

- Technical paper -

## DIFFUSION OF Cl<sup>-</sup> IONS IN PARTIALLY DRY AND SATURATED CRACKED REINFORCED CONCRETE MEMBERS

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**ABSTRACT:** Both of the ingress of chloride (Cl<sup>-</sup>) ions along the movement of NaCl solution due to capillary suction and diffusion through crack were studied. Cracked reinforced concrete specimens were exposed to NaCl solutions and penetrated profiles were tested by Electron Probe Microanalyser (EPMA). Diffusion coefficients (Dap) from crack surface of partially dry samples showed higher than those of exposed surface whereas saturated samples showed almost same from both surfaces. Dap were found to be time dependency as decreasing with time mainly due to continuation of hydration and other mechanisms. An empirical formula was proposed to estimate the notational surface Cl<sup>-</sup> ions concentrations (Cs).

**KEYWORDS:** Cl<sup>-</sup> ions, crack, reinforced concrete, partially dry, ingress mechanisms, Fick's law, diffusion coefficient (Dap), notational surface concentration (Cs), NaCl solution concentration, durability.

### 1. INTRODUCTION

The life spans of the structures exposed to severe environments are found to be comparatively shorter than others. In order to make them durable up to required design life, considerations should be taken carefully on the basic real mechanisms which can occur in those structures. Possessing of such knowledge can lead to be able to prevent or can be done necessary remedial works on time. The prediction of life span of uncracked reinforced concrete structures can be done almost accurately at current knowledge level. However, if some defects such as cracks appeared in the structure mainly due to structural loads, the deterioration and degradation can speedily take place due to the transportation and accumulation of harmful chemical substances such as chloride (Cl<sup>-</sup>) ions.

A detailed study about the Cl<sup>-</sup> ions ingress around a single crack was carried out in two experiments of Exp I and II, by using partially dry and saturated reinforced concrete samples respectively. Based on the results, it was found that the initial moisture content is playing a very important role on the Cl<sup>-</sup> ions transportation into concrete. This fact is in agreement with previous research [1]. Concentration profiles due to various effects such as crack width and cover thickness etc. of Exp I were discussed in detail in reference [2].

### 2. EXPERIMENTAL PROGRAM

#### 2.1 MATERIALS, MIXES AND SAMPLES PREPARATION

A total of 16 samples, 9 from Exp I and 7 from Exp II were tested and details were shown in Table 3. For Exp I, reinforced concrete prisms of size of 100 x 100 x 400 mm as shown in Fig.1 were subjected to three

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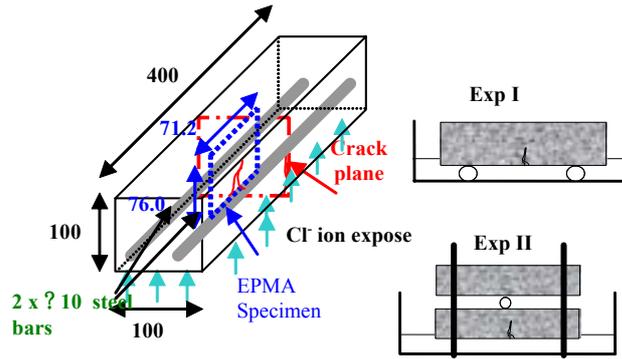
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**Table 1. Composition and Property of Cement**

Density	3.16 g/cm <sup>3</sup>
Specific surface area	3260 cm <sup>2</sup> /g
Initial set (h:min)	2:15
Final set (h:min)	3:40
Soundness	Good
SO <sub>3</sub>	2.02%
IG loss	1.65%
Alkali content	0.54%
Cl content	0.012%
C <sub>3</sub> S	52%
C <sub>2</sub> S	22%
C <sub>3</sub> A	9%
C <sub>4</sub> AF	9%



