www.jcepm.org
https://doi.org/10.6106/JCEPM.2020.10.3-4.025

Vol. 10, No. 3-4 / December 2020
Online ISSN 2233-9582

KICEM Journal of Construction Engineering and Project Management

Necessity to Modify Fick Law considering Liquid Water Front inside Cover Concrete

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Received: Jul 22, 2020
Revised: Dec 22, 2020
Accepted: Dec 31, 2020

ABSTRACT

Most common method for durability analysis of RC structure against chloride attack is the Fick law of diffusion where diffusion coefficient is treated as the base parameter. Inspection data of chloride profile from some real structures does not obey the rule of Fick law for the case of chloride ingress, suggesting the influence of other unknown parameter. Recent research comes up with the conclusion that water penetration front is another key issue regarding cover quality which dramatically change the service life as well as LCC of RC structure. It is found that Fick law can not predict the chloride distribution precisely for very good type of concrete where water can penetrate few millimeters to centimeter. In this aspect, laboratory experiments are done to formulate the behavior of liquid water front considering type of material used in concrete, exposure condition and mix proportion as the parameters. Furthermore, Fick law is modified using the developed model formulas and suitable analysis method is proposed. It is also shown that the Torrent permeability which can easily be obtained from inspection of existing structure can fix suitable analysis method. This work highlights the suitability of analysis methods by modifying Fick's Law using empirical relationship found from experiments, and is therefore, clearly distinguish the concretes based on their cover qualities.

Keywords: Liquid Water Front, Modified Fick Law, Standard Deviation

INTRODUCTION

Fick law of diffusion plays an important role in the prediction of chloride profile in concrete. However, the quality of cover concrete of RC structure influences the analysis method. The structure situated in Okinawa was inspected and the cores were brought to the laboratory to get actual profile of chloride ingress. The immersion tests were conducted for 3 months. This work was done by Takahashi Yuya [7] with the conclusion that water penetration depth is the governing position beyond which chloride does not move. As the chloride can not move inside with the increment of time, Fick law needs to be modified taking liquid water front in consideration for such type of good quality concrete structures.

In this aspect, experiments are done to formulate liquid water front as a function of cement type, exposure condition, w/c ratio as variable parameters. A concept is developed to include these experimental models and verification is shown to prove the applicability of the models.

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Finally modified methods of analysis are correlated with the Torrent permeability which is usually and easily be done at the time of inspection of existing structure so that the range of permeability coefficient can help to select the analysis method to get precise results of chloride distribution.

AIM OF THE STUDY

Chloride profile of the cores taken from OKINAWA and the immersion test result of the same clearly stated that liquid water front stops the chloride ion penetration shown in Figure I(a) and I(b) [7].

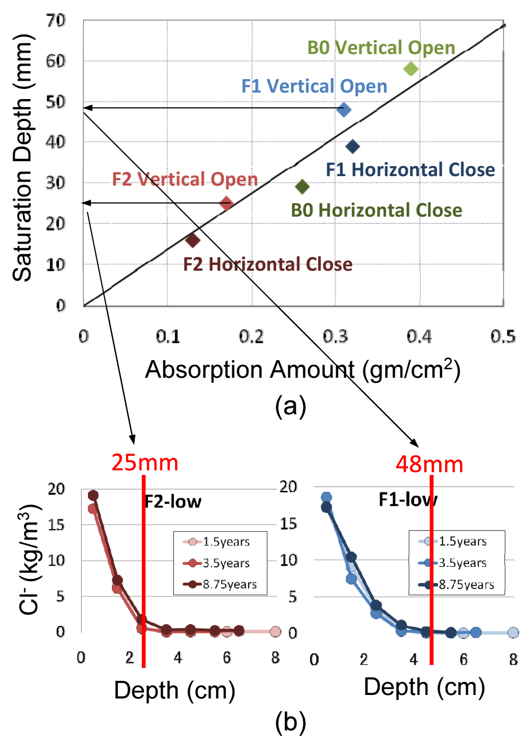


FIGURE I. COMPARISON BETWEEN IMMERSION TEST AND REAL PROFILE

The chloride stopping criterion due to liquid water front (w_f) will change the service life of the structure as explained in Figure II. In this figure liquid water front varies from 2 to 10 cm and the concentration of chloride is computed for depth of 6 cm. We can see a large difference in service life that will affect the life cycle cost also for the concrete having different surface quality in respect of liquid water front.

In some cases of concrete having very bad cover quality, liquid water can penetrate deeper zone inside with no restriction provided by the pores, Fick law can appropriately catch the penetration behavior. However, the profile for concrete like Okinawa structure, Fick law overestimates the profile which reduces the service life of the structure. Therefore, this paper aims to formulate the behavior of liquid water front that can be used in the modification of Fick law.

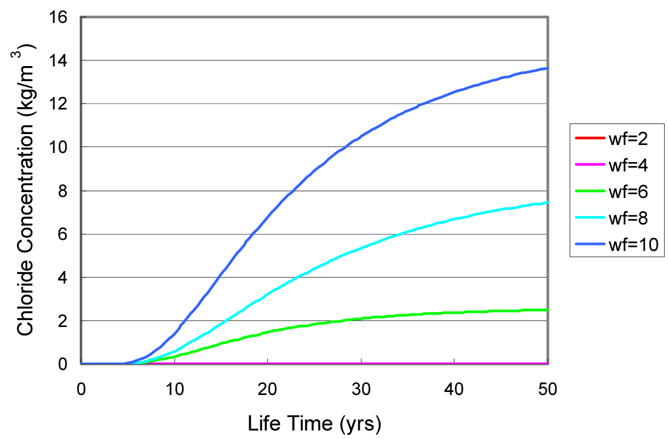


FIGURE II. EFFECT OF LIQUID WATER FRONT ON SERVICE LIFE

FORMULATION

The important parameters governing the flow through concrete can be determined as of the following chart.

