conforming zone II as per IS 383-1970, coarse aggregate with a specific gravity 2.6 and normal potable water.

For each w/c ratio, cylindrical specimens (ø100×200mm) were cast. In addition 150 mm cubes also cast for compressive strength. Table vibrator was exercised to make certain proper compaction. The surface of the specimen is smoothened with the trowel. The 28 day average cube compressive strength are 42 MPa, 57 MPa, 66 MPa respectively for S1, S2, S3 concretes.

Table 1. Mix Details

Set	W/C ratio	Water (kg/m^3)	Cement (kg/m^3)	Fine aggregate (kg/m^3)	Coarse aggregate (kg/m^3)
S1	0.55	170	309	860	1056
S2	0.45	170	378	801	1056
S3	0.40	170	425	709	1056

Rapid Chloride Migration Test

Rapid chloride migration test demonstrated in NT BUILD 492 is used. At the age of 28 days, the (ø100×200mm) cylindrical specimens are sliced for 50mm thick using water-cooled concrete cutting machine denoted as top, middle and bottom. The 50 mm thick sliced specimens are used for RCMT test and the test arrangement is shown in Fig. 1. The slanting position was designed to expel small gas bubbles that appear on the cathode plate during testing [4]. DC Power packs with constant voltage out-puts (variable in the range of 0-60V) are used. The solution level of anolyte chamber (0.3 N NaOH Solutions) and Catholyte chamber (10% NaCl solution) are same. Cathode chamber (10% NaCl) is kept large to prevent build-up of the OH^- and depletion of Cl^-[6,12]. Turn on the power, with the voltage preset at 30V, and record the initial current and initial temperature in anolyte chamber.

Table 2. Voltage and Test Duration for Concrete Specimen (NT BUILD 492)

Initial current I_{30v} (with 30 V) (mA)	Applied voltage U (after adjustment) (V)	Possible new initial current I_o (mA)	Test duration t (hour)
$I_o < 5$	60	$I_o < 10$	96
$5 \leq I_o < 10$	60	$10 \leq I_o < 20$	48
$10 \leq I_o < 15$	60	$20 \leq I_o < 30$	24
$15 \leq I_o < 20$	50	$25 \leq I_o < 35$	24
$20 \leq I_o < 30$	40	$25 \leq I_o < 40$	24
$30 \leq I_o < 40$	35	$35 \leq I_o < 50$	24
$40 \leq I_o < 60$	30	$40 \leq I_o < 60$	24
$60 \leq I_o < 90$	25	$50 \leq I_o < 75$	24
$90 \leq I_o < 120$	20	$60 \leq I_o < 80$	24
$120 \leq I_o < 180$	15	$60 \leq I_o < 90$	24
$180 \leq I_o < 360$	10	$60 \leq I_o < 120$	24
$I_o \geq 360$	10	$I_o \geq 120$	6

During the test, temperature in anolyte chamber should be between 20-25 ^{O}C. The variable such as voltage to be applied and test duration depends on the initial current and is shown in Table 2. Table 3 shows the applied voltage and test duration adopted for different w/c ratio used in the present study. It may be noted that the test duration is 24 hrs for all three sets of concrete. Record the final current and temperature in anolyte chamber before terminating the test. Remove the specimen from the test setup, rinse it with tap water, wipe-off excess water and split them axially into two pieces. Spray 0.1N $AgNO_3$ on the freshly split specimen as represented in Fig 2. Once the white silver chloride precipitation on the axial split surface is apparently evident (nearly about 15mins), the chloride penetration depth has been measured with the help of ruler or Vernier calliper, at an intervals of 10mm.

Table 3. Voltage and Test duration adopted for different Concretes

Concrete	Initial current I_{30}v (mA)	Applied Voltage (V)	New current (mA)	Test duration (hr)
S1	57	30	57	24
S2	66	25	56	24
S3	48	30	48	24