**Fig.1 Location of EPMA Sample in Small RC Beams, Units in “mm”**

**Table 2. Mix Proportion and Property of Concrete**

Sr.No	w/c	Cement kg/m <sup>3</sup>	Water kg/m <sup>3</sup>	Sand kg/m <sup>3</sup>	Coarse Agg kg/m <sup>3</sup>	Agg Vol %	C Strength N/mm <sup>2</sup>	SP
1	0.25	720	180.0	614.40	880.50	57.1	81.04	0.80%
2	0.45	424	190.8	768.00	941.60	67.3	45.04	-
3	0.65	277	180.0	911.40	947.00	71.2	27.86	-

points loading to create cracks. On the other hand, for Exp II, smaller size of beams of 70 x 70 x 400 mm were used and cracks were created by using torque wrenches (loading frames set up) and

the loading frames were fixed to samples through out the exposure period in order to keep the crack width constant. The various concentrations of the NaCl solutions used for exposure tests were shown in Table 3. Cover thickness of 25 mm and crack width of 0.2 mm were kept constant for all specimens.

Ingredients used in concretes were ordinary Portland cement with 5~12.3 mm crushed stone, fine aggregate, tap water and superplasticizer for 0.25 w/c ratio mixes. The superplasticizer (SP) used here has a specific gravity of 1.05 g/cm<sup>3</sup> at 20 °C and Cl<sup>-</sup> content was less than 0.01%. The composition and properties of cement used together with cement clinker compositions are shown in Table 1. Mix proportions and 28-days compressive strength were listed in Table 2.

The specimens were sealed in plastic bags for the first 28 days at 20 °C. After that, for Exp I specimens, load was applied to achieve the required crack width which was measured by using PI strain gauges with 100 mm gauge length while loading and crack gauge after released of loading. Visible crack lengths ranged from 60 to 90 mm. All side surfaces of specimens were coated with 3 layers of epoxy to prevent penetration of Cl<sup>-</sup> ions from the unintended sides. After all preparations, the specimens were kept in the control room at 20 °C and RH of 60% pre-curing and before exposure to NaCl solution for about 2 months. Therefore, exposure for Exp I was started about 3 months after casting in an initially partially dry condition.

On the other hand, after all procedures such as sealed cure for the first 28 days in plastic bags, creation of cracks by torque wrenches, application of epoxy coating etc. were carried out, Exp II specimens were soaked for 3 days in Ca(OH)<sub>2</sub> solution to render them in a saturated condition before expose to 3% NaCl solution. Therefore, the exposure for Exp II was started about 1 month after casting in an initially saturated condition.

## 2.2 TESTING DETAILS

Electron Probe Micro Analysis (EPMA) test was performed on the exposed and cut samples for Cl<sup>-</sup> ion concentration and penetration depth profiles. The specimens were cut by using two different diamond blade cutters without using water or oil to avoid the disturbances to the distribution of Cl<sup>-</sup> ions during

**Table 3. Type of Samples, Exposure Conditions, Notational Cs and Maximum Cl<sup>-</sup> Concentration at Crack-Steel Intersection Region for Exp I and Exp II**

No	(Exp I) Mix ID	w/c	NaCl Concentration (%)	Exposure period	*Cs (%) Exposed	*Cs (%) Crack	**Cl <sup>-</sup> (%)	No	(Exp II) Mix ID	w/c	NaCl Concentration (%)	Exposure period	*Cs (%) Exposed	*Cs (%) Crack	**Cl <sup>-</sup> (%)
1	45-3%-7d	0.45	3	7 days	2.30	1.32	1.45	1	45-7d	0.45	3	7 days	3.00	0.90	0.77
2	45-5%-7d	0.45	5	7 days	3.80	1.80	1.74	2	65-7d	0.65	3	7 days	4.50	1.50	1.56
3	25-8%-7d	0.25	8	7 days	2.92	1.25	0.50	3	25-1m	0.25	3	1 month	2.00	0.75	0.10
4	45-8%-7d	0.45	8	7 days	4.95	2.15	2.34	4	45-1m	0.45	3	1 month	3.00	1.10	1.28
5	65-8%-7d	0.65	8	7 days	7.58	3.25	3.31	5	65-1m	0.65	3	1 month	4.50	1.85	2.77
6	45-3%-1m	0.45	3	1 month	3.00	1.32	1.93	6	25-3m	0.25	3	3 months	2.00	0.75	0.59
7	25-8%-1m	0.25	8	1 month	2.92	1.25	1.20	7	45-3m	0.45	3	3 months	3.00	1.10	1.89
8	45-8%-1m	0.45	8	1 month	4.95	2.15	2.56	<i>Note: *Cs is Notational surface chloride concentration. obtained by extrapolating the calculated concentrations from the Fick's 2<sup>nd</sup> law. **Cl<sup>-</sup> is maximum chloride ions concentration at crack steel intersection level.</i>							
9	65-8%-1m	0.65	8	1 month	7.58	3.25	4.21								