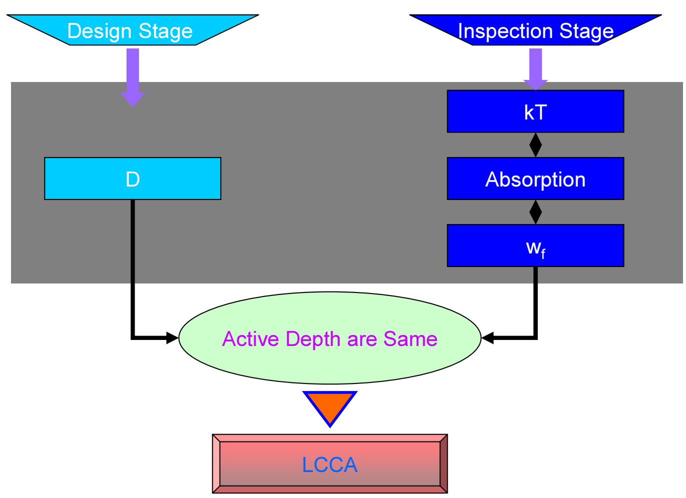


CHART I. CONCEPTUAL FLOWCHART

Parameter D can be set based on w/c ratio and material used in concrete. Usually the health of structure be judged during the inspection by torrent permeability kT that can be correlated with absorption of water as well as liquid water front. To go along with the chart, it is necessary to formulate the behavior of liquid water front based on properties of concrete.

Experimental Plan and Testing

Experiments were set to be done to clarify the effect of liquid water front on chloride ion penetration into concrete. Targeted tests were the titration for chloride profiling and weight measures to know absorption of concrete. The mix proportion is summarized in Table I.

TABLE I. MIX PROPORTION

Type	w/c [%]	Unit weight [kg/m^3]				
		W	C	BFS or FA	S	G
N40	40	180.3	450.9	--	708.6	978.5
N55	55	180.3	327.9	--	805.1	984.5
N70	70	180.3	257.6	--	886.3	960.9
F40	40	172.7	345.4	86.3	694.1	998.6
F55	55	172.7	251.2	62.8	791.6	1007.8
F70	70	172.7	197.4	49.3	873.6	985.8
B40	40	174.9	218.6	218.6	695.9	1001.2
B55	55	174.9	159.0	159.0	792.3	1008.7
B70	70	174.9	124.9	124.9	873.7	985.9

where N is Ordinary Portland Cement Concrete, F is the Fly Ash Concrete where cement is replaced by 25% in weight, B the Blast Furnace Cement Concrete where 50% of cement is replaced by Slag in weight. The direction to exposure is shown in Figure III.

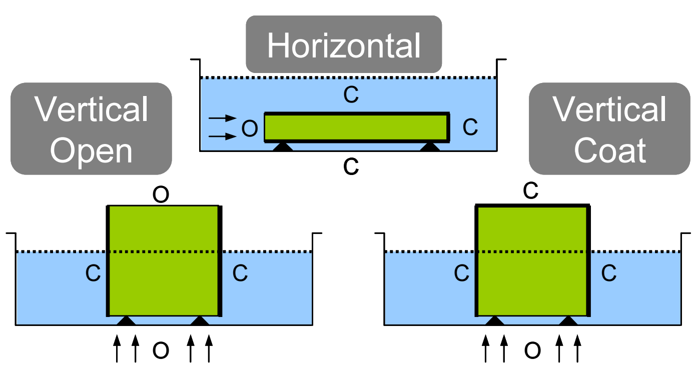


FIGURE III. EXPOSURE DIRECTIONS

where *C* denotes coated and *O* denotes open face. The specimens were put inside tank over angular shape notch to allow free flow of liquid around the specimens.

Steps in Experimental Details

Specimens are of 100 mm in diameter and 200 mm in height. All the specimens were cut in 4 parts. The parts of the specimens were used for 2 different exposure conditions [wet, wet-dry], and for 2 different exposure durations [3 months, 6 months].

All the specimens were coated by primer and let dried for 24 hours. 2 layers of epoxy coating were put on the primer finished surface and kept 24 hours to dry prior to exposure. Coating was done to make the surfaces non penetrable to liquid other than required surface that was kept open as shown in Figure III.

First type of exposure series is to keep the specimen in 10% NaCl solution for total duration of experiment. Another series was kept in cyclic wet-dry condition. Specimens were put in 10% NaCl solution for 1 day and then transferred to drying chamber with 40°C temperature and 60% RH for 6 days.

The weight of the specimens was taken twice a week. The required expose surface was covered by tape before the application of coating. After the drying of the coating the tape was removed and was attached on the blank paper. The area of the tape was made black with ink and the surface area covered by the tape was measured using the software WinROOF. Weight and the surface area were used to calculate absorption capacity of the specimen.

While the absorption shows a tendency of reaching constant value the specimens were broken by compressive strength testing machine. The depth of liquid water front was measured by digital caliper for a number of points.

As it is very difficult to cut the samples by dry cutter @ very small pitch, oil cutter was used to cut at a rate of 1 cm pitch from the exposed surface. Each sample was ground using the machine for about 1 minute.

The powdered samples were 2 days in the laboratory environment to dry. After drying the samples were digested by HNO_3 solution and titrated by $AgNO_3$ solution using Auto titration apparatus.

Durability of concrete is largely dependent on the resistance of cover concrete. Air permeability is an indicator for the resistivity of cover that can easily be quantified at the time of inspection of real structure. Based on the value of air permeability, concrete can be classified from very low to high in the scale of quality.