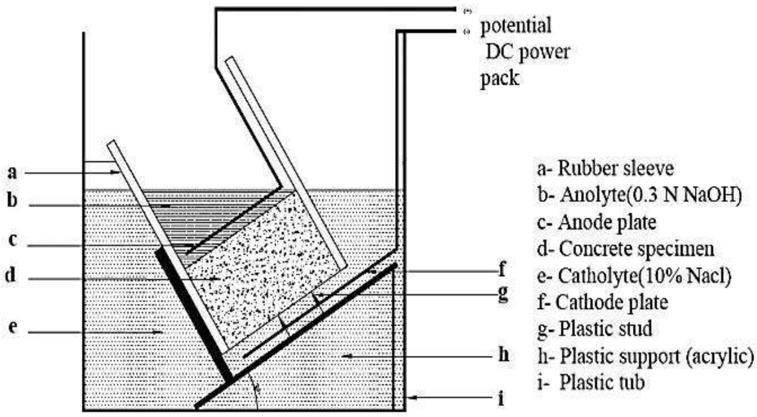

Figure 1. Test arrangement of RCMT

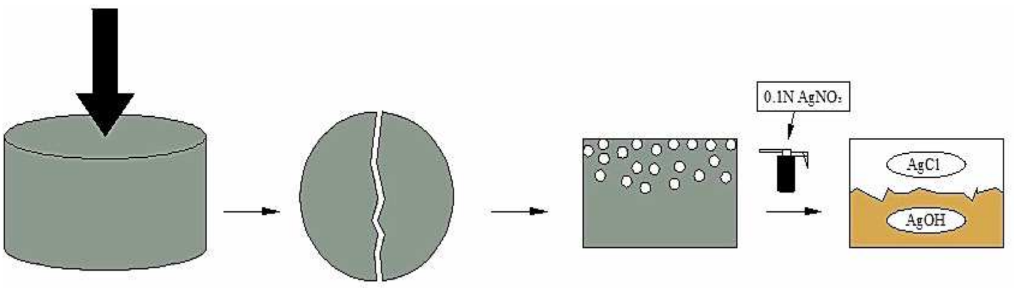

Figure 2. Schematic Representation of Colourimetric Method

Accelerated Chloride Migration Test

Chiang et. al.,[1] and Yang et. al.,[12] used ACMT for evaluating the migration coefficient and the test procedure is described below. Ø100×50mm specimen was positioned in linking two acrylic cells as shown in Fig 3. Each cell with a solution volume of 250ml was used. The anode cell was filled with 0.3mol/l of NaOH solution and the cathode cell was filled with 0.52mol/l NaCl solution. Two mesh electrodes (ø100mm) were located on the ends of the specimen so that the electrical field is applied across the 50mm thick concrete slice. The cells were coupled to 24V DC power pack for a duration of 24-hr, in which cathode is attached to the negative terminal and anode is attached to the positive terminal of the power supply. After switching on the electric field, initial current and initial temperature in an anolyte solution is to be measured. Higher volumes of catholyte and anolyte solutions may minimize the temperature effect on the test results[11]. Before terminating the test final temperature in anolyte solution is measured as 24°C. Colourimetric method was then used on the freshly split specimen to measure the chloride penetration depth.

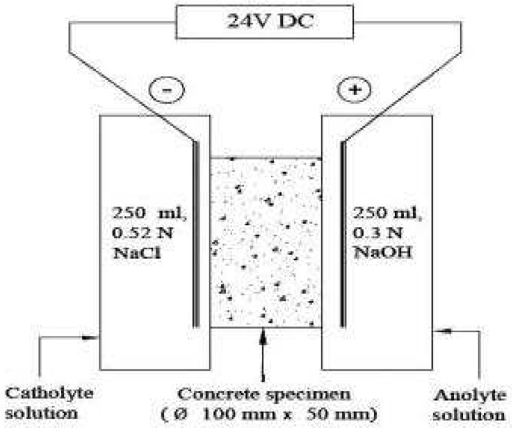

Figure 3. Test Arrangement of ACMT

Results and Discussions

Chloride Migration Coefficient From RCMT

In the RCMT, chloride ions will be transferred through the sample under an applied voltage. The non-steady-state migration coefficient (M_{ns}) was computed from modified Fick's second law which is given in Eq. (1)

$$\frac{dC}{dt} = M_{ns}\left(\frac{d^2C}{dx^2} - \frac{|z|FE}{RT}\frac{dC}{dx}\right) \quad (1)$$

where C is the concentration of chloride ions, z is the electrical charge of chloride (-1), F is Faraday constant (9.648×10^4 J/ (V·mol)), E is the strength of electric between anode and cathode (V/m), R is the universal gas constant (8.314 J/K·mol), T is the average temperature in anolyte solution (K).As shown in equation (1), M_{ns} is relatively constant and has the dimension as m^2/sec. In this case analytical solution to Eq. 2 can be derived, as reported by (Tang et. al., 2012; Crank., 1975).