cutting. The location of the EPMA samples inside the small beam was shown in Fig. 1. The sizes of the specimens for EPMA were <76 mm (Length) x 76 mm (Width) x 18 mm (Thickness). From EPMA test, an array of approximately 400 x 400 numbers of numerical data were obtained for each of the sample tested and they were used for further data analysis.

### 3. RESULTS AND DISCUSSIONS

#### 3.1 MAXIMUM CL<sup>-</sup> CONCENTRATION AT THE CRACK STEEL INTERSECTION REGION

Based on the numerical data resulted from EPMA test, the Cl<sup>-</sup> concentration values were calculated as % by mass of cement. The average of highest concentration values were taken on an area of crack steel intersection zone of 2 mm (around crack) x 10 mm (diameter of steel bar) and represented in Table 3. as maximum possible Cl<sup>-</sup> ions concentration at crack-steel intersection region. According to Glass and Buenfeld (1995), the critical Cl<sup>-</sup> ions concentration to initiate corrosion for the laboratory based trials were noted about 0.4~2.5% [3]. However, no initiation of corrosion was found for all of the samples after all exposure periods in this study although some of the samples showed higher than 2.5% as shown in Table 3. This may be due to insufficient supply of oxygen for the corrosion to initiate and short exposure time.

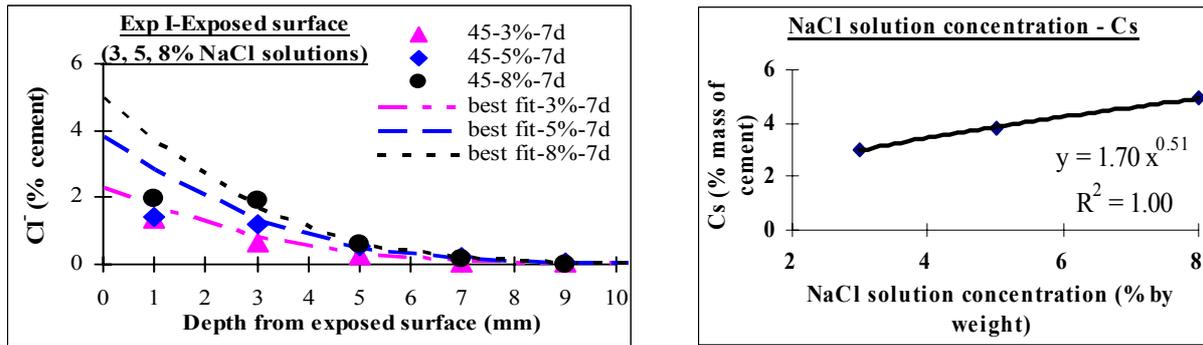
#### 3.2 DIFFUSION COEFFICIENTS (Dap)

The Dap values were obtained by fitting to a solution by Crank for Fick's 2<sup>nd</sup> law of equation (1) to the experimental results. All Cs values from exposed surface were termed as notational surface chloride concentration and were assumed to be constant through out the exposure time. Notational Cs is not the actual concentration at surface of the concrete samples for all the cases but the concentration values those can obtained by extrapolating the calculated concentrations by Fick's 2<sup>nd</sup> law [3]. In that fitting, the concentrations very close to the exposed surface were discarded due to some reasons such as carbonation and richness of motor etc. Diffusion coefficient from the crack surface is obtained by fitting to a curve of average concentration values along the crack length.

$$C(x, t) = C_i + (C_s - C_i) \cdot \left\{ \operatorname{erfc} \left( \frac{x}{2\sqrt{D_{ap} \cdot t}} \right) \right\} \quad (1)$$

Where, C(x,t); total Cl<sup>-</sup> content at depth x at time t, C<sub>i</sub>; background Cl<sup>-</sup> content, C<sub>s</sub>; Cl<sup>-</sup> content at exposed or crack surface, t; exposure time (s), x; depth from surface (mm), erfc; complementary of error function. D<sub>ap</sub>; Diffusion coefficient (m<sup>2</sup>/s).