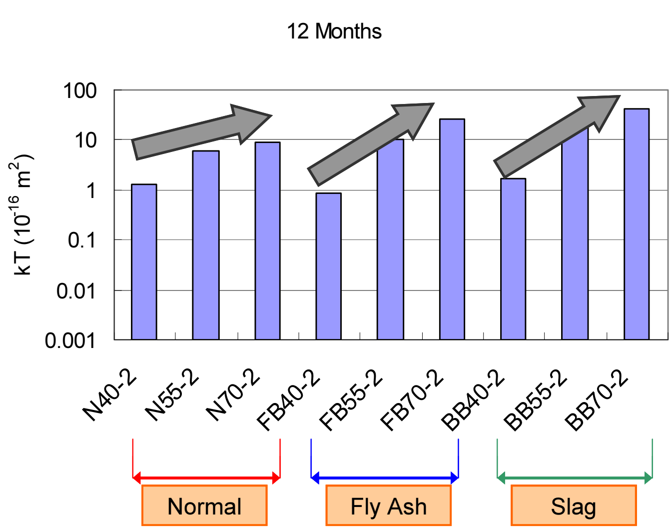
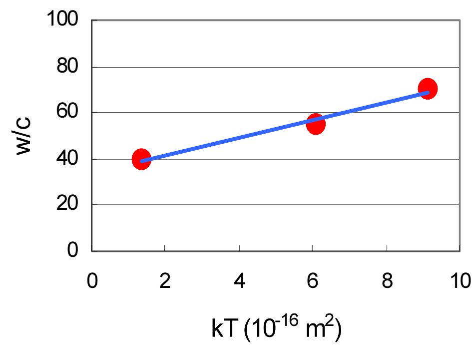


FIGURE IV. PERMEABILITY OF DIFFERENT SPECIMEN

In this study permeability was measured after 1 year of casting. Type of material was varied as normal, fly ash and slag concrete. With the increase of w/c ratio permeability is also getting increased.

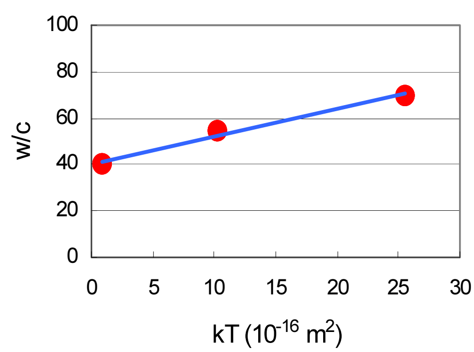
Generation of Basic Models

Figure V to Figure VII is the result that correlates between w/c ratio (as design variables) and torrent permeability (as inspection condition).



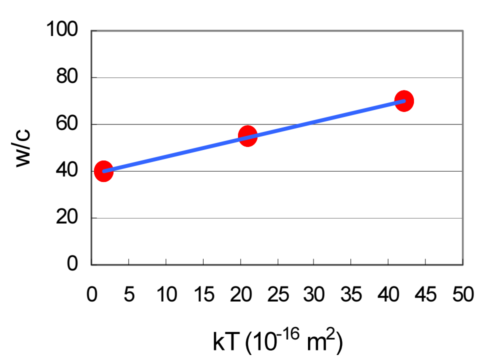
$$w/c = 3.7759kT + 34.125$$

FIGURE V. W/C VS. KT (NORMAL)



$$w/c = 1.1944kT + 40.447$$

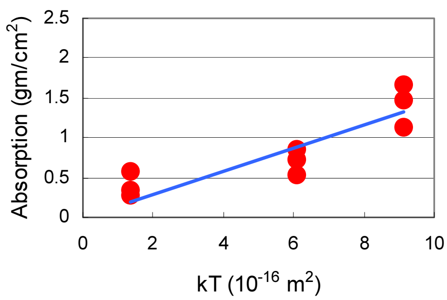
FIGURE VI. W/C VS. KT (FLY ASH)



$$w/c = 0.7438kT + 38.918$$

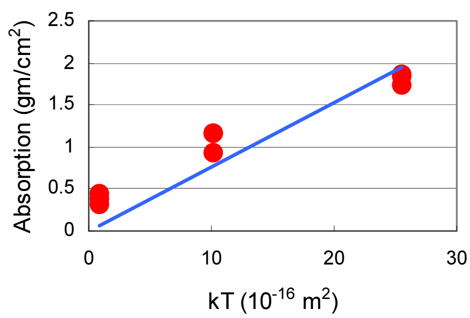
FIGURE VII. W/C VS. KT (SLAG)

Figure VIII to Figure XIII are the results that correlates between absorption and torrent permeability as a function of material type and exposure condition.



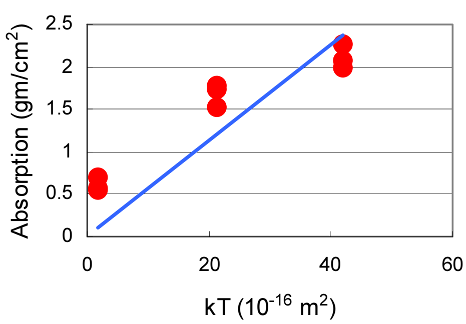
$$Absorption = 0.1452kT$$

FIGURE VIII. ABSORPTION VS. KT (NORMAL, WET)



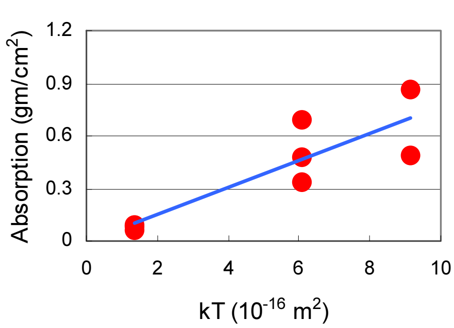
$$Absorption = 0.0765kT$$

FIGURE IX. ABSORPTION VS. KT (FLY ASH, WET)



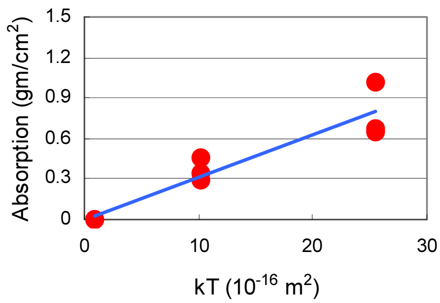
$$Absorption = 0.0567kT$$

FIGURE X. ABSORPTION VS. KT (SLAG, WET)