$$C = \frac{c_o}{2}\left(e^{ax}.\,\mathrm{erfc}\left(\frac{x + aM_{ns}.t}{2\sqrt{M_{ns}.t}}\right) + \mathrm{erfc}\left(\frac{x - aM_{ns}.t}{2\sqrt{M_{ns}.t}}\right)\right) \quad (2)$$

where 'a' is the factor of the electrical potential (a=zFE/RT) and erfc is complement to the error function erf. The non-steady-state migration coefficient can be computed once the electrical field is large enough and the chloride penetration depth x_d as:

$$M_{ns} = \frac{RT}{zFE}\frac{x_{d-\alpha\sqrt{x_d}}}{t} \quad (3)$$

Where ὰ can be taken as laboratory constant

$$\alpha = 2\sqrt{\frac{RT}{zFE}}.\,\mathrm{erf}^{-1}\left(1 - \frac{2c_d}{c_o}\right) \quad (4)$$

where c_d is the chloride concentration when colour changes (0.07N for OPC concrete), c_o is chloride concentration in cathode chamber (2N). The chloride migration coefficient can be computed using Eq. (3) and is presented in Table 4.

Table 4. Test Results from RCMT and ACMT

Concrete	RCMT			ACMT		
	x_d (cm)	M_{ns} $(1\times10^{-12}m^2s^{-1})$	R_p (mm/v-hr)	x_d (cm)	M_{ns} $(1\times10^{-12}m^2s^{-1})$	R_p (mm/v-hr)
S1	4.27	24.97	0.0593	2.38	12.65	0.0413
S2	2.25	12.68	0.0375	1.70	9.55	0.0295
S3	2.06	9.613	0.0286	1.30	7.21	0.0226

Chloride Migration Coefficient from ACMT

In the ACMT, chloride ions move the sample under a constant applied voltage (24V). Same Eq. (3) can be applied to determine the chloride migration coefficient and is detailed in table 3. In which c_0 value from Eq. (4) is changes to 0.52N, because we are using 3% NaCl in the Catholyte solution. Rate of penetration (R_p) is calculated using Eq. (5) and is presented in Table 4.

$$R_p = \frac{x_d}{V.t} \quad (5)$$

Where, x_d is the Average penetration depth (mm), V is applied voltage, t is test duration (hr).

Effect of Water-Cement Ratio on Chloride Migration Coefficient

The chloride migration obtained from two accelerated test methods is evaluated based on colourimetric method. A good correlation is obtained between w/c ratio and migration coefficient, is shown in Fig. 4. It has been examined that as water-cement ratio increases, migration coefficient increased. Using linear regression analysis, the correlation coefficient R^2 value for RCMT and ACMT is 0.8927, 0.9767 respectively.

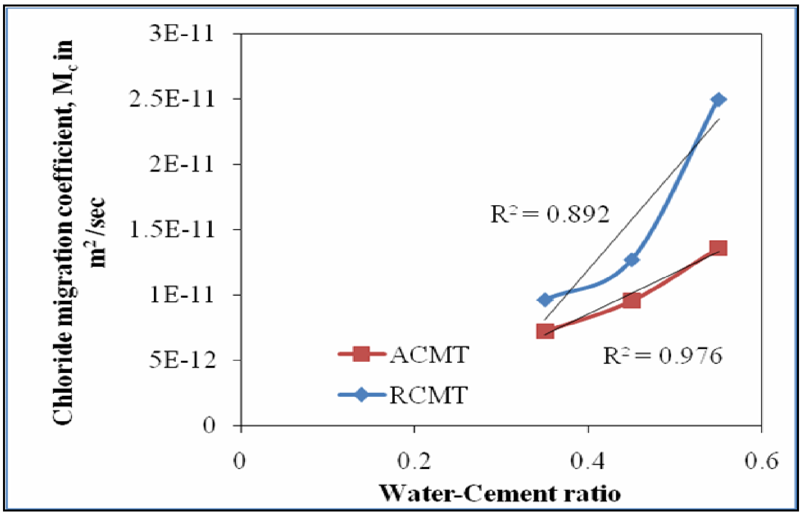

Figure 4. Graph between Water-cement ratio and Chloride migration Coefficient

Correlation between RCMT and ACMT Migration Coefficients

Chloride migration coefficient between two test methods is presented in Fig. 5 (a-c). As the water-cement ratio increases correlation coefficient R^2 value is decreased and highest R^2 value is observed for w/c ratio 0.40. Since, two migration coefficients showing good correlation, ant one method may be used in the evaluation of the chloride migration coefficient.