C<sub>i</sub> values in this study were mainly found from the cement paste and they were taken as 0.011, 0.01 and 0.008 % by mass of cement for three different w/c mixes of 0.25, 0.45 and 0.65 respectively. An

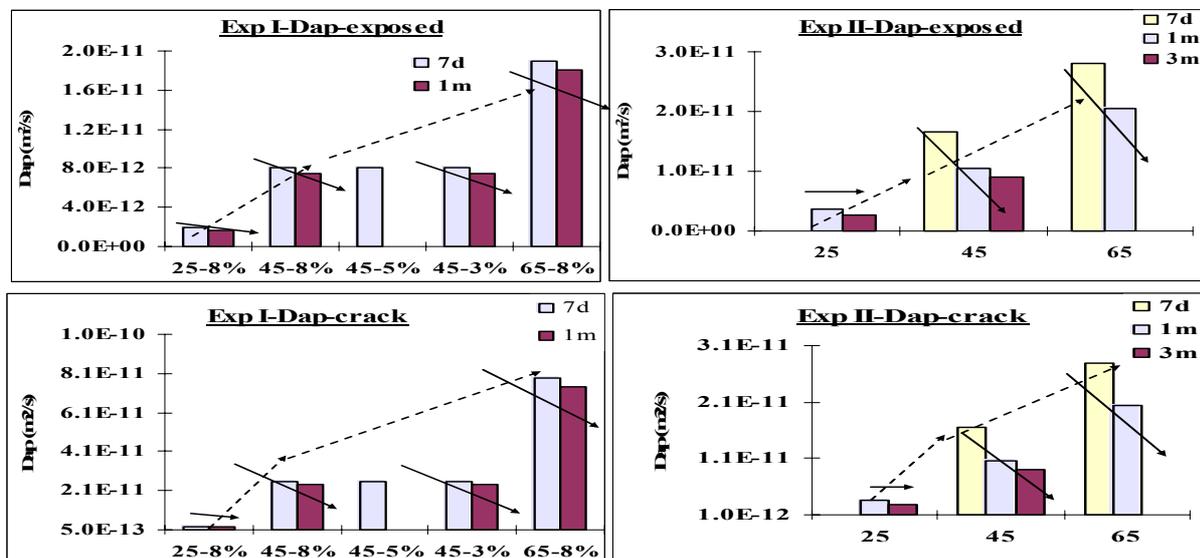


**Fig.2 Example of Experimental Data and Their Best fit Curves for Dap and Cs Determination**

example of fitted curve is shown in Fig. 2 which is for the same concrete samples exposed to three different NaCl solution concentrations. From same Fig.2 and 3, it can be seen that the curves of same 0.45 w/c (7days exposure) concrete can be fitted to be a same  $D_{ap}$  of  $8 \times 10^{-12} \text{ m}^2/\text{s}$  for different exposure solution concentrations with different  $C_s$ . Therefore,  $D_{ap}$  seems to be independent of the severity of  $\text{Cl}^-$  ions concentration in the exposed medium. On the other hand, a power relation of  $C_s$  with NaCl solution concentration was observed as shown in Fig.2.

As shown in Fig. 3, it was found that  $D_{ap}$  values both from exposed and crack surface decreased with time especially in Exp II. Therefore, it should be a function of time. For young concretes, time dependency of  $D_{ap}$  may be due to the combination of processes such as continuation of hydration, blocking effects due to formation of Friedel's salt along the diffusion path and exchanging of magnesium, calcium and hydroxide ions between solution and concrete etc. Apparently, for the mature concretes, effect of continuation of hydration became very less and the other mechanisms led slower diffusion rate with time. Still, to be able to explain it, further observations are needed.