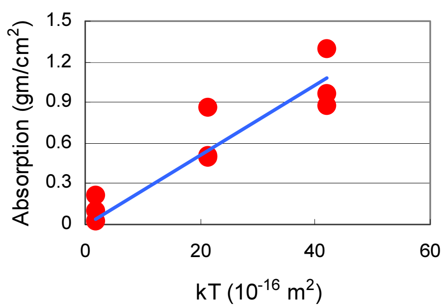
$$Absorption = 0.077kT$$

FIGURE XI. ABSORPTION VS. KT (NORMAL, WET-DRY)



$$Absorption = 0.0312kT$$

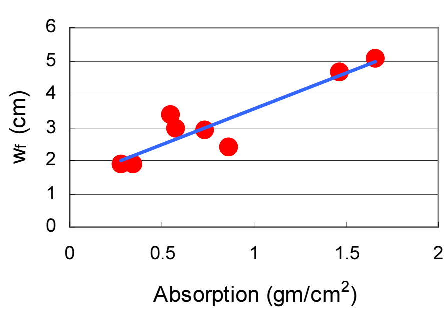
FIGURE XII. ABSORPTION VS. KT (FLY ASH, WET-DRY)



$$Absorption = 0.0259kT$$

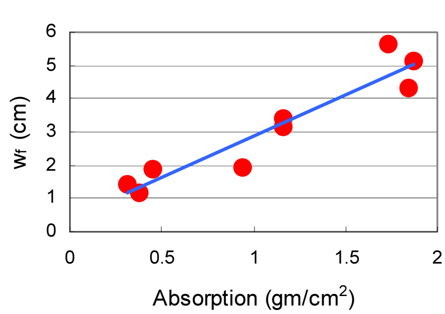
FIGURE XIII. ABSORPTION VS. KT (SLAG, WET-DRY)

Figure XIV to Figure XIX is the correlations between absorption and liquid water front as a function of material type and exposure condition.



$$\omega_f = 2.137 Absorption + 1.427$$

FIGURE XIV. WATER FRONT VS. ABSORPTION (NORMAL, WET)



$$\omega_f = 2.4733 Absorption + 0.4084$$

FIGURE XV. WATER FRONT VS. ABSORPTION (FLY ASH, WET)

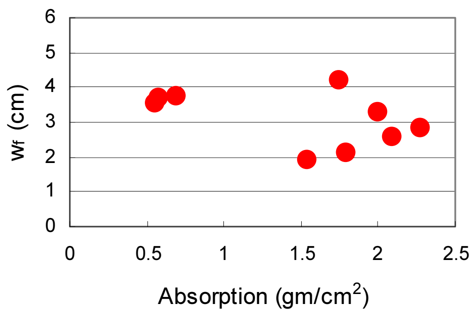
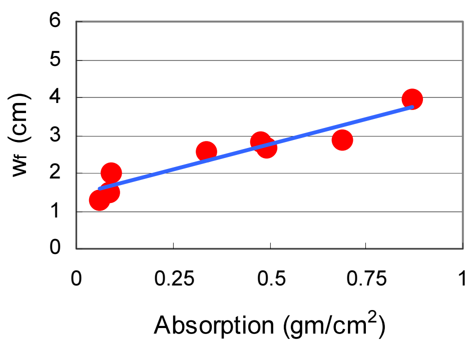
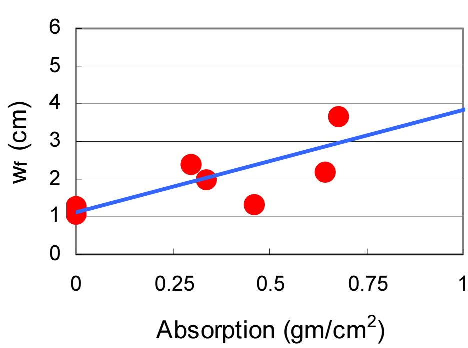


FIGURE XVI. WATER FRONT VS. ABSORPTION (SLAG, WET)



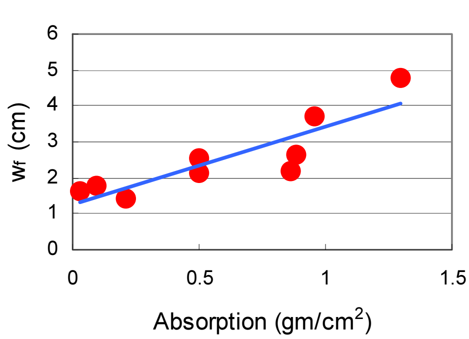
$$\omega_f = 2.7105 Absorption + 1.4051$$

FIGURE XVII. WATER FRONT VS. ABSORPTION (NORMAL, WET-DRY)



$$\omega_f = 2.737 Absorption + 1.1001$$

FIGURE XVIII. WATER FRONT VS. ABSORPTION (FLY ASH, WET-DRY)



$$\omega_f = 2.1697 Absorption + 1.2491$$

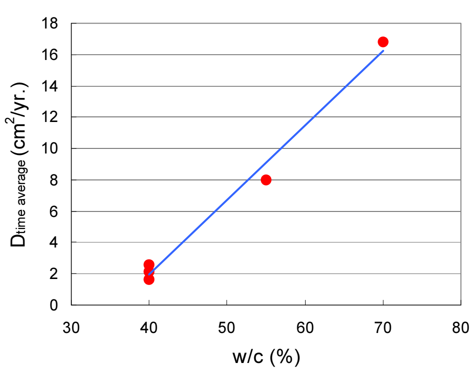
FIGURE XIX. WATER FRONT VS. ABSORPTION (SLAG, WET-DRY)