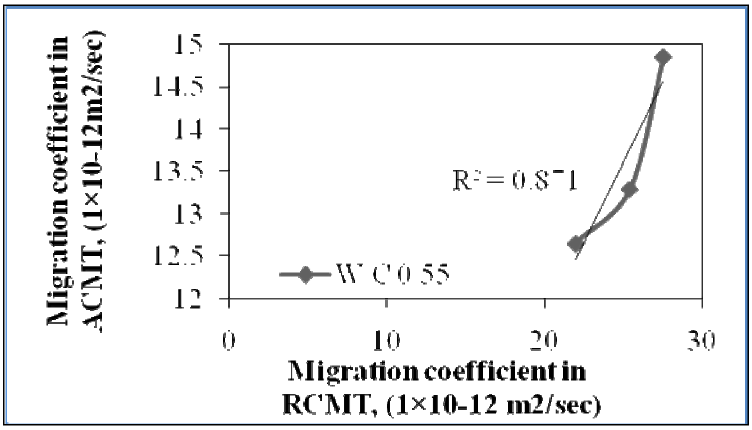

Figure 5a. Correlation between Migration Coefficient in RCMT and ACMT for w/c 0.55

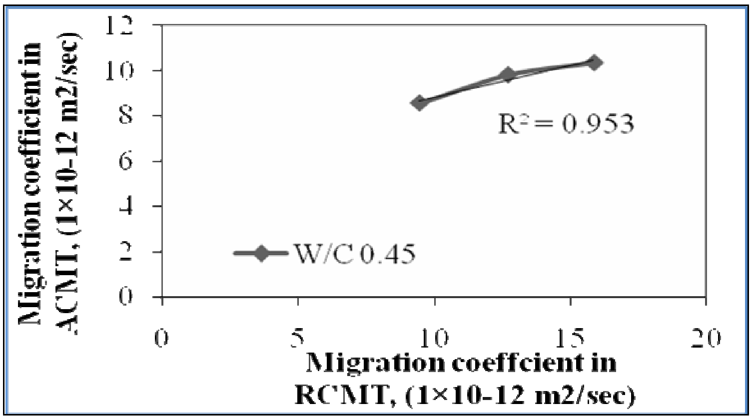

Figure 5b. Correlation between Migration Coefficient in RCMT and ACMT for w/c 0.45

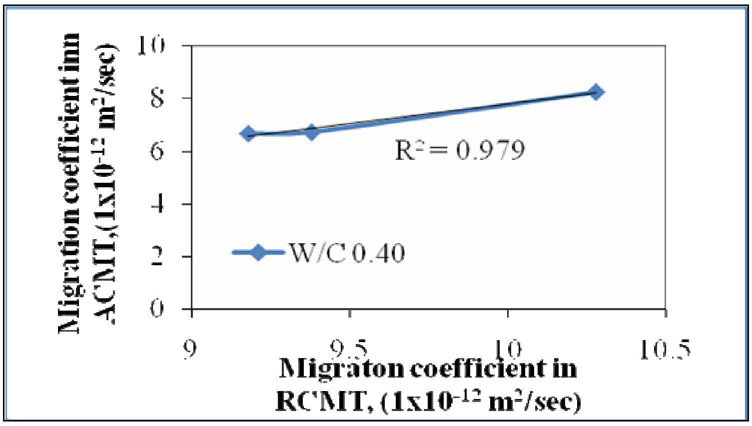

Figure 5c. Correlation between Migration Coefficient in RCMT and ACMT for w/c 0.40

Conclusions

The average penetration depth and chloride migration coefficient were evaluated by two acceleration migration test methods. Based on the experimental investigations, it has been observed that the chloride migration coefficient of concrete is powered by the w/c ratio and increases with increasing w/c ratio.The chloride penetration depth was examined more in RCMT compared to ACMT. Highest R^2 value was observed for w/c ratio 0.40 between RCMT and ACMT.

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