The  $D_{ap}$  from crack of Exp II samples showed almost same as that of exposed surface. However,  $D_{ap}$  from crack of Exp I were higher about 1, 3 and 4 times for w/c of 0.25, 0.45 and 0.65 samples respectively than those of exposed surface. See Fig.3. This may be due to transportation through small micro-cracks (damage which occurred during loading) along the surface of crack. Most of these micro-cracks might be repaired through a process of healing in the case of saturated samples in Exp II [6]. In that case, the formation of new hydration gel products during the saturation period in  $\text{Ca}(\text{OH})_2$  solution might fill in the micro-cracks and heal the concrete to reach almost same condition as exposed surface and leading for the similar  $D_{ap}$  values. At the same time, leaching out of free ions from the pore solution to solution in the crack due to concentration gradient might compensate the effect of micro-cracks.



**Fig.3 Diffusion Coefficients ( $D_{ap}$ ) from both Exposed and Crack Surfaces, Exp I and II**

### 3.3 SURFACE CHLORIDE CONCENTRATION (Cs)

As mentioned in the above section, Cs values were notational concentrations that can effectively estimate the concentration profile inside the concrete. For real structures, depending on the environmental conditions, Cs values can be assumed from the standards such as JSCE. However, there is having no specific values to be assumed for laboratory tests of using different concentrations and salts. Best fit curves were fitted to the apparent Cs values and corresponding Dap values may not be able to reflect the actual mechanisms. There should have a set of most suitable Cs values that can lead to the reliable and similar trends from all of researches. A simple formula for the estimation of Cs for the concretes in contact with Cl<sup>-</sup> ions solutions including structures in submerged and splash zone is proposed in this section. Proposed Cs values were intended for the exposed surface of sound concrete whereas Cs of crack surface depends on time and other factors as well. A basic parameter was developed as “d” (% by mass of cement), which is free Cl<sup>-</sup> ions content in pore solution of concrete when the pore solution near surface reached same concentration as exposed one. It can easily be calculated from the molar mass, density of salt etc. as:

$$d = 0.61 V_p p_{\text{solution}} C_{\text{salt}} / C_e \quad (2)$$

In this study, salt used is NaCl, therefore, 0.61 is the % molar mass of Cl<sup>-</sup> ions in NaCl. Here, V<sub>p</sub>; Open pores volume of the concrete at the time of exposure to Cl<sup>-</sup> ions salt solution (%), C<sub>e</sub>; cement content (kg/m<sup>3</sup>), C<sub>salt</sub>; Concentration of salt in contact solution, p<sub>solution</sub>; density of salt solution (kg/m<sup>3</sup>).

$$p_{\text{solution}} = \frac{(p_{\text{water}} + 1000C_{\text{salt}})}{(1 + C_{\text{salt}}/p_{\text{salt}})} \quad (3)$$

p<sub>water</sub> in this study was taken as 998.2 kg/m<sup>3</sup> at 20°C and p<sub>salt</sub> for NaCl was 2.165. V<sub>p</sub> is from the experimental data carried out by following ASTM C 642-97, standard test method for density, absorption, and voids in hardened concrete. See Fig. 4. After developing the basic parameter “d” as above by considering role of free Cl<sup>-</sup> ions in pore solution of the concrete and based on the knowledge of solution concentration has a power relation to the Cs, equation (4) was developed with a correlation coefficient of R<sup>2</sup>= 0.98 by using experimental data as shown in Fig 5.

$$C_s = 3.9 d^{0.56} \quad (4)$$

For the verification of applicability of the proposed equation (2, 4), some experimental data were collected from the other researchers of Dr. D. D. Higgins [4] and C. Andrade and D. Whiting [5] and expressed in Fig. 6. Dap were obtained from the best fitted curves using proposed Cs values. V<sub>p</sub> values