Diffusion coefficient was calculated by fitting the concentration profile found from titration of 3 months series of specimens. As the diffusion coefficient is high at early age and drastically reduces with the age of structure, it is logical to take the time average diffusion coefficient in the case service life analysis.

$$D_{time\ average} = \frac{\sum_{t=1}^{T} D_t \times t}{\sum_{t=1}^{T} t} \quad (1)$$

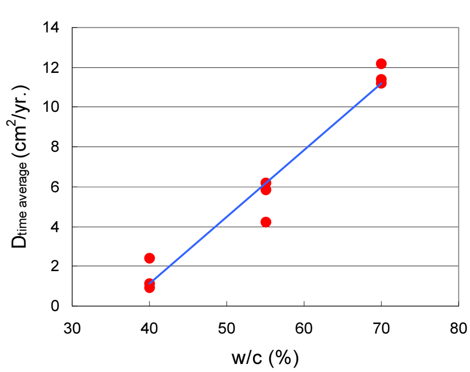
where $D_{time\ average}$ is the average diffusion coefficient throughout the service life, D_t is the diffuision coefficient at any time t, T is the total service life.

Figure XX to Figure XXVI is the correlations between time average diffusion coefficient and w/c ratio as a function of material type and exposure condition.



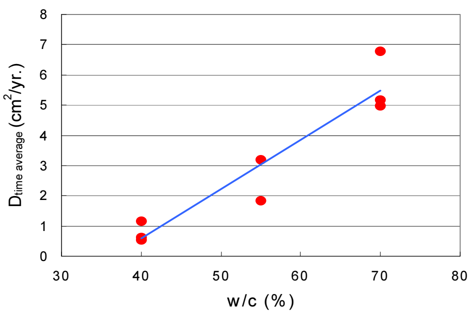
$$D_{time\ average} = 0.4769 w/c - 17.144$$

FIGURE XX. D VS. W/C (NORMAL, WET)



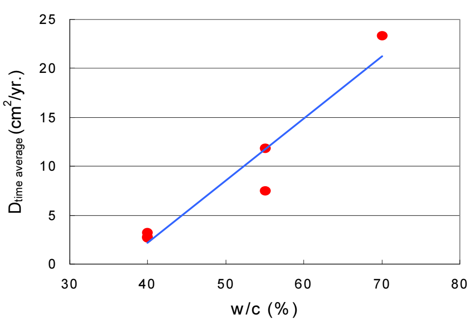
$$D_{time\ average} = 0.3367 w/c - 12.347$$

FIGURE XXI. D VS. W/C (FLY ASH, WET)



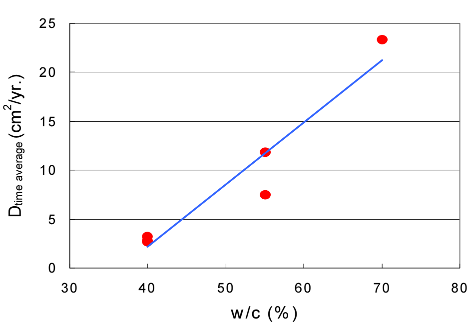
$$D_{time\ average} = 0.1625w/c - 5.9008$$

FIGURE XXII. D VS. W/C (SLAG, WET)



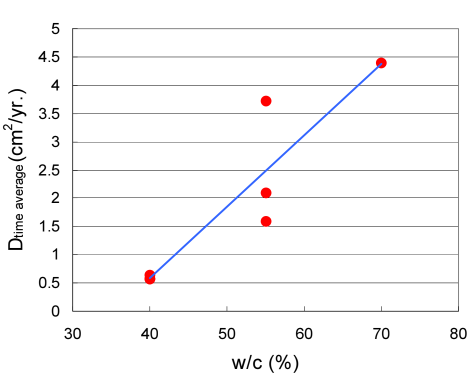
$$D_{time\ average} = 0.6344w/c - 23.168$$

FIGURE XXIII. D VS. W/C (NORMAL, WET-DRY)



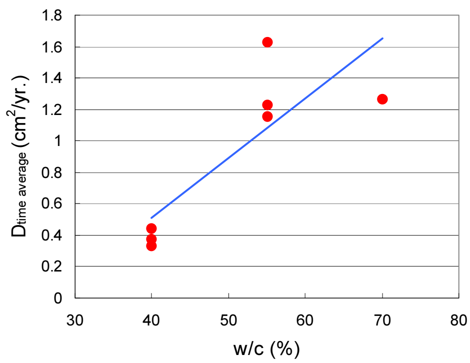
$$D_{time\ average} = 0.6344w/c - 23.168$$

FIGURE XXIV. D VS. W/C (NORMAL, WET-DRY)



$$D_{time\ average} = 0.1261w/c - 4.469$$

FIGURE XXV. D VS. W/C (FLY ASH, WET-DRY)



$$D_{time\ average} = 0.038w/c - 1.0093$$

FIGURE XXVI. D VS. W/C (SLAG, WET-DRY)

Variation Problem

If the concrete cover is not good enough chloride movement goes more than the depth of mean water penetration front. Stopping of chloride ingress at the mean front position of water is not applicable here. At the time of liquid water front measurement it was found that front position is not a straight line rather than it has deviation from the mean front position. This explores new idea of taking a parameter standard deviation from the mean front position.

Risk Model

Figure XXVII shows the distribution pattern of water front for OPC, fly ash and slag concrete in wet-dry condition. The mean front increase means high risk of getting fixed value in comparison with low mean value.

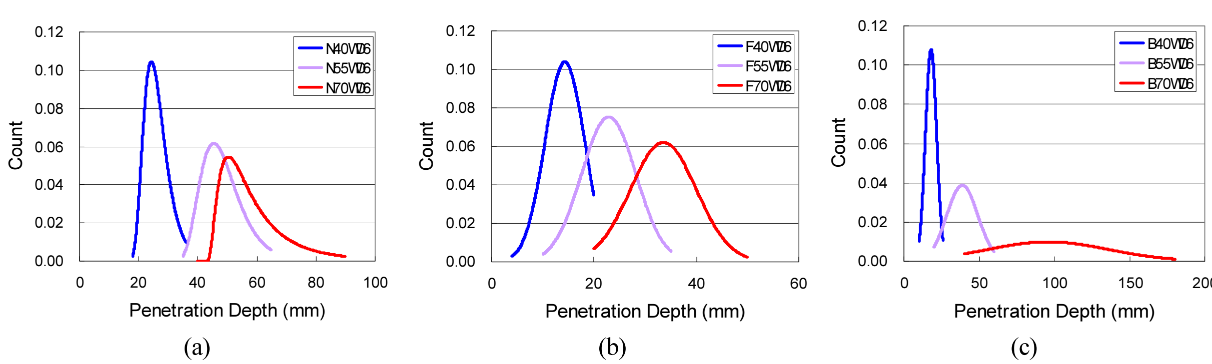
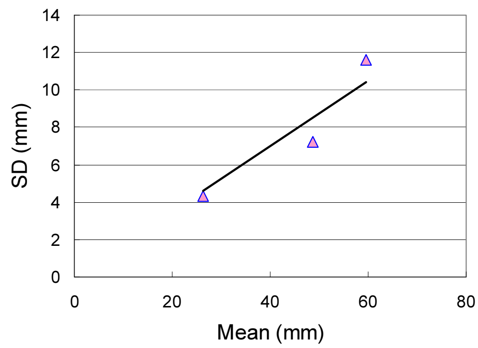


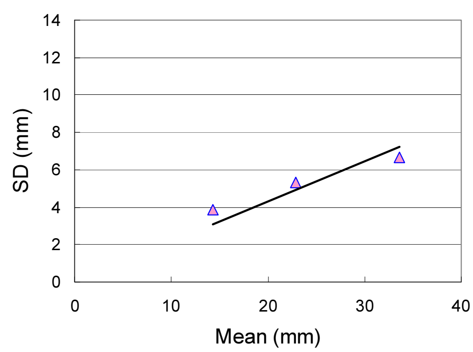
FIGURE XXVII. RISK DISTRIBUTION OF LIQUID WATER FRONT

Figure XXVIII to Figure XXX are the models to quantify standard deviation with a certain mean front position for different types of concrete.



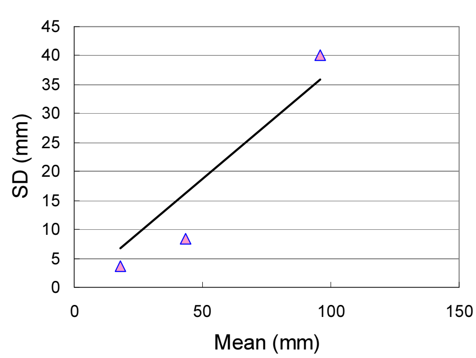
$$SD = 0.1749 \times Mean$$

FIGURE XXVIII. MEAN VS. SD (NORMAL, WET-DRY)



$$SD = 0.2156 \times Mean$$

FIGURE XXIX. MEAN VS. SD (FLY ASH, WET-DRY)



$$SD = 0.3748 \times Mean$$

FIGURE XXX. MEAN VS. SD (SLAG, WET-DRY)

It is found that the value of dependent variables is increasing with the increased value of independent variable used in Figure V to Figure XXVI. The right side of equation [3], discussed later, has two different governing parts, diffusion coefficient *D*, and average linear rate of flow *V*. The design value of *w/c* ratio helps to find the diffusion coefficient *D* and that is presented in Figure XX to Figure XXVI considering difference in materials. It is difficult to find, another parameter used in equation [3], average linear rate of flow *V*, through the experiments. Therefore, torrent permeability *kT* is selected to investigate and is correlated with other parameters. Absorption can easily be obtained from torrent permeability results which are shown in Figure VIII to Figure XIII. Again liquid water front, which has always be obtained by breaking the specimen, can easily be estimated from absorption as shown in Figure XXV to Figure XXX. Figure XXVIII to Figure XXX expresses the risk of uncertainty of liquid water penetration with the change in materials used in concrete. This variation is extremely important need to be considered in modifying the Fick law. However, contributions of this research includes that only torrent permeability data, collected through inspection, can estimate liquid water front inside concrete using empirical equation presented from Figure V to Figure XXX, without conducting any destructive experiments.

MODIFICATION OF FICK'S LAW

Modification of Fick's law to use liquid water front in chloride profiling is described briefly under sections diffusion prediction model and parameters and assumption.

Diffusion Prediction Model

Chloride diffusion into concrete, like any diffusion process, is controlled by Fick's Second Law for non-steady condition.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{2}$$

which includes the effect of changing concentration with time (t). x is the cover depth, C is the chloride concentration in time t and at a depth of x from the surface, D is the diffusion coefficient.

But in actual practice the flow is governed by diffusion and convection manner [1,2] where we have to use following equation.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} \tag{3}$$

where V is the average linear rate of flow (cm/s).

$$V = \frac{k}{\varphi} \frac{\partial h}{\partial x} \tag{4}$$

where $\frac{\partial h}{\partial x}$ is the hydraulic gradient that is considered constant as 0.1 MPa/m in this study, k is the hydraulic permeability (m/s), φ is the porosity of the material. Porosity is dependent on other properties as the following equation [5].

$$\varphi = \frac{1000 \times M}{\omega_f} \tag{5}$$

where M is the absorption capacity (gm/mm2) and wf is the liquid water front (cm).

Hydraulic permeability and critical pore radius are determined by experimental results stated in reference [3].