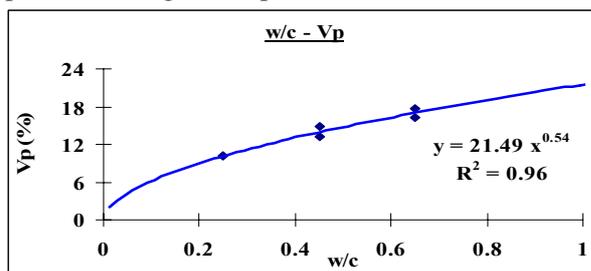


Fig.4 Relation between Vp and w/c

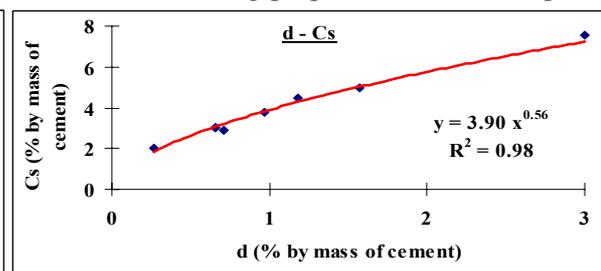


Fig.5 Relation between “d” and Cs

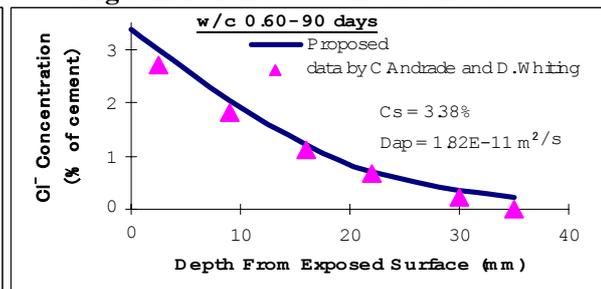
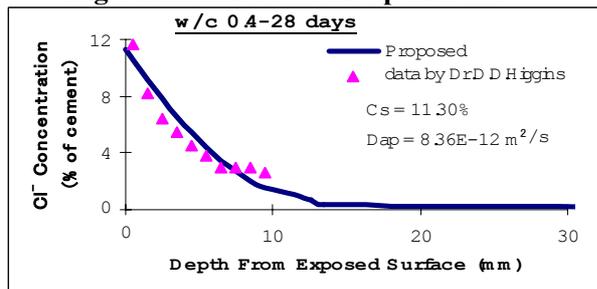


Fig.6 Fitting of Calculated Cs from Equation (2, 4) to Data of Other Researchers

were estimated from the w/c due to similarity of age and nature of concretes at the time of exposure with this research. The calculated values showed good agreement with the experimental data. The NaCl solution used by Dr. D. D. Higgins's research was 5 M (5 moles/liter) which is equivalent to 29.2 % weight of NaCl in solution and which in C. Andrade and D. Whiting was 0.51 M (0.51 moles/liter) equivalent to 3% solution. The concentrations of NaCl solutions used in this study were 3, 5 and 8% only and wider applicability of the proposed equation can be observed.

#### 4. CONCLUSIONS

Partially dry and saturated cracked reinforced concrete specimens were used in this research work. After started exposure to NaCl solution, the Cl<sup>-</sup> ions penetrated in to the exposed surface, through and around the crack and even along the steel. It was found that the penetrations both from exposed and crack surface were higher for higher w/c due to the higher porosity. For same concrete, the higher NaCl solution concentration led to higher Cs with same Dap. Therefore, Dap seems to be independent of severity of Cl<sup>-</sup> ion concentration in the exposed medium. All Dap values were decreased with time basically due to continuation of hydration in combination with some other mechanisms. Time dependency of Dap was more distinct in Exp II. Dap values from crack of partially dry samples showed from 1~4 times higher than those of exposed surface whereas saturated samples showed almost same Dap from both surfaces.

Based on the findings from the best fit curves to all experimental data of this study, a simple empirical formula for the estimation of Cs values for those uncracked concretes in contact with Cl<sup>-</sup> ions solutions including structures in submerged and splash zone was proposed. The free Cl<sup>-</sup> ions content in the pore solution of concrete was used as basic parameter to estimate the notational surface Cl<sup>-</sup> concentration and calculated results could fit well to others experimental data. The calculated values from the proposed equation showed good agreement with the experimental data and the wider applicability was also proven.

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