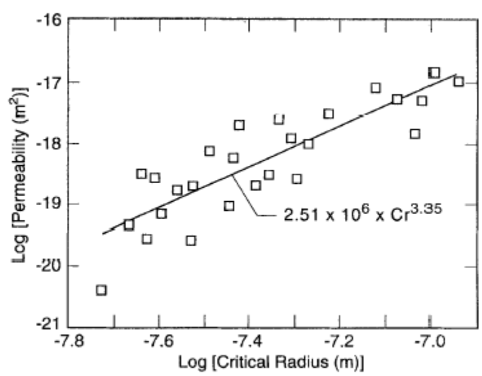


FIGURE XXXI. PERMEABILITY VS. CRITICAL PORE RADIUS

Critical pore radius is termed as *r* in this study which can be determined by capillary theory according to the following equation.

$$r(m) = \sqrt{\frac{4\mu}{P_o}} \times \frac{\omega_f}{\sqrt{t}} \tag{6}$$

where *t* is the time for short term absorption in seconds, w_f is the water front in cm, μ is the viscosity in pa-s, P_o is atmospheric pressure in pa.

In Eq. (3) diffusion coefficient is found from experiments done in the laboratory and the solution is based on Finite Difference Method. Surface chloride concentration C_o is considered to increase with time and is calculated as below [8].

$$C_o(t) = C_o\left(1 - \exp^{-\alpha t}\right) \tag{7}$$

α is the environmental factor adopted as 0.50, *t* is time in years, *Co* is the ultimate surface chloride.

Each of the proposed equations is calculated by using Microsoft Excel to be able to efficiently calculate the concentration distribution and inputting the necessary data at suitable stages the output concentration can be found. Eq. (3) is solved for diffusion-advection of flow using Finite Difference scheme considering three points on the x-axis separated by *dx*. By using Taylor expansion and rearrangement final equation to solve is as follows.

$$C_{t+dt} = C_t + D\frac{dt}{dx^2}[C_{i-1} - 2C_i + C_{i+1}] - V\frac{dt}{2dx}[C_{i+1} - C_{i-1}] \tag{8}$$

Hindmarsh [4] and Sousa [6], showed that the conditions that the finite difference scheme in Eq. (8) is stable are,

$$2D\frac{dt}{dx^2} \le 1 \tag{9}$$

$$\left(\frac{Vdt}{dx}\right)^2 \le 2D\frac{dt}{dx^2} \tag{10}$$

Rearrangement and simplification of both of these conditions gives the restriction on the size of the time step in terms of the parameters and the grid size:

$$dt \le \min\left\{\frac{dx^2}{2D}, \frac{2D}{V^2}\right\} \tag{11}$$

Parameters and Assumption

The main parameters shown in Eq. (3) are rate of flow *'V'* and diffusion coefficient *'D'*. Rate of flow depends on hydraulic permeability and porosity of the material which indirectly is a function of liquid water front *'w_f'* and absorption *'M'* and can beobtained from Eqs. (4), (5), and (6). Diffusion coefficient can be found as a function of design parameter and liquid water front, absorption are computed from inspection data of permeability coefficient as stated in section of generation of basic models.

Diffusion coefficient *D* is assumed to follow the following rule to make compatible with the stopping criterion of chloride ion up to the liquid water front. In Figure XXXII, MFD, MFP and F stand for Modified Fick Deterministic, Modified Fick Probabilistic and Fick respectively.

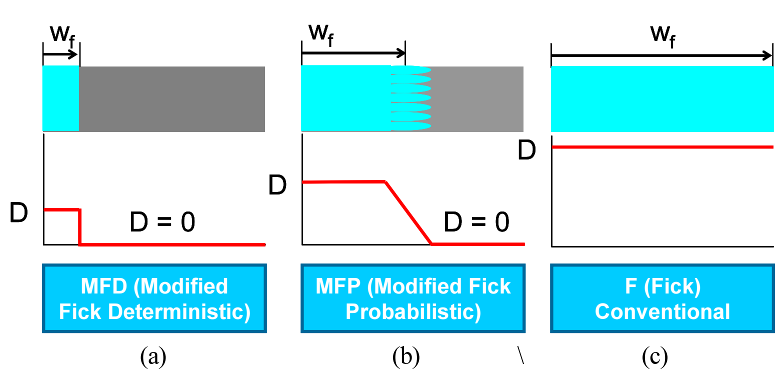


FIGURE XXXII. COUPLING BETWEEN LIQUID WATER FRONT AND DIFFUSION COEFFICIENT

Figure XXXII(c) shows the conventional way of thinking that does not depend on liquid water front and the inclusion of the influence of liquid water front on chloride stopping criterion, diffusion coefficient *D* is set to the value as shown in Figure XXXII(a) and XXXII(b). In conventional Fick's law, diffusion coefficient is set as constant throughout the specimen depth whereas in the case of modification the diffusion coefficient is set different to couple with liquid water front. For concrete with bad quality, saturation drops at the deeper zone from surface where diffusion coefficient drops a slight but for easiness of calculation it assume to be constant throughout the specimen depth that reflects the image of almost all the specimen is saturated. With large pore Cl^- can move through unsaturated zone inside. For good type of concrete saturation drops with sharp front with water also, thus diffusion coefficient needs to take as having two value as in figure. Medium type of concrete has both large and small pores that makes water front to penetrate in a distribution pattern where the diffusion coefficient needs to consider as reducing with a slope and then comes to zero.

Matric pressure or capillary pressure is thought of as the pressure of water in a pore of the medium relative to the pressure of the air. If the matric pressure is close to zero, air-water interfaces are broadly curved, nearly all pores are filled and water content is high. If matric pressure is much less than zero the interfaces are more tightly curved, they can no longer go across the largest pore, and the pores have less water inside. Actually the curvature of the air-water interface is inversely related to the pressure. Tighter curvature is associated with smaller pores with more negative pressure. That is why, bad concrete having many larger pores water front variation is large and Cl^- can move through unsaturated part with less wall friction. But for good concrete, it is difficult to get fully saturated condition and pores inside remain as disconnected. Moreover, good cover concrete having fine pores, sharp front of water is expected and if water can move through the even finer pores Cl^- flow will be restricted by the wall friction.

Verification and Proposal

For the case of verification B55 concrete is selected and the analysis results done by Fick and Modified Fick Probabilistic methods are compared with the actual titration data as shown in Figure XXXIII. Liquid water and its variation is adopted with the formulas stated in sections generation of basic models and in variation problem. The

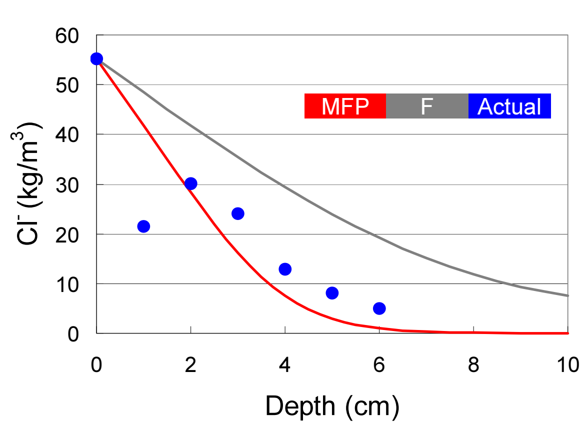


FIGURE XXXIII. VERIFICATION WITH ACTUAL DATA (B55 CONCRETE) concept described in Figure XXXII is included in the analysis. There is no doubt that Fick law overestimates chloride profile which can reduce service life of the structure whereas MFP can reproduce the experimental data in precise way where liquid water front is taken into account.

Thus the proposal of concrete analysis for chloride profiling strongly depends on the quality of cover concrete and it is better to modify Fick law while the concrete quality is really good. The proposal is summarized in following table. Analysis done by MFD can also be simulated by MFP. But in case of concrete having very good surface quality MFD is used for its easiness of application.

TABLE II. PROPOSAL AND CHARACTERISTICS OF ANALYSIS METHODS

Torrent Range	Proposed Quality	Proposed Methods	Liquid Water Front (cm)	
			Mean	Standard Deviation
0.001 ~ 1	Good	MFD	Actual	No
1 ~ 10	Medium	MFP	Actual	Actual
10 ~ 100	Bad	F	Independent of water front	

CLASSIFICATION OF CONCRETE BASED ON TORRENT GRADE

In the proposal concrete is classified in mainly three groups namely good, medium and bad where three different method of analysis are suitable. But the question arise that how to identify concrete as good, medium or bad. European code specifies grades of concrete according to their torrent permeability coefficient. Attempt was taken to correlate the analysis methods with these grades of concrete that can be easily identified by inspection with torrent data.

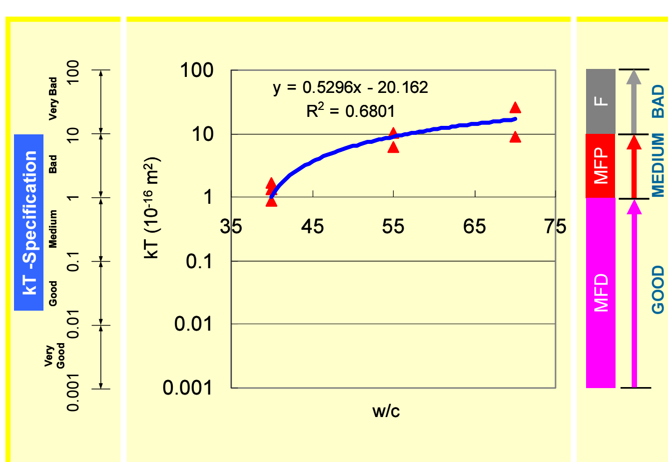


FIGURE XXXIV. SUITABLE ANALYSIS METHOD SELECTION BASED ON TORRENT GRADE

It is found by the analysis done for the experimental specimens that MFD, MFP and F methods of analysis are suitable for concrete with 40%, 55% and 70% of w/c ratio respectively. Permeability coefficients for Normal, Fly ash and Slag concrete with 40%, 55% and 70% w/c ratio are plotted in Figure XXXIV. The trend line of the above graph shows that kT value less than 1 is for concrete with 40% of w/c ratio. 55% w/c ratio concrete lies between 1 to 10 kT value and 70% w/c concrete lies above the 10 as kT value. Thus *very good, good and medium* grades of concrete according to kT specification can be analyzed with MFD method which was specified as Good concrete in previous section. Sequentially *bad* and *very bad* grades of concrete as per kT specification can be analyzed by MFP and F method respectively that was stated as Medium and Bad concrete in previous section.

CONCLUSIONS

Quality of cover concrete, with respect to type of cement, and w/c ratio to correlate the parameters liquid water front, absorption, and torrent permeability, is examined and Fick's Law is modified by coupling liquid water front with chloride ingress into concrete. By applying this concept, following remarks can be pointed out.

Fick law overestimates concentration of chloride for concrete with good surface quality.

Liquid water front and its variation play important role in the prediction of Cl^- profile. For the case of very good concrete having smaller pores, the seepage front of water is stopped sharply and Cl^- can not go beyond the water front position. For the case of medium grade of cover quality concrete, water front is not stopped in sharp but it creates some variation along its mean stopping position due to having small and medium sized pores. Thus Cl^- moves beyond mean position of stopping water front. In the case of bad quality concrete, although saturation drops inside, but water flows deeper with larger pores and creates unsaturated zone through which Cl^- can flow.

Methods of analysis are dependent on the type of concrete.

Formulations are done by laboratory experimental results and a concept to couple water front with chloride movement is proposed.

Methods of analysis can be selected from the Torrent permeability while inspection is carried out.

ACKNOWLEDGEMENT

I would like to express my profound gratitude to the Program for Promoting Fundamental Transport Technology Research from the Japan Railway Construction, Transport and Technology Agency (JRTT) for supporting the project.

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